

# UNITED STATES PATENT OFFICE.

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## PROCESS OF RECOVERING TIN FROM TIN-SCRAP.

SPECIFICATION forming part of Letters Patent No. 322,157, dated July 14, 1885.

Application filed March 23, 1885. (No specimens.)

*To all whom it may concern:*

Be it known that I, CHARLES A. CATLIN, of Providence, in the county of Providence and State of Rhode Island, have invented a new and useful Improvement in the Process of Recovering Tin from Tin-Scrap and other Tinned Metallic Surfaces, which improvement is fully set forth in the following specification.

The present invention has for its object the utilization of waste tinned scrap, old tin, or other tinned metallic surfaces by recovering therefrom the tin in a form capable of commercial use.

In Letters Patent No. 190,550, granted May 8, 1877, to myself and George F. Wilson, a process of recovering tin is described, according to which the scrap to be treated is first sprinkled with common salt (or other chloride) and nitrate of soda (or other nitrate) and then immersed in a hot or boiling solution of caustic soda or potash, whereby the tin is oxidized, and uniting with the soda forms a stannate of soda. The tin is subsequently recovered in that form, either by evaporation of the tin-charged solution to a solid mass or by crystallization of the stannate salt. If metallic tin is desired, it is recovered from the stannate salt by smelting. This process is open to the objection that the smelting operation necessary for the recovery of metallic tin is very difficult and expensive, so much so as to prevent its being commercially successful, and, moreover, the soda of the stannate is lost in smelting, while the uses of stannate of soda in the arts are comparatively few, and there is not, therefore, a demand for its manufacture on a large scale.

The present invention is an improvement upon the process set forth in the aforesaid patent, and is designed to overcome the objections pointed out and to recover the waste tin in an available form, either as metallic tin or as an insoluble stannate.

According to my present process the caustic alkaline bath is prepared, the scrap sprinkled with nitrate of soda or other nitrate, and treated in said bath while boiling or hot, as described in the aforesaid patent. In carrying out the present process the addition of the common salt is preferably omitted. When the charging with tin has reached the

point desired, the boiling of the bath being maintained, I add thereto a proper quantity (depending upon the amount of tin in solution) of an oxide or salt capable of causing precipitation of the tin in the form of an insoluble stannate. The precipitant preferably employed for this purpose is lime in the form of dry slack-lime or milk of lime, though under some circumstances the quicklime may be added directly to the bath. The insoluble stannate thus procured may be readily converted by smelting into metallic tin, or may be converted by subsequent processes into other salts of tin.

In order that the invention may be fully understood by those skilled in the art to which it appertains, I will explain in detail the manner in which the process is or may be carried out.

A caustic alkaline bath is prepared in a suitable boiler and the heat raised to the boiling-point. The strength of the bath may advantageously be about 15° Baumé. The waste tin or scrap is then sprinkled with a suitable nitrate (nitrate of soda is preferred) in the proportions of from three to five pounds of nitrate to every hundred pounds of tin-scrap, and the charging with tin is carried on until the solution (the volume being maintained with water) has a strength of from 23° to 25° Baumé. The boiling of the bath is maintained (though this is not absolutely necessary) and a proportion of lime is added by degrees, the amount depending upon the quantity of tin to be removed.

Should the bath be impaired by the excess of carbonate of soda present, an additional amount of lime may be added to decarbonate the bath; but it is preferred ordinarily to keep the quantity of lime within the saturating capacity of the tin present, thus avoiding excess of lime in the precipitate formed.

When the carbonate of soda becomes a source of trouble, a further addition of lime may be added, after the tin has been removed, to decarbonate the solution, which process being well understood need not be particularly described.

While the lime, preferably in the form of dry slack-lime, or milk of lime, may be added to the bath all at once, it is found better

to introduce it gradually, a little at a time. By this addition the oxide of the tin is taken from the stannate of soda, and uniting with the lime (oxide of calcium) forms stannate of lime, (stannate of calcium,) which, being insoluble in the liquid, on stopping the agitation falls to the bottom, leaving the clear solution of soda above. This solid precipitate is now to be removed to a drainer, either by scooping it out or by drawing off the soda solution and then removing it, or otherwise. By draining it parts with the greater portion of the caustic mother-liquor, and may be entirely freed therefrom by washing, the drainings and wash-water being returned to the bath.

The tin of the insoluble stannate thus produced may readily be reduced to metallic form by smelting; or it may be converted into other salts of tin for which there is an industrial use; or if, instead of using oxide of calcium as the precipitant, a metallic oxide or salt be employed the stannate obtained may, by reduction directly, produce certain valuable alloys—such, for example, as the metal obtained by reduction of stannate of copper.

It will be seen that by the above process the alkali of the solution, as well as the tin, is recovered. In fact, there is no consumption of caustic soda other than that entailed through loss in handling, which, however, will be more than supplied by the soda acquired from the nitrate used in treating the tinned scrap. Under favorable circumstances this acquirement may be so great as to necessitate removal of some of the caustic soda. The bath, therefore, being freed from the tin oxide, may be reused, after first, if necessary, decarbonating with lime, as before explained. When this decarbonating process is to be carried out, all the tin should first be removed; but otherwise it is not necessary to remove all the tin at any one operation, as there would be no loss incurred by allowing a portion of it to remain.

It is obvious that any of the soluble salts of lime may be employed for the removal of the tin from the caustic bath by double decomposition, producing the stannate of lime. Indeed, it is or may be an advantage to use the nitrate of lime, thus providing the nitrate for the treating process and the lime base at the same time; but it will be understood that the invention is not confined to the use of lime, since any other salt or oxide which will cause precipitation of an insoluble stannate either by simple reaction or double decomposition may be used instead—such, for example, as those of the alkaline earths and metallic oxides and salts. Neither is the invention confined strictly to the details of procedure and proportions above set forth, since modifications other

than those indicated may be made therein without departing from the spirit of the invention. It is possible, for example, under certain conditions, to add the precipitants at the outset, and the stripping of the tin and precipitation of the stannate may thus be attained at the same time. It is obvious, moreover, that the use of the improvement described is not confined to the treatment of a stannate solution produced in the manner above set forth, but is equally applicable to the precipitation of valuable products of tin from stannate solutions of any kind.

Having now explained the invention and the manner of carrying the same into effect, it may be observed, in conclusion, that it has long been known as a chemical fact that the alkaline stannates can be decomposed by the alkaline earths—such as lime, for example—but, so far as I am aware, the fact has met with no industrial application, and certainly has not been applied in the manner or connection and for the purposes of the present invention; and it may also be observed that heretofore many methods for recovery of tin from scrap have been proposed in which the tin is to be dissolved and then precipitated, and in some of which lime has been the precipitating agent; but the precipitate has always, so far as I am aware, been an oxide of tin, and when lime has been used its operation is to unite with the acid of the tin compound and go into solution, the tin precipitating as oxide, whereas in the present invention the lime or basic body unites with the tin and is precipitated along with it, leaving the solution free.

What I therefore claim is—

1. The process of recovering tin from tinned metal, scrap-tin, and the like by dissolving the tin in an alkaline bath and precipitating it therefrom in the form of an insoluble stannate, substantially as described.

2. The process of recovering both the tin and alkali from a solution of alkaline stannate by precipitating the tin from the solution in the form of insoluble stannate, leaving the alkali in solution, substantially as described.

3. In the process of recovering waste tin, the improvement consisting in dissolving the tin in an alkaline bath and adding to the solution a suitable oxide or salt, (such as oxide of lime,) whereby the tin is precipitated in the form of an insoluble stannate, substantially as described.

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

CHAS. A. CATLIN.

Witnesses:

EDWARD E. DARLING,  
COURTLAND W. GILMORE.