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METHOD OF DEPOSITING SILVER IN AN ELECTROLYTIC ANODE AND COMPOSITION THEREFOR

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This invention relates to a new and improved method for including in electrolytic electrodes an impregnating oil and a metal, particularly silver.

In a United States patent application, Serial No. 380,104 concurrently filed by Neal J. Johnson and Milton Janes, there is set forth and taught an improvement in electrolytic electrodes consisting essentially of including therein a certain percentage of metallic silver for the purpose of reducing anode wear and lowering cell voltage. This silver treatment is in addition to the known impregnation of such electrodes with an oil such as linseed oil.

The common method of accomplishing such silver inclusion, and the usual laboratory one, is by impregnating the anode with an aqueous silver nitrate solution, followed by drying and subsequent heating of the anode at about a temperature of 250° C. to reduce the nitrate to metallic silver. This is necessarily in addition to the subsequent separate step of impregnating the anode with an oil and then drying the oil. The silver nitrate method has the further disadvantage of not achieving uniform distribution of the silver through the area of the electrode, the silver concentration near the surface of the electrode sometimes being as much as 5 to 7 times that at the center.

The object of this invention is to provide a method whereby a carbonaceous eletrolytic anode may be impregnated with oil and silver in such a manner that the distribution of the silver throughout the anode is nearly uniform. A further object is to improve the present method which necessitates distinct and separate steps for impregnating an anode with both silver and oil.

In the practice of my invention, a suitable impregnating oil, such as linseed oil or other vegetable oil, is mixed with a diluent which is miscible with the impregnating oil and which is also miscible with solution of silver nitrate in a mutual solvent. Such compounds as methyl isobutyl ketone, methyl ethyl ketone, acetone, or chloroform are suitable diluents. A typical mixture would be 70 per cent oil and 30 per cent methyl isobutyl ketone, but the actual proportion used depends on the percentage of oil impregnation of the anode desired. To this mixture is then added a solution of a suitable silver salt, such as silver nitrate, in a mutual solvent, the quantity of solution added being that sufficient to give the desired percentage of silver, preferably 0.4 to 5 per cent silver by weight, in the total impregnating solution which, using silver nitrate, may be in the range of 0.5 to 6.0 per cent silver nitrate by weight. This, in turn, will depend on the percentage of silver it is desired to deposit. Another silver salt suitable for the invention is silver perchlorate. The silver salt used must, of course, be soluble in the mutual solvent employed.

The selection of the proper mutual solvent is essential to the practice of the invention. Such a mutual solvent must be a good solvent for the silver salt and also be miscible with the impregnating oils commonly used. I

have found dimethyl formamide to be an excellent mutual solvent for the invention. It is a powerful solvent for inorganic salts, particularly chlorides and nitrates, with a solvent action on silver nitrate about the same as that of water. It is miscible with most organic liquids and the impregnating oils. Other nitrogen-containing mutual solvents which are suitable for the invention include benzonitrile and dimethylacetamide. Hexylene glycol is also suitable where the percentage of silver desired in the total impregnating solution is not above one per cent by weight.

Using a solution as described above, mutual deposition of silver and impregnating oil is possible by simply immersing the anode to be treated in the solution. The time of immersion would vary with the size of the electrode to be treated. Simple immersion as a method of impregnating is time-consuming, however, and the preferred method comprises using a pressure-vacuum cycle to accomplish the impregnation.

Using this preferred method, a typical procedure is as follows. The anode to be treated is placed in a suitable pressure-tight vessel, air is evacuated from the vessel for 15 minutes or more, and an impregnating solution according to the invention is introduced into the evacuated vessel so as to cover the anode completely with an excess of impregnating solution being introduced to allow for penetration into the pores of the anode. After the vacuum has been released, the vessel is allowed to stand at atmospheric pressure for from 1 to 2 hours. This standing time, which constitutes the soaking or filling time, can be shortened by applying air or inert gas pressure, which method can reduce the filling time to about 30 minutes.

After completion of the vacuum-pressure cycle just described, the now-impregnated anode is heated at a temperature of from 150° to 175° C. in a suitable vessel. The usual time of heating is from 3 to 4 hours. This heating reduces the silver salt to silver and permits recovery of the solvent, an important economy of the process. By the method of the invention just described, the extra operation involved in impregnating and heating the anode twice, once for the silver salt and once for the oil, is entirely eliminated.

Another advantage of my method is the more uniform distribution of the silver through the anode as well as the use of a smaller silver nitrate percentage in the impregnant, for the same quantity of silver deposited. By the old method, due to the poor distribution of the silver involved, in order to have a high enough percentage of silver in the interior of the anode, there was deposited far more silver than was necessary in the outer areas of the anode, with a great waste of silver resulting. These advantages, as well as others, can be seen from the tables which follow.

Table I summarizes tests made on three anodes two inches in diameter, each with a different percentage of silver nitrate in the impregnating solution. For each anode, an impregnating solution was made up by mixing 30 per cent by volume of methyl isobutyl ketone with 70 percent of a liquid raw vegetable oil of uniform quality and similar in properties to linseed oil, and then adding sufficient quantities of a 20 per cent solution of silver nitrate in dimethyl formamide to give the desired percentage of silver nitrate in the impregnation solution. After impregnation, each anode was heated at about 175° C. to remove the solvent and reduce the silver nitrate to metallic silver. Progressive cuts were then made into the anodes at quarter-inch diameter intervals, and the percentage of metallic silver at each depth was measured and recorded.

Table I

Anode No.	Percent $AgNO_3$ in Impregnating Solution	Test Zone	Percent Ag
1	1.5	Outermost, Quarter-inch	0.074
		Second, Quarter-inch	0.074
		Third, Quarter-inch	0.081
		Fourth, Quarter-inch	0.079
		Fifth, Quarter-inch	0.086
2	2	Outermost, Quarter-inch	0.124
		Second, Quarter-inch	0.116
		Third, Quarter-inch	0.120
		Fourth, Quarter-inch	0.121
		Fifth, Quarter-inch	0.108
3	6	Outermost, Quarter-inch	0.384
		Second, Quarter-inch	0.348
		Third, Quarter-inch	0.348
		Fourth, Quarter-inch	0.361
		Fifth, Quarter-inch	0.361

The uniform distribution of metallic silver through electrodes as achieved by my invention is in sharp contrast to the distribution obtained by using a 10 per cent aqueous solution of silver nitrate alone as an impregnant, without oil. Table II below shows the results obtained by testing progressive cuts in an electrode two inches in diameter impregnated with an aqueous impregnating solution of ammoniacal silver nitrate with an ammonia concentration of 7 per cent by weight. The silver nitrate concentration was 10 per cent by weight.

Table II

Zone	Percent Ag
Outermost, 3/16 inch	2.35
Second, 3/16 inch	0.47
Third, 3/16 inch	0.31
Fourth, 3/16 inch	0.31

I claim:

1. In the manufacture of a carbonaceous electrolytic anode containing as impregnants both a fatty drying oil and silver, the improvement which comprises preparing an impregnating solution containing a fatty drying oil, a silver salt, and an organic solvent for said silver salt which solvent is also miscible with said oil, impregnating said anode with said impregnating solution and heating said anode after impregnation for a time sufficient for the purpose of removing said solvent, reducing said silver salt to metallic silver and drying said fatty drying oil.

2. In the manufacture of carbonaceous electrolytic anodes containing as impregnants both a fatty drying oil and silver, the improvement which comprises preparing an impregnating solution containing a fatty drying oil, a silver salt, and an organic solvent for said silver salt which solvent is also miscible with said oil, the quantity of said silver salt being such as to make the percentage of silver in said impregnating solution between 0.4 and 5% by weight, impregnating said anode with said solution and heating said anode at a temperature of from 150 to 175° C., for a time sufficient to remove said solvent, reducing said silver salt to metallic silver and dry said fatty drying oil.

3. An improvement according to claim 1 wherein the impregnation of said anode is accomplished by immersing said anode to be treated in said impregnating solution for the time required by the size of said anode and then heating said anode after impregnation for a time sufficient for the purpose of removing said solvent, reducing said silver salt to metallic silver and drying said fatty drying oil.

4. An improvement according to claim 1 wherein the impregnation of said anode is accomplished by placing said anode in a pressure-tight vessel, evacuating the air from said vessel, maintaining the vacuum for at least 15 minutes, introducing said impregnating solution into said vessel, releasing said vacuum, allowing said anode to remain in said vessel at atmospheric pressure for from one to two hours, removing said anode from said vessel and heating said anode at a temperature of from 150° to 175° C. for from three to four hours for the purpose of removing said solvent, reducing said silver salt to metallic silver and drying said fatty drying oil.

5. An improvement according to claim 1 wherein the impregnation of said anode is accomplished by placing said anode in a pressure-tight vessel, evacuating the air from said vessel, maintaining the vacuum for at least 15 minutes, introducing said impregnating solution into said vessel, releasing said vacuum, introducing a pressure of air or inert gas above atmospheric pressure into said vessel, keeping said anode under said pressure for at least 30 minutes, releasing said pressure, removing said anode from said vessel and heating said anode at a temperature of from 150° to 175° C. for from three to four hours for the purpose of removing said solvent, reducing said silver salt to metallic silver and drying said fatty drying oil.

6. An improvement according to claim 1 wherein said solvent is a nitrogen-containing organic compound selected from the group consisting of dimethyl formamide, benzo nitrile, and dimethyl acetamide.

7. An improvement according to claim 6 wherein said solvent is dimethyl formamide.

8. An improvement according to claim 6 wherein said solvent is benzo nitrile.

9. An improvement according to claim 6 wherein said solvent is dimethyl acetamide.

10. An improvement according to claim 3 wherein said solvent is a nitrogen-containing compound selected from the group consisting of dimethyl formamide, benzo nitrile, and dimethyl acetamide.

11. An improvement according to claim 4 wherein said solvent is a nitrogen-containing compound selected from the group consisting of dimethyl formamide, benzo nitrile, and dimethyl acetamide.

12. An improvement according to claim 5 wherein said solvent is a nitrogen-containing compound selected from the group consisting of dimethyl formamide, benzo nitrile, and dimethyl acetamide.

13. An impregnating solution for impregnating electrolytic anodes comprising a solution of a fatty drying oil, a diluent, and a sufficient quantity of a silver salt dissolved in a solvent, which solvent is miscible with said fatty drying oil, so as to make the percentage of silver in the impregnating solution between 0.4 and 5 per cent.

14. An impregating solution for impregnating electrolytic anodes comprising a solution of a fatty drying oil, a diluent, and a quantity of silver nitrate in a solvent, which solvent is a nitrogen-containing organic compound selected from the group consisting of dimethyl formamide, benzo nitrile, and dimethyl acetamide, sufficient to make the percentage of silver in the impregnating solution between 0.4 and 5 per cent.

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