

UNITED STATES PATENT OFFICE.

ELIAS A. SMITH, OF ANACONDA, MONTANA.

ELECTROLYTIC REFINING OF COPPER.

SPECIFICATION forming part of Letters Patent No. 617,886, dated January 17, 1899.

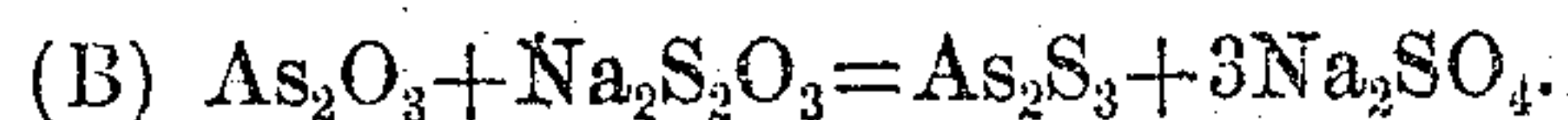
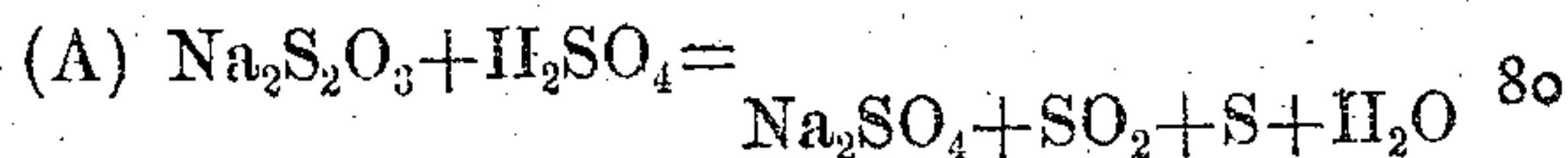
Application filed May 19, 1898. Serial No. 681,129. (No specimens.)

To all whom it may concern:

Be it known that I, ELIAS A. SMITH, a resident of Anaconda, Deer Lodge county, Montana, have invented certain new and useful Improvements in the Electrolytic Refining of Copper, of which the following is hereby declared to be a full, clear, and exact description.

In the electrolytic method of refining copper by immersion of copper anodes in a suitable bath of acid electrolyte the impurities associated with the copper in the anodes and which are composed mainly of iron, arsenic, and antimony become affected electrochemically and by virtue of the reactions pass in part into solution and in part are thrown down to settle with the slimes. Such of the impurities as remain in solution tend in measure to deposit with the copper or are apt otherwise to affect injuriously the quality of the copper yield. Since these impurities are being continuously supplied from the anodes, the gradual accumulation of the objectionable ingredients suffices to compel a periodic renewal of the electrolyte solution. In most refineries the practice now is to evaporate the impure electrolyte, and thus to recover the bulk of the copper salts, (blue vitriol.) The blue vitriol crystallizes out of the cool concentrated solution and being redissolved is restored again to the refinery bath, whereas the "mother-liquor" which still retains the impurities is generally rejected and allowed to run to waste. The invention aims to utilize this refuse mother-liquor by regenerating it for restoration to the electrolyte substantially as follows: After removal of the bulk of the copper salts (blue vitriol) by aid of a regular crystallizing plant the solution which remains—i. e., the refuse mother-liquor—is further evaporated. A system of lead pans, such as is commonly used for concentrating sulfuric acid, can be conveniently employed for the purpose. During this secondary evaporation the liquid becomes heated to a high degree. It presents a large surface to air exposure and may be constantly agitated with advantage by aid of hand-stirrers. Owing to the exposure and to the gradual concentration of the sulfuric acid the iron salts are thrown down in the pans as an insoluble oxy-sulfate. From the pans it is easy to periodically remove the precipitated iron salts.

The impure mother-liquor should be continually fed in usual manner to advance progressively along the system of evaporating-pans, as well understood. Eventually the concentrated acid there contained may reach a strength somewhere about 55° Baumé. Emerging from the pans the acid runs through a set of water-jacketed cooling-tanks, thence along troughs for settling, and ultimately discharges into big precipitating-vats. Under quiet clarification the remnants of copper sulfate, if any, and some part of the ammonium sulfate, if this be present in the original electrolyte, will crystallize out. To the clear and concentrated acid yet remaining and left quite cool, comparatively, within the tank are now added crystals of sodic or calcic hyposulfite. These additions are mechanically stirred in and effect the precipitation of the antimony and arsenic. A supply of free sulfurous acid is also liberated, but owing to the cool temperature of the sulfuric-acid bath the liberated supply remains intimately blended or dissolved in such bath. Typical examples of the two sorts of reaction may be stated by equations thus:



The equations show that the hyposulfite crystals react in part directly with the sulfuric acid, the result being to release sulfurous acid which is detained as such in the bath and also to generate nascent sulfur, which latter effects precipitation of the arsenic and antimony. On dilution the arsenic and antimony compounds resulting from the treatment proceed to settle away. A minor portion of the sulfur also separates out, leaving the sulfuric acid clarified and regenerated, free from all impurities and in readiness to be restored anew to the electrolyte bath at the refinery. By allowing the concentrated sulfuric acid to cool down before adding the crystals of hyposulfite the precipitation of the arsenic and antimony is more certainly accomplished. Besides, except for such cool state, the retention of the liberated sulfurous acid could not otherwise be assured. The free sulfurous acid thus dissolved as an incident of the regener-

ation treatment has a tendency to reduce the electrolyte. Hence at the refinery it prevents the arsenic from passing into solution as arsenate of copper, the almost insoluble
5 arsenous acid which forms being retained as such, and thus being compelled to settle down with the silver slimes. The free sulfurous acid also tends to reduce ferric to ferrous sulfate. The latter salt requires a higher ten-
10 sion current for decomposition than is requisite for copper sulfate. Hence under the reducing influence of the sulfurous acid less iron deposits on the cathode along with the copper than would occur were this reducing
15 agent absent from the bath.

Obviously the details can be varied according to the mechanic's skill without departure from the essentials of the improvement.

Having thus described my invention, what
20 I claim as new, and desire to secure by Letters Patent, is—

1. The electrolytic method of refining copper which consists in depositing the copper from anodes thereof immersed in an acid-bath,
25 concentrating the resultant impure electrolyte to recover by crystallization the bulk of the copper salts (blue vitriol), further treating the "mother-liquor" by progressive shallow
evaporation at high temperature, under air
30 exposure, to throw down the iron salts and

to gradually concentrate the free acid, and upon subsequent cooling then adding suitable hyposulfite to remove the antimony and arsenic while retaining liberated sulfurous acid
35 in solution, and thereupon diluting to complete the precipitation of antimony and arsenic prior to the return of the free acid to the refinery-bath, substantially as described.

2. The electrolytic method of refining copper which consists in depositing the copper
40 from anodes thereof immersed in an acid-bath, concentrating the resultant impure electrolyte to recover by crystallization the bulk of the copper salts (blue vitriol), further treating the "mother-liquor" by progressive shallow
45 evaporation at high temperature, under air exposure, to throw down the iron salts and to gradually concentrate the free acid, and upon subsequent cooling then adding suitable
50 hyposulfite to remove the antimony and arsenic while retaining liberated sulfurous acid in solution, so that the same may serve as a reducing agent on return of the regenerated acid to the refinery-bath, substantially as described.

ELIAS A. SMITH.

Witnesses:

THOS. F. TOOMEY,
JOHN C. SALOR.