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UNITED STATES PATENT OFFICE

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METHOD OF DETINNING

No Drawing. Application filed August 30, 1928. Serial No. 303,125.

This invention relates to detinning; and it comprises a method of detinning or recovering tin from tin scrap or other tin bearing material in which the bulk of the tin is present in the metallic form with recovery of tin as such and with a cyclic use of solutions wherein scrap is detinned by solution of the tin in a caustic alkali bath of low concentration containing nitrogen oxids, the bath is removed after substantial exhaustion of the oxidizing power of said oxids and an accumulation of soluble tin in the bath, is electrolyzed to regain metallic tin and form a solution of caustic alkali, the solution is treated with nitrogen oxides and is returning for use in detinning; all as more fully hereinafter set forth and as claimed.

In the detinning art, tin scrap or other tin bearing materials are often freed from tin by the dissolving action of strong alkali solutions. Oxidation is required and as accelerated by the addition of oxidants to the bath. With the oxidants ordinarily used, such as sodium cholarate, manganese dioxide, etc., strongly alkaline solutions are regarded as necessary; concentrations of 20 to 30 per cent NaOH being ordinarily employed. These highly alkaline liquors however will not hold much tin in solution; a 30 per cent solution carrying a maximum probably of 1.5 per cent tin. As the action goes on the dissolving tin crystallizes out as sodium stannate.

In the ordinary routine operation, this separated stannate is removed from time to time, the strength of the bath being maintained by replenishing additions of caustic soda or by evaporation or by both. An inconvenience of this method is the gradual accumulation by the bath of CO_2 from the air. The sodium carbonate thus formed is useless in detinning and must be removed from the bath and be recausticized by lime from time to time.

The removed solid stannate is now treated in various ways to recover the tin. One is to remove the alkaline bath liquor from the solid stannate as far as possible and then dissolve it in water. This gives solutions containing less alkali and more tin and these are electrolyzed, giving metallic tin and a solution of NaOH. The latter is concentrated to the alkaline strength considered necessary in detinning and goes back for reuse together with the drainings and washings of the stannate.

This cycle of operations is expensive and cumbrous and is attended with the difficulty of absorption of CO_2 at every stage. It is however considered necessary since the detinning bath liquor is not adapted to electrolysis because of its high content of alkali and its low content of tin.

It is well known in the industry that the highest concentration of caustic in a tin plating bath, consistent with efficient electrolysis and adherent deposits, is in the neighborhood of 5 per cent sodium hydroxide. It is also known that the plating efficiency is greatly reduced by the presence or oxidizing agents in the plating bath. Thus the presence of oxidizing agents, while advantageous in detinning is highly detrimental in the plating bath. I have found that by using a low caustic alkali concentration and a more highly reactive oxidizing agent in a cyclic process the disadvantages of prior processes have been obviated. A high tin content is obtained in the detinning bath and the oxidizing agent substantially diappears before the liquor is transferred to the tin plating bath.

In my invention the same body of liquid is used alternately in detinning and in electrolysis. The detinning bath contains a concentration of sodium or potassium hydroxid, usually sodium, sufficiently low so that it may be used later for electrolysis. To this bath is added a portion of the same bath which has been gassed with gaseous nitrous oxids until the caustic has been neutralized. It is advantageous to use nitrous oxids of such composition that the resulting product in solution is principally sodium nitrate, as this is a very efficient oxidant, much more so than those now in common use. Such nitrous oxids may be formed in various ways, but I regard those formed by the catalyzed oxidation of NH_3 by air as most satisfactory. These gases on absorption by soda solution give sodium nitrite with a small amount of sodium nitrate.

This solution I have found will detin satisfactorily and may be used until the tin con-

centrations reach five to six per cent. In the solution of the tin, the nitrogen acids existing as salts in the solution are reduced, their oxygen serving in the formation of sodium stannate. Reduction may go as far as to form ammonia which escapes from the bath and can be collected if desired. The solution at this time is one of sodium stannate containing some free alkali.

The stannate solution is transferred to an appropriate electrolytic bath and electrolyzed to deposit metallic tin on the cathode. As the tin is deposited the combined alkali of the stannate remains in the bath as free caustic alkali. The tin may be completely removed by electrolysis or the electrolysis may be stopped when the efficiency becomes low. A portion of this solution is returned to the detinning bath to supply the free caustic necessary to dissolve the tin. The balance is gassed with nitrous oxides in any convenient way. Contact of gas and liquid may be in a tower if desired. The nitrous oxids form sodium nitrite and some sodium nitrate. Any CO_2 which may have been picked up by the alkali solution is expelled by the action of the nitrous oxids. The gassed solution is returned to the detinning bath to supply the necessary oxidant.

While I have spoken more specifically of a soda solution, it will be understood that potassium salts may be used in its lieu. The present bath being used cyclically there is no necessary loss of alkali and potassium salts may therefore be used in spite of their higher cost. The use of the same bath for dissolving tin in one operation and for electrolytic recovery of tin in another is an important simplification of the detinning process. It obviates the usual necessity of using a strong bath for detinning and a weaker bath for electrolysis. It also obviates the necessity for a separation and washing of the stannate crystals, dissolving the crystals in the plating bath and for concentrating the spent plating bath and causticizing the liquor preparatory to reconstituting the detinning bath. By completely neutralizing the alkali in the portion of the bath gassed with nitrogen oxids all the CO_2 in that portion of the solution is expelled. This obviates much expense and inconvenience incident to causticizing with lime.

What I claim is:

1. In detinning material containing metallic tin, the process which comprises dissolving the tin in a solution of caustic alkali containing reaction products of vitrous gases with said alkali.

2. In detinning, the process which comprises contacting nitrous gases with a solution of caustic alkali and detinning tin bearing material with the bath so formed.

3. In detinning, the process which comprises oxidizing ammonia by air to form nitrous oxids, dissolving said oxids in caustic alkali solution and detinning tin scrap with the bath so formed.

4. In a cyclic process of detinning, the steps of dissolving tin from tin scrap in a caustic solution containing nitrites, separating the solution from the scrap when the tin concentration has reached the neighborhood of 5 to 6 per cent and the nitrites have substantially disappeared, removing tin from the solution by electrolysis, adding nitrites to the solution and repeating the cycle.

5. In detinning tin scrap and recovering metallic tin, the process which comprises detinning the scrap in a nitrite containing caustic alkali solution of such a concentration that upon tin plating a substantial current efficiency and adherent deposits of tin are obtained, separating the solution from the scrap when the solution contains a substantial concentration of tin and plating out the major portion of the tin.

6. In detinning tin scrap and recovering metallic tin, the process which comprises detinning the scrap in a caustic alkali solution containing the reaction products of nitrous gases and said alkali, separating the solution from the scrap when the solution contains a substantial concentration of tin, removing the major part of the tin from the solution by electrolysis, adding nitrous gases to at least a portion of the solution and repeating the process.

7. In a process of detinning by means of caustic alkali solutions containing oxidizing agents, the step which consists in dissolving tin in an electrolyte comprising a caustic alkali solution containing nitrites, of such a caustic alkali concentration that upon tin plating a substantial current efficiency and adherent deposits of tin are obtained.

8. In detinning material containing metallic tin, the process which comprises dissolving the tin in a solution of caustic alkali containing nitrites.

In testimony whereof I affix my signature.

EMANUEL KARDOS.

CERTIFICATE OF CORRECTION.

Patent No. 1,798,607.

Granted March 31, 1931, to

EMANUEL KARDOS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 24, for the misspelled word "cholarate" read chlorate; same page, line 91, for "nitrate" read nitrite; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of June, A. D. 1931.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.