UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING TIN-BEARING MATERIAL.

1,018,734. Specification of Letters Patent. Patented Feb. 27, 1912.

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To all whom it may concern:

Be it known that I, JOSEF WEBER, subject of the King of Prussia, German Emperor, and resident of Essen-on-the-Ruhr, in the Province of the Rhine, Germany, have invented a new and useful Process of Treating Tin-Bearing Material, of which the following is an exact specification.

The process consists in a treatment of tin-bearing material, as for instance tin scrap, with an alkaline solution containing an oxidizing material as for instance saltpeter.

It has already been proposed to act upon tin-bearing material, especially tin scrap, by means of an alkaline solution to which have been added oxidizing reagents. But according to most of the proposed processes it has not been possible to completely separate the tin from the tin-coated waste. Only when subjecting the tin-bearing material in a closed vessel under a high pressure to the action of a hot alkaline solution, it was possible to remove the tin. But when treating the material under a high pressure, as for instance from 7 to 15 atmospheres, considerable drawbacks resulted, which are to be avoided when working according to the present process, that is to say, without any pressure or maintaining only a slight pressure and using a greater amount of alkali and oxidizing reagent.

In order to obtain a good output it is absolutely necessary to carefully prepare the material before being subjected to the detinning process. If, for instance, old tins are to be treated, they are first perforated, then washed with a diluted alkaline solution, preferably a solution of caustic soda, and with water, whereafter the solder is removed. If colored tinned sheet is to be treated, it must be cleaned from lacquer by means of an alkaline solution, for instance of caustic soda, and is then washed with water, whereafter it is ready for being subjected to detinning. Also white tinned sheet must be carefully washed, if it is to be subjected to this new process of detinning, in order to remove the adhering sand, alumina, lime, etc., as otherwise part of these impurities will be dissolved by the caustic soda lye and thus contaminate the solution. The thus prepared material is subjected to the action of a highly heated alkaline solution, preferably a solution of caustic soda which contains an excess of free alkali and especially also an excess of oxidizing means, as for instance saltpeter, over the theoretical amount calculated to the equation

$$2Sn+3NaOH+NaNO_3=2Na_2SnO_3+NH_3;$$

avoiding during the whole detinning process a considerable increasing of pressure in the detinning apparatus.

The process is carried out in the following way: The material, after having been subjected to the different preparing actions, is brought into a solution containing say 20 per cent. by weight of sodium hydroxid and say 10 per cent. by weight of saltpeter. The solution is boiled during about 3 hours whereafter the material is lifted out and placed into a second detinning bath containing the same amount of sodium hydroxid and of saltpeter. In this second solution the material is also left during about 3 hours, the solution being boiled, whereafter it is subjected to a treatment with water in two different tanks. During the washing action the material must be constantly agitated in order to facilitate the removing of the adhering lye, saltpeter, lead, etc. This washing water serves to fill up the detinning baths after some water has evaporated so that the original volume of the detinning baths is always maintained. In the washing water there is always formed a considerable amount of slime, containing tin, lead, iron particles, silica, lime, etc., therefore it is advisable to use this washing water for filling up the detinning baths only after the impurities have been removed. The slime is accumulated, whereafter it may be reduced by means of carbon, in order to obtain the tin and lead in metallic form, or the slime may be reduced at a low temperature and the produced metallic tin is treated with dry chlorin in order to obtain anhydrous chlorid of tin. The detinning baths may be used until a considerable amount of crystals of stannate of sodium is formed in the first bath, then the second bath is used as first bath, and a fresh solution, which is prepared in the meantime, serves as second bath. The solution saturated with stannate of sodium is concentrated so as to obtain a specific gravity of say 1.4. Nearly the whole amount of stannate of sodium will get the form of crystals, which are drawn off and subjected to centrifugal action. The remaining mother lye is diluted so as to have

a specific gravity of 1.2, whereafter such an amount of caustic soda and saltpeter is added that the solution contains say 20 per cent. of caustic soda and say 10 per cent. of saltpeter, the volume being the same as in the beginning. This solution is used as second bath, as described above, and in the further course of treatment as first bath. The stannate of soda obtained may be subjected to a further treatment by dissolving it with water and precipitating the oxid of tin by means of bicarbonate of sodium. The solution of soda obtained after the precipitation of this oxid of tin, is newly introduced in the course of the detinning operation. For this purpose it is made caustic by boiling, according to any known method, as for example with lime so as to obtain a rather clean solution of caustic soda, containing still the saltpeter crystallized together with the stannate of soda, and after addition of the necessary amount of saltpeter and after having arrived at the necessary degree of concentration, it is newly fit for the purpose of detinning. Therefore, according to the above described process, a pure oxid of tin is obtained from the tin-bearing material, whereby the alkali used in this process is always recovered and reintroduced in the course of the operation, so that only those very small losses result which are practically unavoidable. Also the saltpeter used in this process is recovered at the end of the operation, with the exception of the amount which has been necessary for the oxidation according to the equation

$$2Sn+3NaOH+NaNO_3=2Na_2SnO_3+NH_3.$$

Therefore the whole process is to be called a cyclic one.

What I claim is:

1. Process of treating tin-bearing material, which consists in reacting upon same with a highly heated alkaline solution containing a great amount of free alkali and a large excess of an oxidizing reagent over the amount required according to the equation representing the separative reaction.

2. Process of treating tin-bearing material, which consists in preparing same by washing and then reacting upon it with a highly heated alkaline solution containing a great amount of free alkali and a large excess of an oxidizing reagent over the amount required according to the equation representing the separative reaction.

3. Process of treating tin-bearing material, which consists in reacting upon same with a highly heated solution of sodium hydroxid containing a great amount of free sodium hydroxid and a large excess of saltpeter over the amount required according to the equation representing the separative reaction.

4. Process of treating tin-bearing material, which consists in preparing same by washing and then reacting upon it with a highly heated solution of sodium hydroxid containing a great amount of free sodium hydroxid and a large excess of saltpeter over the amount required according to the equation representing the separative reaction.

5. Process of treating tin-bearing material, which consists in reacting upon same with a highly heated solution containing about 20 per cent. of sodium hydroxid and about 10 per cent. of saltpeter.

6. Process of treating tin-bearing material, which consists in preparing same by washing and then reacting upon it with a highly heated solution containing about 20 per cent. of sodium hydroxid and about 10 per cent. of saltpeter.

7. The process of treating tin-bearing material, which consists in treating same with a highly heated alkaline solution containing a great amount of free alkali and a large excess of an oxidizing reagent over the amount required according to the equation representing the separative reaction, and placing the material, when the solution gets more and more saturated, into another bath containing a fresh solution of the same composition as the first, in order to effect complete detinning.

8. The process of treating tin-bearing material, which consists in preparing same by washing, then treating it with a highly heated alkaline solution containing a great amount of free alkali and a large excess of an oxidizing reagent over the amount required according to the equation representing the separative reaction, and placing the material, when the solution gets more and more saturated, into another bath containing a fresh solution of the same composition as the first, in order to effect complete detinning.

9. The process of treating tin-bearing material, which consists in treating same with a highly heated solution of sodium hydroxid containing a great amount of free sodium hydroxid and a large excess of saltpeter over the amount required according to the equation representing the separative reaction, and placing the material, when the solution gets more and more saturated, into another bath containing a fresh solution of the same composition as the first, in order to effect complete detinning.

10. The process of treating tin-bearing material, which consists in preparing same by washing, then treating it with a highly heated solution of sodium hydroxid containing a great amount of free sodium hydroxid and a large excess of saltpeter over the amount required according to the equation representing the separative reaction, and placing the material, when the solution gets more and more saturated, into another bath

containing a fresh solution of the same composition as the first, in order to effect complete detinning.

11. The process of treating tin-bearing material, which consists in reacting upon same with a highly heated solution containing about 20 per cent. of sodium hydroxid and about 10 per cent. of saltpeter, and placing the material, when the solution gets more and more saturated, into another bath containing a fresh solution of the same composition as the first, in order to effect complete detinning.

12. The process of treating tin-bearing material, which consists in preparing same by washing, then reacting upon it with a highly heated solution containing about 20 per cent. of sodium hydroxid and about 10 per cent. of saltpeter, and placing the material, when the solution gets more and more saturated into another bath containing a fresh solution of the same composition as the first, in order to effect complete detinning.

13. A continuous process of treating tin-bearing material, which consists in reacting upon same with a solution containing free alkali and an oxidizing reagent in large excess over the amount required according to the equation representing the separative reaction, recovering substantially all the alkali and oxidizing reagent and restoring said recovered reagent to the bath during the course of the reaction, substantially as described.

14. A process of treating tin-bearing material, which consists in reacting upon the same with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction.

15. A process of treating tin-bearing material, which consists in thoroughly cleaning said material, and reacting upon said cleaned material with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction.

16. A process of treating tin-bearing material, which consists in reacting upon the same with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction while said materials are maintained under substantially normal pressure.

17. A process of treating tin-bearing material, which consists in reacting upon the same with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction while said materials are maintained under substantially normal pressure, and repeating said operation in another bath containing a fresh solution in order to effect complete detinning.

18. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, converting the resulting sodium stannate into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

19. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, separating the resulting sodium stannate from the mother lye, returning said mother lye to the bath, converting said sodium stannate into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

20. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, concentrating the resulting sodium stannate solution and separating the sodium stannate from the mother lye, returning said mother lye to the bath, converting said sodium stannate into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

21. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, washing the remaining solid material, separating the slime from the solution, and recovering the tin content of said slime, converting the sodium stannate resulting from the main reaction into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

22. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, washing the remaining solid material, separating the slime from the solution and recovering the tin content of said slime,

converting the sodium stannate resulting from the main reaction into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

23. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, washing the remaining solid material, separating the slime from the solution and recovering the tin content of said slime, utilizing said wash-water solution to fill up the bath, converting the sodium stannate resulting from the main reaction into oxid of tin, restoring the remaining solution to its original caustic condition, and returning said caustic solution to the bath.

24. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, repeating said operation in a second bath containing a fresh solution in order to effect complete detinning, converting the resulting sodium stannate of the first bath into oxid of tin, and restoring the remaining solution to its original caustic condition for re-use.

25. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, repeating said operation in a second bath containing a fresh solution in order to effect complete detinning, converting the resulting sodium stannate of the first bath into oxid of tin, restoring the remaining solution to its original caustic condition, returning said caustic solution to the second bath, and utilizing the second bath as a first bath when the first bath becomes substantially saturated.

26. A process of treating tin-bearing material, which consists in subjecting said material to the action of a bath containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, repeating said operation in a second bath containing a fresh solution in order to effect complete detinning, washing the remaining solid material, separating the slime from the solution and recovering the tin content of said slime, utilizing said wash-water solution to fill up the baths, separating the sodium stannate resulting from the reaction in the first bath from the mother lye, utilizing said mother lye in the second bath, converting said sodium stannate into oxid of tin, restoring the remaining solution to its original caustic condition, utilizing said caustic solution together with said mother lye in the second bath, and utilizing the second bath as a first bath when the first bath becomes substantially saturated.

27. A process of treating tin scrap, which consists in perforating said scrap, cleaning said scrap, and reacting upon said loose cleaned scrap with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction.

28. A process of treating tin scrap, which consists in perforating said scrap, washing said scrap with an alkaline solution, then washing said scrap with water, and reacting upon said loose cleaned scrap with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction.

29. A process of treating tin scrap, which consists in perforating said scrap, washing said scrap, de-soldering said scrap, and reacting upon said loose cleaned scrap with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction.

30. A process of treating tin scrap, which consists in perforating said scrap, washing said scrap, de-soldering said scrap, reacting upon said loose cleaned scrap with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, and repeating said operation of detinning said loose perforated scrap in another bath containing a fresh solution in order to effect complete detinning.

31. A process of treating tin scrap, which consists in perforating said scrap, cleaning said scrap, reacting upon said loose cleaned scrap with a solution containing free alkali and an oxidizing reagent largely in excess of the amount required according to the equation representing the separative reaction, and washing said tin scrap.

In witness whereof I have hereunto set my hand in the presence of two witnesses.

JOSEF WEBER. [L. S.]

Witnesses:
OTTO KÖNIG,
CHAS. J. WRIGHT.