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DISCUSSION.

Mr. W. C. Prebble said there were one or two criticisms he would venture to make. He thought the author's method of removing the tin paste by scraping it away with a T-square very crude. Something of the nature of an endless band which could be worked from the same motor as the pump would surely be preferable, and such a device would probably do away with the necessity of "agitating the cathode in a special way" referred to in one of the papers. Mr. Gelstharpe spoke of using a lead or block tin pump. That would hardly be satisfactory with an hydrochloric acid solution; one of Doulton ware or copper would probably meet his requirements better. The author also remarked, "tin paste is deposited best in an acid solution," and the hydrochloric acid must be arsenic free. Now in the production of zinc paste, a process analogous to that of tin paste, it was found advantageous to use an alkali solution, and the presence of arsenic actually favoured the formation of sponge in an acid solution. In the case of zinc paste, it was found necessary to dry *in vacuo*, otherwise the paste would fire. Had the author experienced the same difficulty with tin? He thought it hardly probable that an alloy of either sodium or hydrogen was formed under the

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conditions mentioned ; hydrogen was probably merely held mechanically by the paste.

Dr. O. J. Steinhart in referring to the numerous attempts that had been made to practise successfully detinning, said that it used to be objected that there was no tin scrap to be had. But there was a process now at work in London, at the London Electron Works, Limehouse, where about ten thousand tons of scrap were being treated annually, and treated economically and well. Perhaps a few of the experiences in connection with this process he had obtained from Mr. de Back, might be put before the meeting. He quite bore out the contention of Mr. Gelstharp as to the value of agitating the cathodes ; he could not agree, however, that the deposited tin-mud floated to the top of the baths ; on the contrary, in practice it always dropped to the bottom. One of the chief difficulties was how best to utilise the product. If it were simply removed from the vat, washed, and dried in air, it oxidised to a large extent, and was difficult to smelt. Could any one suggest how to get over this trouble in a practical way, as the method would be of undoubted value ? The tin-mud could not just be melted down, because in that case it nearly all drosses or oxidises.

The current efficiency of the process he was referring to was very remarkable, being sometimes higher than that allowed by Faraday's law. Here again he was unable to suggest a satisfactory explanation. The voltage used was very low, and a current density of 10-15 amperes per square foot was employed.

Dr. J. C. Cain, speaking from the point of view of the pure chemist, objected to the author's supposition that sodium was thrown down in an alloyed form with the tin paste. The evolution of gas observed was much more likely to be due merely to occluded hydrogen.

Dr. F. M. Perkin thought that the apparently high current-efficiency referred to by Dr. Steinhart was caused by the presence of oxide and other impurities in the deposited tin. He had examined some tin-mud, and found in it considerable quantities of iron and copper. (Dr. Steinhart explained that the high current efficiency he had spoken of was calculated on assays of the tin actually present in the deposit, so that impurities were taken account of.)

He agreed with previous speakers in doubting whether sodium could be deposited from a dilute aqueous solution, even as an alloy. Perhaps the effects noticed by Mr. Gelstharp were due to finely-divided zinc, which was also able to decompose water with evolution of hydrogen.

The Chairman, in moving a vote of thanks to Mr. Gelstharp, said that several years ago he had worked at detinning. He always found that the chief difficulty encountered was not to recover the tin but to get hold of the scrap.

Referring to the author's suggested use of iron in contact with the tin scrap in order to start the reaction, there was one rather curious thing he had noticed. If a piece of tin and a bit of iron nail be put together into a test tube with some dilute caustic soda, tin will be deposited on to the nail, and the peculiar part about the action is that it does not necessarily stop, as one would expect, as soon as the nail has any deposit of tin. There appears to be a stannate and a stannite of soda.

He disagreed with the speakers who had doubted the possibility of sodium being deposited along with the tin. Sodium was readily deposited into mercury from an aqueous caustic solution, and there was no reason why it should not similarly be deposited alloyed with tin.

Mr. H. Sayer said he would have liked to put one or two questions to

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the author had he been present. In the first place he would like to ask what percentage of the total tin present was recovered by Mr. Gelstharp's process. He was inclined to think that the alkali process would leave untouched the iron-tin alloy that exists at the surface junction of the metals because the iron hydrate formed would tend to prevent the complete solution of tin, and the iron scrap would thus retain a quantity of tin, probably quite sufficient to prove deleterious in steel manufacture.

He referred to the published statements in connection with detinning processes that tin scrap carries from 3-9 per cent. tin, and stated that for ordinary tin plate only 2 lbs. 4 oz. to 2 lb. 6 ozs. per box of 112 lbs. is actually used.

Dr. O. J. Steinhart : Light scrap usually contains about 1.7 or 1.8 per cent., and heavy scrap about 2 per cent. of tin. In the process I have already referred to the recovery is about 95 per cent. Regarding the question of contamination raised by Mr. Sayer, I can assure him that the scrap iron is all sold to steel-makers, who take it most readily.

Mr. H. Sayer, continuing, said that, referring to the paper on tin paste, he had recently heard of a patent process, in which the stripping was done in an alkaline solution under conditions which gave a thick adherent deposit on tin on the cathode. The deposit on removal from the bath was compressed and made the anode in a bath of hydrochloric acid, and the tin recovered in the form of paste on tinned iron cathodes.

Mr. A. C. Bawtree (*communicated*) : In 1899 I had to carry out experiments with the object of producing tin in the form of a fine powder by electrolysis at a cheaper rate than by the zinc reduction method. I made very numerous tests with varying compositions of electrolyte and under different conditions as to temperature, current density, agitation, etc. The great difficulty was to avoid the production of crystalline deposits. I obtained the best results with an electrolyte containing SnCl_2 0.5 per cent., SnCl_4 0.33 per cent., temperature 15°C . Relative area of anode to cathode 1 to 3, agitation of solution once every hour. The solution remained clear. A little gas was evolved at the cathode. The tin fell continuously to the bottom of the vat as a mud, from whence (the vat being funnel-shaped) it would be readily tapped off. E.M.F. between electrodes 2.32 volts. The process was rendered still more continuous by the substitution for the anode of a celluloid crate with fine perforated sides, into which dipped conductors of tin rod, and which was frequently filled up with feathered or granulated tin.

In the firm where it was proposed to introduce this process the chemical production of tin powder was entirely carried out by one labourer at 15s. a week, and upon the firm's receiving an offer of a very good price for the zinc chloride produced, it was found that it would be impossible to produce the electrolytic deposit at a cheaper rate, and the matter was therefore abandoned.

Mr. H. S. Coleman (*communicated*) : I have read the advance copy of "Notes on the Electrolytic Recovery of Tin" by Mr. F. Gelstharp with much interest. About five years ago I tried a similar process for the recovery of tin from tinned scrap iron. My solution consisted of sodium hydrate in water, sp. gr. 1.07, temperature about 90°C . When the current was switched on I experienced the same effect as the one now mentioned. I carefully considered the whole process, and decided to try what would be the effect of the following. (1) Adding a small percentage of potassium hydrate. (2) Increasing the current density. (3) Working the solution at a lower temperature. The result was quite satisfactory when the solution was kept at a

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temperature between 50° C. and 60° C. The scrap was stripped clean in about twenty minutes, leaving the surface of the de-tinned iron a good colour. I found that all the trouble was caused by working the bath at too high a temperature.

Mr. F. Gelstharp (*communicated*): In reply to Mr. W. C. Prebble, the continuous removal of the tin paste does not favour the formation of the desired deposit that will float after being detached from the cathodes. By using an endless band scraper, as suggested, the deposit would be partly held in suspension in the electrolyte; this would be objectionable.

As regards the circulating pump, block tin or lead is not appreciably attacked by dilute solutions of hydrochloric acid of 1.025 sp. gr.

The deposition of tin paste can hardly be compared with zinc paste, as the latter is so easily oxidised, especially when detached from the cathode.

If arsenic be present in the hydrochloric acid, it will be precipitated as arsenide of tin, and remain in suspension in the electrolyte.

Referring to the possibility of some sodium being alloyed with the deposited tin when using an electrolyte of sodium hydrate, I will repeat that the deposited tin was first squeezed to rid it of free hydrogen gas and then placed in water, when I observed a small quantity of hydrogen gas was liberated. I see no reason why some sodium should not be deposited and alloyed with the tin, for it is well known to electrochemists that sodium is deposited into mercury cathodes in some electrolytic alkali processes; and I have been able to deposit sodium in a similar way into a cathode of fusible alloy from a hot aqueous solution of sodium hydrate. It is not probable that the tin and sodium are deposited at the same time; but I think it is very probable that it is deposited on or into the tin after the stripping of the scrap is finished, and while the current is being continued till the scrap is coated with a reddish deposit.

In reply to Dr. O. J. Steinhart, when the hydrochloric acid process is used, the deposited tin under proper conditions is always deposited in a spongy form, which floats on the surface for an hour or so before it falls to the bottom. But in the case of the sodium hydrate process the deposit does not float.

In working with an hydrochloric acid electrolyte, I have experienced the same difficulty of treating the deposited tin to produce ingots, and it was overcome by compressing the freshly deposited tin into blocks under a pressure of one ton per square inch, and then melting them down under a suitable flux in a special reverberatory gas furnace daily, so that oxidation could only be very slight.

Dr. F. M. Perkin suggests that finely divided zinc might account for the effect noticed by me. There was no possibility of zinc being present.

In reply to Mr. H. Sayer, if the stripping is allowed to continue till the scrap is seen to be coated with a reddish deposit, the whole of the tin can be recovered. I have only been able to find traces of tin on the stripped cuttings. My experience of the percentage of tin on scrap agrees with the statement of Dr. Steinhart.

In reply to Mr. H. S. Coleman, I cannot agree with him that the temperature of the bath had anything to do with the passive effect of the tin scrap I noticed, as the experiment was repeated at various temperatures, the results always being the same; with this difference only, that when the reaction did commence it was more energetic at higher than at lower temperatures.
