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PROCESS FOR PRODUCING FLUORIDES

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This invention relates to methods for reducing the tin content of stannates to stannous form, and is more particularly related to processes in which an alkali fluostannate is converted to a stannous fluoride and an alkali fluoride by effecting contact of the fluostannate with molten tin, preferably in the presence of residual stannous fluoride.

In aqueous solutions for the electrodeposition of tin, it is desirable that the tin be in stannous form in order to achieve a maximum current efficiency. An excellent tin electrodepositing solution may, for instance, contain stannous fluoride and preferably also sodium fluoride. Unfortunately, in the large-scale use of such a solution as, for instance, in a continuous strip plater for depositing the tin on sheet steel, it is practically impossible to avoid a certain amount of oxidation of the stannous salts present. It is necessary, for instance, in most strip platers to agitate the solution at a rapid rate, and while the rate of oxidation may be minimized by excluding air as much as possible during such agitation, the oxidation cannot be prevented entirely.

The result of the oxidation in a sodium fluorides stannous salt bath is the formation of a sludge of sodium fluostannate. While this sludge does not seriously interfere with the operation of the bath, nevertheless, the tin in the sludge is no longer available for electrodeposition and eventually the sludge must be removed for best operation of the bath. Ordinarily, the removal of the fluostannate sludge presents no difficulty, since it may be settled out or filtered out of the bath. The recovery of the tin content of the sodium fluostannate baths, however, presented a difficult problem.

Now I have found that if sodium fluostannate is brought into contact with molten tin, preferably in the presence of stannous fluoride, the stannic tin is reduced to the stannous form and there is obtained a mixture of stannous fluoride and sodium fluoride which may be reused to advantage in sodium fluoride-stannous salt electroplating solutions.

By the use of a process of this invention, the entire tin content of a sodium fluostannate sludge, such as results from oxidation in a sodium fluoride-stannous salt electroplating bath, may be completely recovered in a form suitable for adding directly to the bath. The bath thus becomes self-sustaining; that is, the salts recovered from the sludge replace electrolyte lost by dragout from the solution. The products of my recovery processes may be in the form of a complex compound of stannous fluoride and sodium fluoride, but this complex is readily soluble in the bath and its use presents no difficulty.

In carrying out a process of my invention, I prefer to use the sodium fluostannate in a dry form since danger is involved if there is moisture present in the material added to the molten tin. The molten tin may advantageously be contained in a nonmetallic receptacle, such as a graphite crucible. The fluostannate may be added in any suitable manner, but it is preferred that the addition be gradual and that the tin and fluostannate be mixed thoroughly after each addition. Continuous mixing in combination with continuous addition of fluostannate gives the best results.

The tin should be maintained in a molten condition at all times, but it is preferred to have the temperature not substantially higher than is necessary to maintain this molten condition. Account must be taken of the cooling effect of the foregoing stannate additions. I have found that ordinarily excellent results may be obtained by maintaining the tin in a temperature range of about from 300 to 500° C.

The fluostannate should be allowed to remain in contact with the molten tin for a time sufficient to reduce the stannic tin to stannous form. Once intimate mixture of the fluostannate and molten tin has been obtained, the reduction proceeds rapidly and is usually complete in a few minutes.

The proportions of fluostannate and tin used may be widely varied, depending on the manner of operation, but in any event the tin should be at least stoichiometrically equivalent to the fluostannate; that is, one mol of tin for one mol of fluostannate. It may be desirable in some circumstances to maintain a residue or heel of molten tin, tapping the reduced product off the top of the residue.

The nature of my invention and its manner of application may be more readily understood by reference to the following illustrative example.

Example

This sample was carried out in a graphite crucible heated by gas and fitted with a tap tube about 3 inches above the bottom for removal of the reduced material.

Two pounds of molten tin was placed in the crucible, melted, and maintained at a temperature in the range of 300 to 500° C. Two pounds of sodium fluostannate, obtained as a sludge from a sodium fluoride-stannous salt electrodepositing

bath and dried at a temperature of 100° C., was added to the tin in small increments over a period of one hour with periodic stirring to insure contact between the molten tin and the sludge. The reaction products were very fluid and were removed through the tap tube. The reduced product was found to be readily soluble in water and by analysis was found to contain the following:

	Per cent
Stannous tin	50.6
Stannic tin	4.8
Fluoride	23.0
Sodium	10.7
Insoluble	10.0

While in the foregoing description of this invention, I have shown certain specific processes, it should be understood that without departing from the scope of my invention, one skilled in the art may employ numerous processes for reducing sodium fluostannate with molten tin.

I claim:

1. In a process for converting the tin content of sodium fluostannate to the stannous form, the step comprising bringing the sodium fluostannate into contact with molten tin.

2. In a process for converting the tin content of sodium fluostannate to the stannous form, the step comprising bringing the sodium fluostannate into contact with molten tin in the presence of stannous fluoride.

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