UNITED STATES PATENT OFFICE.

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PROCESS OF DETINNING TIN SCRAPS AND PRODUCING TIN COMPOUNDS.

943,508. Specification of Letters Patent. Patented Dec. 14, 1909.

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To all whom it may concern:

Be it known that I, OTTO K. ZWINGENBERGER, a citizen of the Empire of Germany, and resident of New York, in the county of New York and the State of New York, have invented certain new and useful Improvements in the Process of Detinning Tin Scraps and Producing Tin Compounds, of which the following is a specification.

The invention is based on the chemical reaction between chlorin gas and metallic tin which forms tin-tetrachlorid.

The process for the recovery of tin from tin-scraps by means of chemicals as acids, acid salts and by means of electricity in alkaline liquids have all the shortcomings that they require relatively much labor. The chemicals attack iron and this action on the iron increases in the degree the layer of tin decreases so that finally the process must be interrupted because it would be too difficult and uneconomical to separate the tin products from the iron-products in order to bring the former into merchantable form. The electrolytic process with a solution of sodium-hydrate takes off very easily the upper layer of tin, but the taking off of the layer close to the iron plate, which represents an alloy of tin and iron, requires the application of a higher electric energy whereby other metals present in the sheet-plate participate in the process and in the long run of the process the carbonic acid gas of the air acts on the sodium-hydrate solution raising difficulties too. The detinning of tin-scraps by means of chlorin gas is free from all these shortcomings, for the tin-scrap is handled in bundles and the process is completed in one single operation delivering the tin-compounds directly in a marketable condition. The detinning by this chlorin-process is more complete than by any other process and no tin is lost in washing or while handling the detinned iron-scraps.

Many details of the preparation of tin-scraps for the detinning processes and the treatment of the detinned iron-scraps were long known. Already in 1883 Reinecken described his method of cleaning tin-scraps and the like material from fat, varnish and the like impurities by treating the tin-scraps with sodium-hydroxid (D. R. P. 21,628.) It was early found out that both the chlorin gas and the tin-scraps must be absolutely dry.

The low temperature is essential for the success of the process and is often maintained by artificial cooling. I have now found out that this low temperature can be successfully maintained by giving the chlorin a larger surface of tin-scraps to work on, as the elevation of the temperature is especially caused by the action of chlorin which owing to its excessive supply to one place works like a blast-flame and the heat generated spreads quickly all over the mass thus inviting a still greater action of the chlorin and increasing the loss as much iron may be attacked and decreasing the value of the obtained tin-tetrachlorid. I have found out that the low temperature is fully guaranteed by creating a partial vacuum in the receptacle containing the raw-material, whereby when observing a suitable connection of the receptacles the chlorin gas is more equally distributed over the receptacles and cannot raise the temperature over a due degree.

I am aware that it has been proposed to apply low-pressure in the detinning process by connecting the detinning apparatus with an exhausting device. This process is used for the removal and recovery of the residue of chlorin gas and tin-tetrachlorid when all or nearly all of the tin has been dissolved so that the flow of chlorin gas upon the tin-scrap is discontinued (Seely, U. S. P. 127,375). The method of carrying out this part of the process consists in connecting the exit-pipe of the vessel 1, at the stage when all tin is dissolved, with the inlet-pipe of vessel 2. A similar method applies exhausting devices (Sperry, U. S. P. 872,092) especially to dry the tin-scraps before the detinning and to remove the surplus of chlorin gas and the residue of tin-tetrachlorid from the reaction vessel after finishing the detinning process.

It may be obvious to use exhausting devices for forwarding gases from one receptacle to another or to remove the residue of gaseous products from one vessel as demonstrated by those two processes mentioned above, but it is not obvious at all to use a partial vacuum for distributing gases over a plurality of vessels in order to moderate the heat produced by a chemical process and to

improve the quality of the obtained goods simultaneously saving labor and affording like advantages.

Though the application of low-pressure in detinning operations is known *per se* the difference between my process and those above is great and important because in the old style any detinning vessel connected in series is in a different stage of operation and pressure or low-pressure respectively. It is evident, that a process, in which on account of the special connection of the vessels and the equal distribution of chlorin gas over all the vessels any of the latter is exactly at the same stage of operation and will be finished at the same time, is a great improvement for its easy control and the great division and saving of labor.

The division of work is very convenient, for if a series of for instance 12 vessels is finished at the same time the residue of chlorin and tin-tetrachlorin contained in the first vessel will be driven off by compressed air in the time the workmen are going to connect the other vessels with the conduit for compressed air etc. One gang of workmen is therefore kept busy all the time by emptying the detinning vessels and handling the iron-scrap until it is ready for delivery to the smelting-works. The workmen waste no time by waiting for the finishing of the process in a vessel as it happens often in the processes having the vessels connected in series thus finishing each vessel separately at an uncertain time.

The detinned iron-scrap must be washed for two reasons. The one reason is to save the last traces of tin-tetrachlorid and the other is to save the clean and bright iron-scrap from rusting. Washing with water dissolves simultaneously the iron-chlorid with the tin-tetrachlorid and from this solution tin can be recovered but with great difficulties and the tin will be lost. As even these little quantities lost daily amount in the long run to a considerable quantity I tried several ways and found washing the detinned iron-scrap with a solution of sodium-sulfate as the most suitable method to recover the last remains of tin contained as tin-tetrachlorid in the spongy layer of iron chlorid. Now this sodium-sulfate solution dissolves iron-chlorid as well as tin-tetrachlorid, but the tin-tetrachlorid is precipitated out of the washing fluid in the form of tin-hydroxid according to the equation:

$$SnCl_4 + 4Na_2SO_4 + 4H_2O = Sn(OH)_4 + 4NaCl + 4NaH.SO_4.$$

This tin-hydroxid is completely precipitated by heating the washing-fluid and after filtering it from the liquid it is dissolved in sodium hydrate to sodium tannate in which form it is much used in the cloth-printing industry. Since by the washing with sodium-sulfate the detinned iron is exposed to the corrosive action of sodium-bisulfate, the detinned iron-scraps are thereupon washed with water and to be sure to neutralize the last traces of acid salt adhering to the bundles of detinned iron the latter are dipped in a bath of sodium-carbonate solution.

The precipitation of tin in the form of tin-hydroxid only takes place when the sodium-sulfate solution is of neutral reaction. As sodium bisulfate is formed by the precipitating process the washing fluid is neutralized by caustic soda or quick lime before it is used for another washing-process.

I will now completely describe my process.

The bundles of tin-scrap are first submitted to a separating process provided the manufacturing concerns do not supply the tin-scrap with varnish and other impurities separated from those free of varnish etc. The tin-scraps are washed in a bath of caustic soda, rinsed with water and then dried in a drying chamber. The bundles of tin-scraps are then packed into a suitable receptacle which may be of iron, stone or brickwork and in which the action of chlorin on the tin scrap takes place. It is the first requirement that the chlorin gas be absolutely dry and that besides the naturally required openings for the entrance and exit of the chlorin gas all other openings are duly closed in order to protect the attendants against the effects of the chlorin gas and fuming tin-tetrachlorid and to avoid any losses of materials.

The chlorin gas may be used in the concentrated or diluted form and is introduced into the receptacle at the bottom, passes through the receptacle and leaves, if it is not absorbed by the tin, through an opening on top of the receptacle. The tin-tetrachlorid generated by the reaction is drained off through the bottom into a collector. Special care is taken that the temperature caused by the reaction does not rise too high and steps have to be taken to keep it as low as possible.

In order to distribute the chlorin equally over all the vessels the latter are joined parallel in the same way as the elements of a galvanic battery so that they have both the main-supply-pipe and main-exhaust-pipe in common. There escapes a varying quantity of chlorin gas which depends on the degree to which the detinning process has progressed. For most of the time the detinning process is going on only a moderate quantity of chlorin gas is entering the main exhaust-pipe.

If the process is nearly finished then a greater quantity of chlorin gas will escape

unused to the main exit pipe and that is corrected either by reducing the production of chlorin by the electrolytic cells or one forwards this unused gas to another main line of detinning vessels which were emptied and prepared again for the process and which must be ready again for their turn.

The partial vacuum in the detinning vessels is maintained by a vacuum-pump. The reserve detinning vessels taking up the last traces of chlorin gas are not directly connected with the vacuum-pump. For greater security against losses a small tower of suitable material is inserted between the reserve-vessels and the vacuum-pump. This tower of moderate size is filled with granulated tin or any other granulated metals, the chlorid of which is soluble, over which just enough water is running from top to the bottom to keep the granulated tin moist enough. Liquids for the absorption of traces of chlorin gas are not reliable enough as such liquids, when approaching the point of saturation do not absorb chlorin gas fully and must be too often renewed, whereas a granulated metal like tin, always kept moist, readily absorbs the last traces of chlorin gas and besides has the great convenience, that one filling of granulated tin goes for a considerable long time. The resulting solution of tin-tetrachlorid may be made the basis of marketable products by enriching it with more tin-tetrachlorid.

As soon as the process is finished one detaches the collector below, the bottom, introduces compressed air through the top of the vessel whereby the remaining detinned iron-scraps are freed of the tin-tetrachlorid vapors, and the chlorin gas is driven out too. The detinned iron-scraps are then given a wash with a sodium-sulfate solution whereby the thin layer of iron chlorid is dissolved as well as the tin-tetrachlorid which is kept back by the spongy iron chlorid and is not always fully given off. This washing-fluid, containing now both iron chlorid and tin-tetrachlorid, is then occasionally heated until the tin is completely precipitated in the form of tin-hydroxid, a form which allows easily its working up into marketable form. After this washing with sodium-sulfate solution the iron scrap bundles are well washed with water to remove the sodium bisulfate from the bright surface and in order to counteract any corrosion by this acid salt the bundles of iron-scrap are finally dipped in a bath of sodium carbonate.

The advantages of my process are demonstrated by the following description:

The applying of a vacuum has long been done in the chemical industry when chemicals of high boiling point could not be distilled except with decomposition of the chemical matter. The losses sustained by this decomposition consist both in direct loss of raw material and in the inability of producing a pure chemical stuff the resulting products being mostly spoiled by such decomposed matter to a great extent.

There has come into use therefore the method of distilling such perishable chemicals under partial vacuum thereby lowering the boiling point to such a degree that the distillation goes on without decomposition. The situation in the detinning process is a strikingly similar one. By maintaining the partial vacuum in the detinning vessels the chlorin gas is in a kind of diluted state and the action of the chlorin gas goes on in a moderate way keeping down the temperature and avoiding the generation of iron-chlorid so that I can determine my process as "a process for distilling off tin under a partial vacuum by means of chlorin gas."

The process is carried out in a dry state. Owing to the absence of water the chlorin gas acts only on the upper layer of tin and finally on the very thin layer formed by the alloy of tin and iron reducing thus the generation of iron-chlorid to a minimum.

The partial vacuum maintained in the detinning vessels throughout the process allows most conveniently the control of the temperature and the keeping of it as low as possible. The vacuum is easily maintained in the same degree over all the detinning vessels and the necessary regulations do not require much time and can be done in a very short time by a single man. This method saves therefore a good deal of labor. A most important factor is involved in the application of vacuum, as it excludes the many and most serious troubles which in case of a leak take place with the application of pressure to the vessels. In case the chlorin gas, in whatever form it may be used, is acting on the tin-scraps while the vessels are standing under pressure and an accident should occur the health of the attendants is exposed to the most serious danger which with great probability may result in either death or permanent injury. In the pressure process all gaseous products coming in question have in case of a leak the tendency to escape into the open air whereas in my vacuum process those gaseous products have the tendency to remain in the vessel instead of escaping to the outside and this tendency extends even to the gaseous chlorin generated in the electrolytic cells. It is evident that the vacuum process not only avoids losses of raw-materials but is a great safeguard in regard to the health of the attendants.

The low temperature maintained by the vacuum-process produces the tin-tetrachlorid in the possible greatest purity. The washing of detinned iron-scraps with a solution of sodium-sulfate permits the recovery even

the least traces of tin from the washing fluid containing simultaneously iron-chlorid and tin-tetrachlorid and furthermore the obtaining of this tin in a chemical form which easily admits of its transformation into a marketable form.

The bright surface of the tin-scraps, essential for their use in the steel-furnace, is perfectly obtained by the wash with sodium-sulfate solution and water respectively and by neutralizing the last traces of sodium-bisulfate with sodium carbonate.

Having thus fully described the nature of my invention, I claim as new and desire to secure by Letters Patent:

1. Process of detinning tin-scrap and the like raw-material and recovering the tin in form of chemical compounds and the iron in form of iron-scrap, consisting in treating the tin-scrap or the like material with dry chlorin gas in receptacles, in giving the chlorin gas the largest possible surface of tin by delivering simultaneously the chlorin gas in as far as possible equal quantities into all of said receptacles by equally and simultaneously maintaining a partial vacuum in said receptacles during the time the action of chlorin gas on tin takes place, in removing the chlorin gas and the tin-tetrachlorid out of the receptacles and in afterward washing the iron-scrap for recovering the last traces of tin-tetrachlorid and removing the chlorid of iron from the iron-scrap.

2. Process for detinning tin-scrap and the like raw-material and recovering the tin in form of chemical compounds and the iron in form of iron-scrap, consisting in treating the tin-scrap or the like raw-material with dry chlorin gas in receptacles, in giving the chlorin gas the largest possible surface of tin by delivering simultaneously the chlorin gas in as far as possible equal quantities into all of said receptacles by maintaining equally and simultaneously a partial vacuum in said receptacles, in joining said receptacles in parallel for maintaining the partial vacuum simultaneously in all vessels, in removing the chlorin gas and the tin-tetrachlorid out of the receptacles and afterward washing the iron-scrap for collecting the last traces of tin-tetrachlorid and removing the chlorid of iron from the iron-scrap.

3. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scrap with dry chlorin gas in a receptacle, removing afterward the chlorin gas and the residue of tin-tetrachlorid by compressed air and washing the iron-scraps with a solution of sodium-sulfate to collect the last traces of tin-tetrachlorid and removing the chlorid of iron adhering to the detinned iron-scrap.

4. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scrap with dry chlorin gas in a receptacle and removing the chlorin gas and the residue of tin-tetrachlorid by compressed air, washing the iron-scrap by sprinkling them in the receptacle with a solution of sodium sulfate, treating them afterward in a separate vessel with a solution of sodium-sulfate and agitating the sodium-sulfate solution either to completely collect the last traces of tin-tetrachlorid and removing the chlorid of iron from the detinned iron-scrap.

5. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scrap with dry chlorin gas in a receptacle, removing the chlorin gas and the residue of tin-tetrachlorid by compressed air, washing the detinned iron-scraps with a solution of sodium-sulfate and afterward washing the detinned iron-scraps with water for removing the sulfate washing-fluid from the detinned iron-scraps.

6. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scrap with dry chlorin gas in a receptacle, removing the chlorin gas and the residue of tin-tetrachlorid by compressed air, washing the detinned iron-scrap with a solution of sodium-sulfate, then rinsing the detinned iron-scraps with water and afterward dipping them into a solution of soda to neutralize any trace of sodium-bisulfate may adhere to the iron-scrap.

7. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scraps with dry chlorin gas in a receptacle, removing the chlorin gas and the residue of tin-tetrachlorid by compressed air, washing the detinned iron-scraps with a solution of sodium-sulfate, afterward rinsing the iron-scrap with water, then dipping the iron-scrap into a bath of soda solution and in heating the sodium-sulfate bath for completely precipitating the tin in the form of tin-hydroxid from the solution.

8. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scraps with dry chlorin gas in a receptacle, removing the chlorin gas and the residue of tin-tetrachlorid by compressed air, washing the detinned iron-scraps with a solution of sodium sulfate, afterward rinsing the iron-scrap with water, then dipping the iron-scrap into a bath of soda solution and restoring the neutral reaction of the sodium-sulfate washing fluid by treating it with alkalies or earth-alkalies or carbonates.

9. Process for detinning tin-scrap and the like raw-material, consisting in treating the tin-scraps with dry chlorin gas in a receptacle, absorbing the chlorin gas supplied in excess and escaping through the exit in a tower filled with granulated tin or other metals forming soluble chlorid-compounds,

moistening such metal in the tower by introducing water or steam through the tower on top of the metal, removing the chlorin gas and the residue of tin-tetrachlorid after finishing the process by compressed air, washing the detinned iron for saving the last traces of tin and removing the iron chlorid adhering to the detinned iron-scrap.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

OTTO K. ZWINGENBERGER.

Witnesses:
CELIA WOLF,
JOEL H. RIBETH.