XVII.—*On a Process of refining Tin.*

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It is well known that the grain tin of Cornwall sells for a much higher price than the block tin, which is produced in the same county; and that this difference in their value arises from the greater purity of the former, which renders it more fit for a variety of purposes.

The causes of this difference in the purity of the two sorts, are generally supposed to be of such a nature as not to be removed or modified; stream tin alone, as it is said, being fit for the production of grain tin, and the quantity of grain tin being necessarily limited by the supply of that fuel which is peculiarly adapted to it.

This, I believe, is the popular opinion, and with all the respect which is due to it, I am nevertheless disposed to think that it is fallacious.

For although it be true that the produce of a blowing-house must necessarily depend on the supply of that sort of fuel which is fit for it; yet it is by no means clear that coak may not be substituted for charcoal, and that block tin may not be converted by a process of refining into grain tin

I was led to form this conclusion by a short view which I took of the operations in a blowing-house in the autumn of 1791.

It appeared to me that as tin was specifically lighter than most metals, and more fusible than most, some advantage might be taken of these two combined circumstances to refine even the impurest mixture of tin by precipitation

As I had no opportunity of submitting my ideas to the test of experiment, the observations which I drew up and communicated to my friend, Mr. William Gregor, would have remained in that oblivion which results from a pursuit long since abandoned, had I not been informed that the attention of this Society was by no means exclusively directed to an object (the mineral history of Cornwall) which, under the direction of its zealous and enlightened secretary, it was so well calculated to promote; but that no hint which might be offered for the improvement of the mining and metallurgical operations of this county, would pass unregarded.

The question, indeed, whether block tin may be refined in the way that I have suggested, is so intimately connected with the interest of Cornwall, that I need no apology for submitting to the Society the result of my imperfect endeavour to answer it.

It is fair, however, in this place to state, that I found I had been anticipated in the ideas which suggested this improvement, by two very able French chemists, Messrs. Bayen and Charlard, who, in the course of their enquiries into the causes of those poisonous effects which were ascribed in France to the use of pewter, made the following observations on the quality of our Cornish tin.

Messrs. Bayen and Charlard found the West Cornish grain tin, the Banca tin, and the Malacca tin, to be equally malleable; and that they could be bent a long while in different directions without breaking. They possessed this flexibility and softness to such a degree, that tin alloyed with the minutest portions of arsenic could not be put into any sort of competition with them. Bayen affirms that these three sorts of tin are pure, i. e. free from all natural and artificial admixture, and as perfectly equal in this respect, as gold of 24 carats, or silver of 8 ounces, from the European or South American mines.

On the other hand, Geoffroy observes of the block tin, that it varies in fineness in different parts of the same block; "the upper part, he says, is very malleable, and so pliable as not to be fit for working before it has had a mixture of copper in the proportion of 3, and sometimes of 5 lb. in the cwt. The middle part of the block is harder, and requires only 2 lb. in the cwt. and the bottom part is so brittle as to require lead before it can be worked."

This perhaps gave occasion to the common opinion in France, that the exportation of pure English tin was prohibited, and that a certain portion of alloy was prescribed by law.

The observation of Geoffroy induced Mr. Bayen to express a wish to procure more information concerning the smelting of tin in Cornwall. "For instance," says he, "whether the English have any other means of producing pure tin than *the separation of the upper part of these blocks*, and whether merely for the reason cited by Geoffroy, they add a portion of copper and lead. Does not the precipitation of a heavier substance to the bottom of the mass, and this spontaneous purification of it, require a more circumstantial explanation? And may we not suppose that some time is required to effect this separation, and even the art of preserving the moulds hot to a certain degree, in order to prolong the fluid state of the metal; by which means the extraneous and more heavy substances are completely separated from the upper part of the block, less completely from the middle part, precipitated to the bottom, and there fixed by refrigeration."

Mr. Bayen suspects this to be the most secret part of the process of tin-smelting in Cornwall, and confirms the idea of the spontaneous precipitation by some experiments of his own.

After holding several masses of tin 24 hours in fusion, he invariably observed that all those which contained copper, bismuth, and lead, contained tin of two kinds at least. The upper part held little of this mixture, the lower much. He was assured by the pewterer, in answer to his enquiries, that sometimes after smelting a considerable quantity of tin at once, they found at the bottom of the mass some pounds of the metal so brittle as not to be fit for use. To prevent which separation from taking place, they were accustomed to stir it gently round from time to time, during the fusion, with the iron ladle with which they afterwards pour it into the moulds.

With the same view to preserve an equal mixture in the mass, I have observed that the Saxon blowers do not permit it to subside in a mould like other metals, but after a careful stirring of the fluid tin in the float, pour it over a broad sheet of iron, where it instantly coagulates in the form of a thin plate.

The above-mentioned observations shew how quickly the precipitation of the heterogenous metals takes place, and how early it must have occurred to the rudest empiric that some use might be made of it. Accordingly, this principle seems to have long been the basis in some measure of the process of refining grain tin in Cornwall, although unfortunately, from a total want of science, and a blind adherence to traditionary practice, the Cornish blower has not availed himself of it, to the extent to which he might have carried it, as will appear from the following account of his process.

The Cornish refiner *teams* the metal from the float into a cauldron of cast iron, and maintains its fluidity by a small fire beneath, during the space of four hours. During this time, green branches previously attached to the bottom of the kettle by a mechanical contrivance, produce a great ebullition in the fluid mass.

At the end of three hours, the wood being removed, the ebullition ceases, and the mass is suffered to rest one hour, in which time the heavier parts of the fluid subside. The upper part (about $\frac{1}{2}$) is then carefully laded off and poured into moulds.

It is difficult to conceive what good effects in the purification of the mass, so long a heat and this ebullition can produce. It appears then, that the principles upon which the process ought to be founded, are very imperfectly, if they are at all understood by the Cornish refiner. The true process, as I have already observed, is a precipitation which spontaneously takes place in every mass of fluid tin which contains an admixture of other metals, in consequence either of their greater specific gravity, or of the greater degree of heat which is necessary to keep them in a state of fluidity: those metals which cannot be separated from tin by the difference in their specific gravity alone, (as is the case I believe with zinc) being readily precipitated by refrigeration.

It is well known, in fact, that tin longer retains its fluidity than almost any other metal, and that most metals are heavier in a fixed than in a fluid state. This last is the case, according to Reaumur, with silver, copper, lead, and tin; for if you cast into a mass of either in fusion a piece of the hard metal, it will immediately sink to the bottom. But it is not the case, I believe, either with iron or with antimony: for whatever may be the law of dilatation by heat in fluid metals, their greater or less solidity, when fixed, must depend in some measure upon a certain crystalline arrangement which the particles assume at the moment of coagulation. Now antimony rarely, if ever, occurs in the mixture which is exposed to fusion; and the specific gravity of iron compared with that of tin, is, according to Sir Humphry Davy, (vide his Chemistry) as 7.70 to 7.29; and the difference must be greater when both arise in a fluid state, as iron expands while tin contracts by setting. It follows therefore from all these considerations, that a partial application of heat to the superior parts of the fluid mass, if it could be effected, and a partial removal of it from the lower and impurer, must greatly promote this precipitation of the heterogeneous metals*.

I proceed now to consider in what manner, a process which is founded on these principles, may best be carried into effect.

1st.—In order that a more complete division of the different qualities of the mass may take place, I propose that the refining vessel should be of a higher and a more narrow form than that which is at present in use: for if we suppose the sides of this vessel to be exposed to an equal heat, the degrees of this separation will extend in proportion to the protraction of the cylinder.

2dly.—The fire should be applied not to the bottom of the vessel as at present, but to its whole circumference.

It appears to me that this is a necessary consequence of the alteration in the form of the vessel; otherwise, the metal, although fluid at bottom, might have a tendency to coagulate at top, where, in order to facilitate the precipitation of the heavier and heterogeneous parts, a greater degree of fluidity ought to prevail.

3dly.—It would greatly conduce to the success of the preceding operation, if the diameter of the vessel were made gradually to diminish

* This is precisely the reverse of the process of eliquation.

from the bottom to the orifice, by which means the upper part would be exposed to the nearer action of the fire. The duration of the fluidity depends on the degree of purity of the mass, and may be regulated by experiments.

4thly.—In order to enable the refiner to draw off the purer parts of the mass without disturbance, I would recommend that tap-holes should be applied at different elevations, to the sides of the cylinder.

5thly.—Previous to the tapping, the external heat should be diminished, and a gradual refrigeration take place from the bottom to the surface of the mass, the different qualities of which may be tapped off in succession.

Having had no opportunity of submitting to the test of experience the process which I here recommend to the notice of practical men, I am well aware of the possibility that the result may prove somewhat different from what is here contemplated.

Some causes of obstruction may arise from the attractions of metals to each other in a fluid state, not being perfectly understood. Some metallic mixtures too possess a less degree of density than might be inferred, by calculation, from the density of the several ingredients. It is true, likewise, that tin most readily unites with iron, and dissolves it in a heat far less than that in which iron by itself melts: it will consequently retain the iron longer in fusion. I suspect too that the contraction which is usually the consequence of a metal passing from a fluid into a fixed state, must depend in some measure upon the period of refrigeration. The following useful remarks on this process are contained in a letter from Mr. Wm. Gregor, of the date of 1793. "I should think that experiments on the alloy of iron and tin would be useful, in order to discover the maximum of iron which a given quantity of tin would take up. I should also like to know, whether, in a long perpendicular cylinder of tin which is alloyed with iron and kept in different heats, the specific gravity increases in any determinate ratio, according to the distance from the surface, and at what distance is the maximum. As the iron over and above the quantity which tin can take up in a heat that will keep it in a melted state, is only kept from precipitation by the friction which its particles meet with in their descent, would any mechanical motion, such as a smart concussion, communicated to the melted mass, contribute in any way to the further descent of the particles of iron?"

On consulting the very elaborate work on iron by Rinman, I found that the dissolution of one part of raw iron requires 22 parts of tin, and that this mixture is somewhat harder than tin. He says too, that sulphur much facilitates this combination, i. e., it enables portions of each metal more nearly equal, to unite; and that the same effect is produced by arsenic in a reguline state, when added to the mixture of the two metals.

According to Rinman, the change which is most observable in tin which is alloyed with the least portion of iron, is, that it does not crackle when bent. An easy trial too of its purity may be made by its flexibility; for small round bars of tin, a line in thickness and six inches long, may be bent 80 times backwards and forwards in an angle of 90 degrees, without breaking.