

Patented July 7, 1925.

1,544,726

UNITED STATES PATENT OFFICE.

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ELECTROLYTIC REFINING OF METALS.

No Drawing.

Application filed August 28, 1924. Serial No. 734,798.

To all whom it may concern:

Be it known that I, FRANK F. COLCORD, a citizen of the United States, residing at New York city, in the county of New York and State of New York, have invented certain new and useful Improvements in Electrolytic Refining of Metals; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The invention relates to the electrodeposition of metals and more particularly to the electrolytic refining of metals such as lead, copper and tin.

It is the practice in electrolytic refining of metals to use so-called addition reagents in the electrolyte and the present invention is based on the discovery of a new reagent of this character which may be used with marked advantage over prior reagents in the electrodeposition or electrolytic refining of certain metals. This reagent is a sulfite liquor concentrate comprising the solid or viscous materials obtained from the waste sulfite liquors produced by treating certain woods with sulfite solutions. The evaporation of these liquors leaves a colloidal substance which may be designated as sulfite lignose. The principal constituents of this substance are or may be lignin-sulfuric acid, lignin sulfonic acid, aldehyde sulfonic acids, furfural, and plant sugars. This substance is cheaply made from the waste sulfite liquors produced in the manufacture of paper pulp and is known under the trade names "lignol" and "goulac".

I have discovered that sulfite lignose may be used as an addition reagent in certain acid electrolytes with remarkably advantageous results. It may be used to replace many of the addition reagents commonly used weight for weight and owing to its extremely low price, a substantial economy may be effected. It can be used alone or in partial replacement of some of the commonly used addition reagents effecting not only an economy thereby, but permitting the substitution to take place in an old electrolyte and thus avoid the cost of new electrolyte when changing over to this addition

reagent. In many cases it produces a cathode deposit superior to deposits obtained with other additional reagents, increasing thereby the efficiency of the operation and resulting in an important economy in the power consumption. In refining metals where precious metals and/or deleterious impurities are present in the anode slime the superior cathode deposit offers lesser opportunity for floating slime to deposit on the cathode, resulting in the production of a purer cathodic metal and a smaller loss of precious metals. No accumulation in the electrolyte of substances which might finally cause the deposit to form non-adherent and crystalline deposits has been noticed with this addition reagent, as in the case with some of the prior addition reagents commonly used.

The use of this addition reagent has given particularly excellent results in the electrolytic refining of lead with a fluosilicate electrolyte. While the composition of the electrolyte can vary considerably without materially affecting the character of the deposit, excellent results have been obtained with an electrolyte containing 8.5 grams of lead as lead fluosilicate per 100 c. c. and 4.2 grams of hydrofluosilicic acid per 100 c. c. The common addition reagent has been glue, but complete substitution of this new addition reagent can be effected. In actual practice this addition reagent when used alone is added daily to the electrolyte in the form of a water solution at the rate of one to two pounds of the dry reagent per ton of lead produced, while if used in conjunction with glue, the total quantity of the two reagents added daily is one to two pounds per ton of lead produced, with the glue and the new reagent varying in such proportion as desired. It may also be used in the electrolytic refining of lead using electrolytes of fluosilicates and fluoborates or fluoborates alone. It may also be used in the electrolytic refining of lead using electrolytes of lead cresol-sulfonate, containing for example, 80 grams of lead as $Pb(C_6H_5.CH_3.OH.SO_3)_2$, and approximately 70 grams of free cresol-sulfonic acid per liter sp. gr. equals 1.21; and also with electrolytes of mixed cresol-sulfonate and fluosilicate elec-

trolyte, containing 80 grams of lead as $\frac{1}{2}$ part $\text{Pb}(\text{C}_6\text{H}_5\text{CH}_2\text{OH}\text{SO}_3)_2$ and $\frac{1}{2}$ as PbSiF_6 , and approximately 40 grams of free acid (estimated as H_2SiF_6) per liter
5 sp. gr. equals 1.26.

Sulfite lignose, either alone or with glue, may be used as the addition reagent in the electrolytic refining of copper with sulphuric acid electrolytes. In this case the
10 new reagent has a replacement value for glue of at least weight for weight. An additional benefit resulting from its use in the refining of copper is that the presence of a large amount of the reagent, or say an
15 excess, has no detrimental effect which is not the case when using the common addition reagent glue in electrolytic copper refining. The new reagent also imparts a higher throwing power to the electrolyte
20 and forms smooth, finely crystalline and tougher deposits than glue and nodules and dendritic crystals are restrained.

The new reagent may also be used in the electrolytic refining of tin with sulphuric,
25 sulphuric and sodium sulfate, or fluosilicate electrolytes in conjunction with other addition reagents, especially replacing glue when used with other reagents. Single addition reagents have not been particularly
30 successful in electrolytic tin refining and it has been the practice to use two or more addition reagents simultaneously, some of the addition reagents being glue, cresol, curacao aloes, and nicotine sulfite. Glue
35 when used with either cresol, aloes or nicotine sulfate has given in practice satisfactory deposits. The new reagent can however be substituted for glue in any of these combinations, effecting thereby superior deposits
40 in that they are less crystalline, more adherent and denser.

What is claimed is:

1. That improvement in the electrolytic deposition or refining of metals such as lead, copper or tin, with acid electrolytes which
45 consists in the use in the acid electrolyte of sulfite lignose as an addition reagent.

2. That improvement in the electrolytic deposition or refining of metals such as lead, copper or tin, which consists in the use as
50 an addition reagent in the acid electrolyte of sulfite lignose in conjunction with glue or other addition reagents.

3. That improvement in the electrolytic deposition or refining of lead which consists in the electrodeposition of the lead
55 from acid electrolytes containing sulfite lignose as an addition reagent.

4. That improvement in the electrolytic deposition or refining of lead with acid
60 electrolytes such as fluosilicate, fluoborate or fluosilicate and fluoborate electrolytes which consists in the use alone or in conjunction with other reagents of sulfite lignose as an
65 addition reagent.

5. That improvement in the electrolytic deposition or refining of copper with sulphuric acid electrolytes which consists in the use in the electrolyte of sulfite lignose
70 as an addition reagent, either alone or in connection with other reagents.

6. That improvement in the electrolytic deposition or refining of tin with acid electrolytes such as sulphuric, sulphuric and
75 sodium sulfate, or fluosilicate electrolytes, which consists in the use in the electrolyte of sulfite lignose in connection with other addition reagents.

In testimony whereof I have signed my name to this specification.

FRANK F. COLCORD.