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The Conductivity of Electrolytes Used in the Electrolytic Separation of Silver and Gold

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THE electrolytic separation of silver and gold has been practiced by the refineries in the United States for a good many years; and probably because of frequent visiting between officials of plants and the consequent exchange of views, operations in the various silver and gold refineries are very similar. We find, for instance, they practically all use electrolytes of approximately the same composition, which, no doubt, is more the result of experience than of studies of electrolytes. At the new electrolytic parting plant of the U. S. S. Lead Refinery, Inc., East Chicago, Ind., considerable attention has been given to the composition of electrolytes, especially to their conductivity and their effect on the character of the silver deposit. We are not aware that anything has been recently published on this subject and are, therefore, presenting such data as we have with the idea that, although it will not be wholly new, it may stimulate interest in the subject.

EFFECT OF COPPER CONTENT ON CONDUCTIVITY

The first work was to determine the specific conductivity of silver nitrate and copper nitrate solution. Concentrated solutions of silver nitrate and copper nitrate were prepared by dissolving analyzed chemically-pure salts in distilled water, and determining the silver and copper in each. Definite amounts of the concentrated solutions were taken, mixed and diluted to a definite volume. The silver and the copper were determined in each of these solutions and the conductivity was then determined. The plotted results are shown in Fig. 1 and 2. The effect of increasing quantities of silver and copper is readily seen. A comparison of the two sets of curves shows conclusively the benefit of holding the copper content of the electrolyte above 50 g. per liter, as its

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effect is to increase greatly the conductivity in an approximate proportion, one unit of copper to one and one-half unit of silver, in electrolytes containing from 30 to 60 g. each of silver and copper.

An electrolyte composition of approximately 60 g. of copper and 60 g. of silver was adopted for the parting plant at East Chicago. This composition proved satisfactory in practice, both as to the conductivity of the electrolyte and the character of the silver crystals. The crystals were heavy and dense and the average voltage drop per cell was approximately 3 volts.

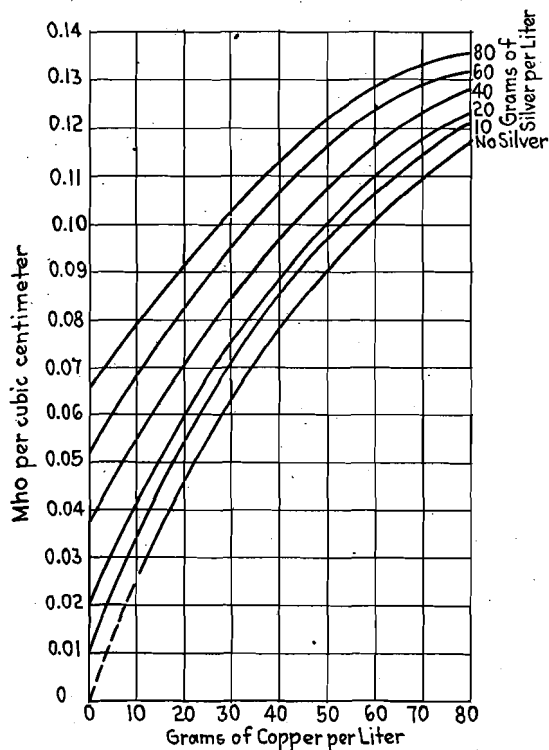


FIG. 1.—SPECIFIC CONDUCTIVITIES OF SILVER NITRATE AND COPPER NITRATE SOLUTIONS AT 25° C. (77° F.).

PRESENCE OF AMMONIA IN ELECTROLYTES

It is commonly known that old electrolytes perform better than new electrolytes, and this was borne out by our experience. At first the character of the deposit varied in different cells, but in the course of time like deposits were obtained. It was then discovered that the electrolyte contained a considerable quantity of ammonium nitrate. Two samples taken after the electrolyte was four months old showed 19.36 g. and 17.29 g. of ammonia per liter.

The question arose as to why ammonia was present. The usual reactions when copper or silver or silver-copper alloys are dissolved in fairly concentrated warm nitric acid solutions, and the acid is in excess, are:

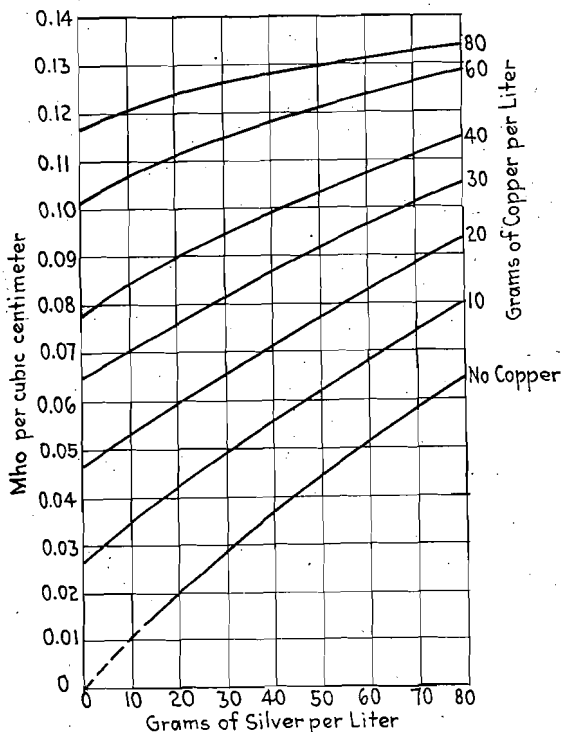
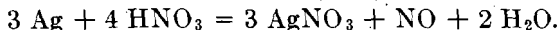
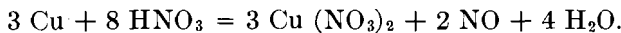
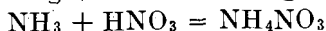
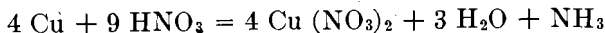


FIG. 2.—SPECIFIC CONDUCTIVITIES OF SILVER NITRATE AND COPPER NITRATE SOLUTIONS AT 25° C. (77° F.).

The reactions, however, are very different if the metals are in excess and the nitric acid solutions are dilute, and not heated, under these latter conditions ammonium nitrate will be one of the products, as shown by the following reactions:



As a rule it is not possible to have reducing conditions with such a strong acid as nitric acid, but when the metal is in great excess, and the acid is comparatively dilute, ammonium nitrate will be produced.¹ The

¹ Reference to this reaction is given in Prescott & Johnson's "Qualitative Chemical Analysis" under Division 6, Reactions A, With Metals, Part III, Nitric Acid.

second set of reactions seemed to explain the presence of ammonia in the electrolyte, as it was the practice to add daily small quantities of nitric acid to the electrolyte.

EFFECT OF AMMONIUM NITRATE ON CONDUCTIVITY OF ELECTROLYTES

It was also noted as the electrolyte became aged that its conductivity increased and the next tests were run to see if ammonium nitrate was the reason thereof. Concentrated silver nitrate and copper nitrate solutions

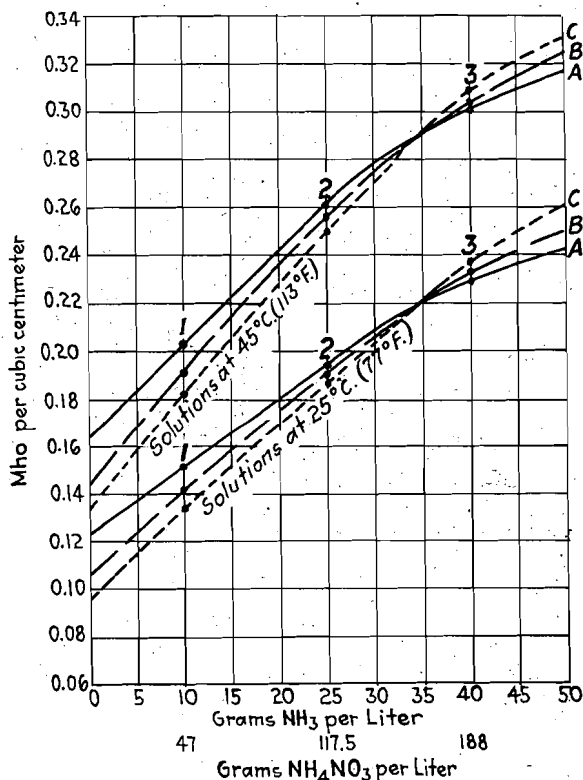


FIG. 3.—SPECIFIC CONDUCTIVITIES OF SILVER AND COPPER NITRATE SOLUTIONS WITH ADDITIONS OF AMMONIUM NITRATE.

Solution	Grams per Liter				Specific Gravity
	Ag	Cu	NH ₄ NO ₃	NH ₃	
A-0	60	60	0	0	1.218
A-1	60	60	47	10	1.233
A-2	60	60	117.5	25	1.260
A-3	60	60	188	40	1.280
B-0	60	40	0	0	1.172
B-1	60	40	47	10	1.191
B-2	60	40	117.5	25	1.214
B-3	60	40	188	40	1.239
C-0	40	40	0	0	1.145
C-1	40	40	47	10	1.163
C-2	40	40	117.5	25	1.191
C-3	40	40	188	40	1.215

were made up as in the first test, and the ammonium nitrate solution was prepared by dissolving a weighed amount of chemically pure salt in distilled water. Definite amounts of the concentrated solutions were taken and then mixed and diluted to a definite volume. The silver and copper were determined in these solutions, but the ammonia was not, as the dry chemically-pure salt was used. The conductivity of these solutions was then determined. Fig. 3 shows the results.

The results showed conclusively that the presence of ammonium nitrate greatly increases the conductivity of silver-copper nitrate parting-plant electrolyte, and that its effect upon the conductivity is the greatest when the copper and silver content of the electrolyte is the lowest. With 165 g. of ammonium nitrate, equivalent to 35 g. of ammonia per liter, the variation in the silver and copper content does not affect the conductivity as indicated by the crossing of the curves. In this respect, the presence of the ammonium nitrate in silver-parting electrolytes acts similarly to free acid in copper, zinc, lead and tin electrolytes.

Tests on a Commercial Scale

It was then decided to test this effect of ammonium nitrate in regular operations. Two cells were taken and new electrolyte of approximately

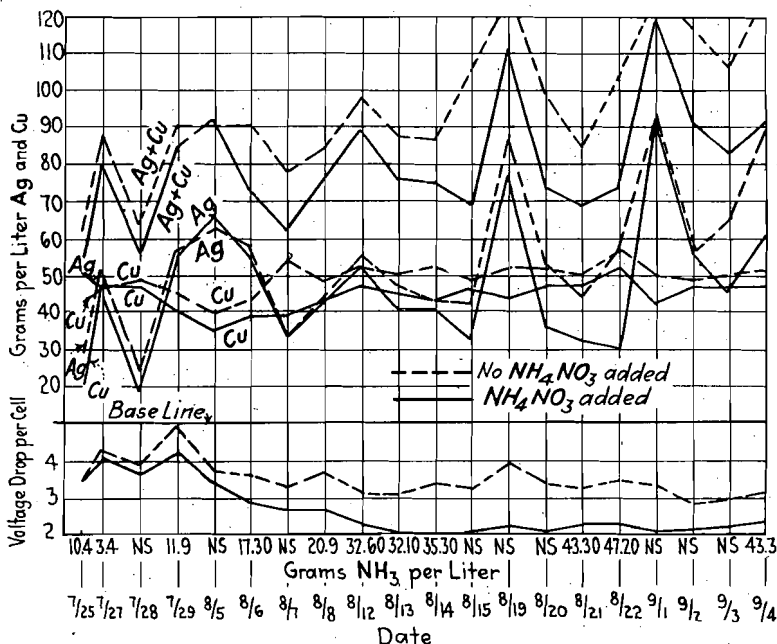


FIG. 4.—CURVES SHOWING VOLTAGE DROP AND COMPOSITION OF ELECTROLYTES USED IN TESTS OF THE EFFECT OF THE PRESENCE OF AMMONIA.

the same composition was made for each. These cells were then put into regular operation, and parallel conditions were maintained as nearly as

possible on a commercial scale. The electrolyte in the two cells varied from day to day principally because of the copper in the anodes, but by additions of silver nitrate or copper nitrate they were brought back to approximately the same composition. To one of the cells, ammonium nitrate was added from time to time and the amount of ammonium nitrate present was checked by analysis of the electrolyte for ammonia. The temperature and specific gravity of the electrolyte and voltage-drop readings of the cells were taken regularly. The character of the deposit was also recorded. The voltage-drop readings and the composition of the electrolyte were plotted as shown in Fig. 4.

It will be noted in Fig. 4 that the copper content of the electrolyte was maintained fairly constant throughout the test, but that the silver content varied considerably. This variation in silver content was due to the copper content of the dore' anodes and to the operating conditions under which the tests were conducted; but the silver content as well as the copper content as between the two cells was practically the same.

The copper-plus-silver content of the electrolytes shows a gradual increase as the tests proceed. It will be noted that as the copper-plus-silver content increased, the resistance of the cells was reduced, which is shown particularly by the voltage-drop curve of the cell to which no ammonium nitrate was added. The curve for the cell to which ammonium nitrate was added clearly shows the effect of ammonium nitrate in decreasing the resistance. It also shows that after 35 g. of ammonia per liter were present in the cell, the difference in voltage drop of the two cells was fairly constant. In other words, beyond 35 g. of ammonia per liter, there is no beneficial effect from the ammonium nitrate in so far as conductivity is concerned.

Effect on Character of Silver Crystals

The presence of ammonium nitrate apparently had an effect on the crystalline character of the deposited silver, but not to such an extent as a variation in the amounts of silver nitrate and copper nitrate in the electrolyte. When the silver was below 40 g. per liter the deposit was of a fine crystalline nature; and when the silver content was under 35 g. per liter the crystalline formation was very fine. The effect of ammonium nitrate was to cause the formation of more compact and finer crystals, and was more apparent as the silver content of the electrolyte was low. At times the crystals tended to form very compactly and to adhere to the cathodes. The results indicated, however, that with high-copper and high-silver content (each above 50 g. per liter), the presence of ammonium nitrate has a beneficial effect on the character of the silver crystals.

Laboratory Tests of Effect on Silver Crystals

Work was resumed in the laboratory to study further the effect of ammonium nitrate on the character of the crystals, as better control is

possible there than in commercial-scale tests. Five electrolytes were prepared by dissolving the pure salts of silver nitrate, copper nitrate, and ammonium nitrate in water and diluting so as to give solutions having the compositions as follows:

Solution	Grams per Liter			Grams Equivalent per Liter			Specific Gravity
	AgNO ₃	Cu(NO ₃) ₂ ·3H ₂ O	NH ₄ NO ₃	Ag	Cu	NH ₃	
III	79			50			1.070
II	79	230		50	60		1.215
III	79	230	83	50	60	17.5	1.248
IV	79	230	165	50	60	35	1.275
V	79	230	215	50	60	45	1.300

Pure cast-silver anodes and sheet-silver cathodes were used. The latter were coated with a film of oil so as readily to permit the removal of the deposited crystals of silver at periods about 4 hrs., in the case of all except the deposits formed in solution I., from which the cathode crystals were removed at about 1-hr. intervals to prevent short circuiting. The anodes and the cathodes were suspended 2½ in. apart in beakers holding 600 cc. of the electrolyte.

TABLE I.—Results of the Laboratory Tests

Period of Test	Drop between Electrodes, 2.5 in. apart, Volts					Temperature, °C.
	Cell I	Cell II	Cell III	Cell IV	Cell V	
Start.....	3.20	1.20	0.80	0.65	0.54	21
4th hr.....	3.19	1.18	0.79	0.64	0.53	24
8th hr.....	3.19	1.18	0.79	0.64	0.53	26
12th hr.....	3.20	1.20	0.82	0.65	0.54	23
16th hr.....	3.19	1.19	0.80	0.64	0.54	25
20th hr.....	3.20	1.21	0.82	0.66	0.56	23
24th hr.....	3.20	1.20	0.80	0.65	0.55	26
28th hr.....	3.25	1.21	0.83	0.67	0.57	23
32nd hr.....	3.22	1.20	0.82	0.66	0.56	26
36th hr.....	Stopped test					
Current efficiency, per cent.....	83	98	98	98	98	
Specific Gravity of Electrolytes						
Cell	I	II	III	IV	V	
Start.....	1.070	1.215	1.248	1.275	1.300	
Finish.....	1.070	1.215	1.245	1.270	1.295	

The current density selected was 32 amp. per square foot of exposed electrode surfaces, and the temperature of the electrolytes was between 20° and 26° C. The duration of the test was 36 hr. The voltage drop between the electrodes was measured at the start of the 4-hr. periods, after the electrodes were stripped of the deposited silver crystals. Table 1 gives the data.

The difference in the weights of the cathode silver and the loss in weights of the anodes gave the weight of the anode residue as about 0.4 per cent. in the case of anode I, and about 0.6 per cent. for anodes II, III, IV, and V.

The character of the cathode silver was as follows:

Cell I.—Long slender branching needles, which rapidly grew towards the anode, and unless pushed back to the cathode would short-circuit the electrodes within an hour.

Cell II.—Short thick single and dendritic crystals which formed close to the cathode. An occasional dendrite would slowly grow towards the anode, but in no case caused short circuiting of electrodes.

Cell III.—Heavier thick crystals than those formed in cell II; the tendency of the crystals was to form compactly.

Cell IV.—Heavier crystals than those formed in cell III. The dendrites which formed on the edges of the cathode, had a tendency to turn back toward the surface of the cathode; the crystals in general were compact.

Cell V.—The crystals were similar to those formed in cell IV but in general were more compact and of smaller size; the dendrites on the edges of the cathode formed close to the surface.

The anode residue which formed in cell I was of lighter color than that which remained on the anodes in cells II, III, IV and V; in each test it was removed from the anodes when the electrolyte was stirred.

CONCLUSION

The conclusions deduced from the results of the test conducted in the plant and in the laboratory are as follows:

A. The conductivity of the electrolyte depends upon the silver and the copper content; and the higher the silver and copper content within limits, the greater is the conductivity.

B. Copper in the electrolyte is more effective than silver in increasing the conductivity.

C. The presence of ammonium nitrate materially increases the conductivity of the electrolyte.

D. The effect of ammonium nitrate on the conductivity of the electrolyte reaches a maximum when about 165 g. of ammonium nitrate per liter is present, equivalent to about 35 g. of ammonia.

E. A low-silver and low-copper content of the electrolyte causes the silver to deposit as fine crystals. With very low-silver content the deposited crystals will either be finer or will assume a long slender branching needlelike shape.

F. The greater the amount of silver in the electrolyte, up to about 60 g. per liter, the coarser the crystal formation becomes, if copper is present; and with an increase of the copper content, up to 80 g. per liter, the coarser and more compact will be the crystal formation.

G. The presence of ammonium nitrate has a tendency to change the crystalline character of the deposited silver causing it to form more compactly in electrolytes that contain between 40 and 60 g. each of silver and copper per liter.