

# UNITED STATES PATENT OFFICE.

ADOLPHE JEAN MARIE THIROT, OF BOURGES, FRANCE, ASSIGNOR TO HIMSELF, AND LOUIS AUGUSTE MAGE, OF AVIGNON, FRANCE.

## ELECTROLYTIC PRODUCTION OF PURE TIN.

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*To all whom it may concern:*

Be it known that I, ADOLPHE JEAN MARIE THIROT, of 83 Rue Bourbonnoux, Bourges, Cher, Republic of France, engineer of arts and manufactures, have invented an Electrolytic Production of Pure Tin, of which the following is a full, clear, and exact description.

The present invention has for its object a process relating to the extraction of tin, in the form of pure metal, either from stanniferous slimes or from natural tin ores which have previously undergone a mechanical preparation, as energetic oxidizing roasting and lixiviation, or again from all products capable of yielding stannate of soda, by the wet or the igneous process, such as tin drosses, tin work waste or old tin plate.

If the product treated is bronze, nearly all of the tin derived therefrom is found in the form of stannous hydrate, which it is advisable to preliminarily transform into stannic hydrate. This oxidation takes place after washing the slimes, being effected naturally, at the surrounding temperature, in the course of exposure of the slimes to the air, with a view to their desiccation, by atmospheric action.

The impurities found, will always be constituted, whatever the origin of the product operated upon, by hydroxids, oxids, sulfates, arsenites, arseniates, antimonites, antimoniates, of common metals, such as copper, lead, iron, bismuth, &c. In the case of slimes resulting from bronze, there might be found appreciable traces of silver and of gold. If the product treated is tin work waste, or tin dross, it will contain as impurities principally iron, lead and copper.

The process which forms the object of the invention, comprises three principal operations; first, the formation of a solution of stannate of soda; second, purification of this solution; and third, electrolysis of the solution.

To obtain the solution of stannate of soda, when dealing with hydroxids of tin, they are treated at the boiling point, with a ten or twelve per cent. solution of caustic soda, in iron vessels, basing the process on the fact that one liter of a twelve per cent. sodic solution can dissolve from 45 to 50 grams of tin.

The solution of caustic soda may be used again and again, it being only necessary to retain it at the normal concentration above

indicated. After electrolysis, the liquid will yet contain a certain proportion of stannate of soda corresponding to about ten grams of tin per liter.

To obtain the solution of stannate of soda, it is necessary to retain the mixture at the boiling point for about one and one-half hours, stirring it during ebullition.

To facilitate the operation, several vessels are ordinarily employed, and a methodical enrichment of the liquor is practiced, the liquid passing successively from one vessel to the other.

If the product treated is tin oxids or metallic tin partly oxidized (tin dross, tin work waste, &c), instead of tin hydroxid, the same process may be employed, but the formation of the stannate is more difficult, and it may be necessary in certain cases to form the stannate of soda by the igneous process and then dissolve it.

Except tin, there enters into the solution, only very small quantities of other metals, and of these metals copper and lead are the only ones whose presence causes difficulty. Antimony for the major part, enters into solution in the form of antimonite of soda, but in the course of electrolysis, under the action of oxygen which is disengaged at the anodes and under the action of the temperature of the electrolyte, this salt is transformed into antimoniate of soda, which is deposited in the first vats or vessels of the series during the electrolysis, on account of its insolubility in the sodic liquor. Arsenic forms arsenite and arseniate of soda, both of which are soluble. Arsenite is converted into arseniate in the same manner as the antimonite is converted into the antimoniate. The arseniate however does not electrolyze in the sodic liquor and hence accumulates in the liquor.

The precious metals remain in the waste, which may constitute a sub-product somewhat strongly argentiferous if the product treated is constituted by slimes obtained from bronze by electrolysis.

The second operation consists in the purification of the stannate solution, and is carried out while hot, about 70° centigrade usually, in an iron vessel heated by steam, or in any other suitable manner.

When the solution is at the proper temperature, sodium sulfid is added, monosulfids in preference to polysulfids, by which copper



and lead are precipitated. In practice a very concentrated solution of sodium sulfid is made use of, the amount necessary to add being approximately determined beforehand, 5 by adding a known amount of sodium sulfid to a sample of the solution, filtering, and adding more sodium sulfid to the filtrate. When no precipitate appears in the filtrate the proper amount of sodium sulfid has been 10 determined. A slight excess of sodium sulfid is however immaterial.

The liquor should be well stirred during the addition of the sulfid. After the adding of the sulfid, the liquid is permitted to clarify 15 and is decanted. The precipitate may be collected and filtered, constituting a sub-product whose composition depends on the primitive materials employed. The mother waters which are rich in stannates of soda 20 are also collected.

The electrolysis of the purified solution may be effected in iron tanks with insoluble anodes of iron and cathodes of sheets of tin or even of tin plate. It is important to 25 maintain the solution during the electrolyzing at a minimum temperature of 80 degrees centigrade, and if steam circulation is employed for the heating it will of course be necessary to guard against the steam pipes 30 placing the vats in short circuit with each other. This end may be attained by threading on the tubing short lengths of tubes of insulating material, caoutchouc for example.

The voltage necessary to electrolyze the 35 solution will be about 2.4 volts with an amperage of 300 to 400 per square meter of cathode, a single side only being counted. Twenty-five vats may be easily placed in series, one being limited in this respect only 40 by difficulties of insulation, which commences to arise when the total voltage exceeds approximately sixty volts.

In the present process, the electrolysis is effected under the following essential conditions 45 necessary to obtain a good deposit.

1st. The temperature of the electrolyte should be maintained as high as possible, at the least at 80 degrees centigrade;

2nd. An excessive amperage of current 50 should be avoided;

3rd. The electrolyte should be maintained sufficiently concentrated in stannate of soda;

4th. The electrolyte should be maintained in a fairly active circulation;

55 5th. Insoluble anodes should be employed.

The third condition requires that the solution be not exhausted by electrolysis, the concentration below which a good deposit 60 cannot be easily obtained being approximately ten grams of tin per liter. A good arrangement for this purpose consists in arranging the apparatus so that the electrolyte circulates from one vat to another through 65 tubes of caoutchouc, grouping the vats into

one or several series in each of which they are arranged cascade-wise.

The rich liquor proceeding from the purification is introduced into the upper vats and the speed of circulation is regulated so that 70 the concentration is a little above the minimum concentration permitting the obtaining of a good deposit. In practice the speed of circulation of the electrolyte is diminished until the deposit of tin on the cathodes of 75 the lower vats commences to become slightly black.

It is advisable to compensate for evaporation by a continuous addition of water in certain proportion into the liquid which 80 leaves the lower vats, so that the quantity of free or combined soda per liter be restored to the same proportion as at the commencement. By means of the above precautions and a regular conduct of the operation, there 85 can be obtained an excellent deposit of tin of a clear gray color very adherent and coherent and comparable to the electrolytic deposits of copper. If the bodies of the cathodes are of pure tin, the cathodes can be 90 stored or enter into commerce, after a simple washing in water as hot as possible.

In cases where cathodes of tin plate are employed, they can after washing and drying, be very readily cleared of the tin de- 95 posit, by a simple immersion in a bath of tin in fusion. The surplus tin fuses, and the bodies remain tinned and are capable of serving anew.

By the above process tin can be obtained 100 containing less than a thousandth of impurities.

The quantity of tin per ampere-hour may attain to 0.8 grams, when the amperage is not too strong; but when it is desired to 105 raise the amperage, the voltage is raised, the water commences to be electrolyzed, and the yield is less.

The process presents economic superiority over existing methods of electro-deposition 110 of tin, in that there may be obtained by direct deposit upon the cathodes pure tin in the form of adherent and coherent metal. Consequently the increase of expense for electric energy, due to the employment of insoluble 115 anodes and to the fact that the quantity of tin deposited per ampere-hour is rather small, is largely compensated by the suppression of operations consecutive to the electrolysis and necessary in old processes, 120 such operations consisting in washings of spongy precipitates, agglomeration by hydraulic pressure, and fusion, during which processes important losses take place due to oxidation, and in addition a spongy metal 125 even after agglomeration is the result.

The electrolyte slightly carbonates under the action of the carbonic acid of the air during the manipulations to which it is sub- 130 jected, but this carbon does not in any way



hinder the operation even when it is very appreciable. On the other hand if the primitive matters treated are slimes obtained from bronze, they contain sulfates which give rise to the formation of sulfate of soda, and this also does not hinder the other operations. In addition it is easy to separate parasitic salts, carbonate and sulfate of soda, by cooling, the fluid after electrolysis before reusing. During this cooling, the excess of sulfate and carbonate crystallizes and can be collected.

I claim:—

1. A method for producing pure tin, which consists in treating the tin compound with boiling caustic soda to form sodium stannate, purifying the sodium stannate by the addition of concentrated sodium sulfid, separating the precipitate from the solution and subjecting the solution to electrolysis.

2. A method for producing pure tin from its compounds which consists in treating the tin compounds with boiling caustic soda, purifying the resulting sodium stannate and subjecting the solution to electrolysis.

3. A method for obtaining tin from its compounds which consists in treating the compounds with caustic soda, purifying the solution and subjecting the solution to electrolysis.

4. A method for obtaining tin from its compounds, which consists in treating the compounds with caustic soda to form sodium stannate, purifying the solution, and subjecting the solution to electrolysis while maintaining the electrolyte at at least 80° centigrade.

5. A method for obtaining tin from its compounds, which consists in treating the compounds with caustic soda, purifying the solution, and subjecting the solution to electrolysis, with a current of 300 to 400 amperes per square meter of anode surface.

The foregoing specification of my electrolytic production of pure tin signed by me this 12th day of March, 1907.

ADOLPHE JEAN MARIE THIROT.

Witnesses:

HERNANDO DE SOTO,  
MAURICE H. PIGNET.