

ELECTRO-SILVER PLATING.

PART I. EARLY TECHNICAL HISTORY.

PART II. THE AUTHOR'S INVESTIGATIONS.

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PART I.

The purpose of this paper is to present a brief summary of the technical development of electro-silver plating together with a survey of our present knowledge of the subject and the investigations still needed to deal adequately with its problems.

The recent publication of a paper by Mr. R. E. Leader¹ has placed on record a really authoritative account of the discovery by Wright, in 1840, of the cyanide solutions which form the basis of all industrial silver plating, and the introduction of the resulting processes into commercial practice by the Elkingtons.

But apart from a number of patent specifications—most of them valueless—relatively little systematic investigation of the varied phenomena of silver plating practice is to be found in literature until towards the end of the nineteenth and beginning of the twentieth century.

It may be said indeed that not until the pioneer work of Hittorf, Ostwald, Arrhenius, Haber, and others had laid the foundation of the modern science of electrochemistry, was any adequate scientific survey of the subject possible.

In spite of this, however, we owe more than perhaps is readily understood to a few workers of the nineteenth century.

Messrs. Glassford and Napier in 1844 investigated the chemistry of the double cyanides, and threw considerable light on the reactions involved in making up the plating bath.

Smee, in 1843, published the second edition of his "Elements of Electro-metallurgy"—the first scientific treatise on the subject. This revised edition is well worth the study of electroplaters even now. It contains much of permanent value, and is particularly interesting in its treatment of the subject of the physical characteristics of electrodeposited metals. While taking a mistaken view of the exact influence and bearing of hydrogen liberation on deposits, Smee grasped very clearly the importance of current density; and—considering the state of electrochemical knowledge in his day—showed quite remarkable insight into the question of the relationship between metal concentration and current density.

He states, *e.g.* "to obtain with certainty any particular metallic deposit we must regulate the galvanic power actually passing to the strength of

¹ *Journ. Inst. Metals*, vol. xxii., pp. 305-26.

the metallic solution".¹ Farther on he says, "the quality of the metal depends on the regulation of the quantity of electricity to the strength of the metallic solution".²

An interesting statement on silver deposits is the following:—

"The silver will be thrown down in somewhat different states according to circumstances. If thrown down very slowly, it will assume a beautiful dead appearance, if still more rapidly, it will be brighter."³

Gore, whose scientific career covered a considerable portion of the latter half of the nineteenth century, is the chief contributor on the subject to scientific and technical literature, and his position as technical adviser to the Elkingtons, and general consultant to the trade in Birmingham, entitles him to the careful attention of all workers in the art.

Even Gore, however, does not appear to have published any detailed observations bearing on practical problems, although he investigated largely the electro-chemistry of many silver compounds.

For the most part, his views are embodied in his "Art of Electro-Metallurgy" (Longmans, 1877, and subsequent editions) and his "Electro-Chemistry" (Electrician Publishing Company, 1887), both of which works are still available in libraries.

Another author of the same period deserving at least brief mention is Dr. Georg Langbein, the first edition of whose "Vollständiges Handbuch der Galvanischen Metall-niederschläge," appeared in 1886. Langbein, however, contributes little of importance, except to be more definite than his contemporaries in giving exact values of current density and E.M.F., as also in stating the relative proportion of free cyanide to be recommended for practical work. On the other hand, it must be said that he is a little misleading in some respects, as *e.g.* in his references to the use of carbon bisulphide in "bright" plating vats.⁴

It was not until the early part of the present century that any really systematic investigations into the various factors of technical importance began to appear in scientific and technical journals.

The period 1900-1910 is much more prolific than any other in the history of the art in this direction, and during these years work of first-rate importance has been published.

In 1904 Bancroft⁵ published a paper of considerable interest entitled "The Chemistry of Electro-Plating," in which a number of problems awaiting solution were discussed. Amongst these was the question of the exact cause of the variation in the structure of deposited metals when varying current densities were employed. Bancroft put forward the interesting explanation that the structure of metals deposited by high current densities was exactly analogous to the structure of precipitates produced rapidly by purely chemical reactions. This view has been widely endorsed,⁶ and is of importance as rendering intelligible at least in some degree the widely varying physical structures of deposits it is possible to obtain from identical solutions.

Of still more importance, however, was the publication by Brunner in Germany in 1907 of his "Beiträge zur Kenntnis der Elektrolytischen Abscheidung der Metalle," Dresden.

¹ "Elements of Electro-Metallurgy," 2nd edit., 1843, p. 114.

² *Ibid.*, p. 127.

³ *Ibid.*, p. 217.

⁴ Langbein, "Vollständiges Handbuch der Galvanischen Metallniederschläge". Leipzig, 1886, p. 179.

⁵ *Trans. Amer. Electrochem. Soc.*, 1904, pp. 27-43.

⁶ See Miller, *Trans. Amer. Electrochem. Soc.*, 1913, vol. xxiii., p. 18.

This work deserves extended reference, particularly since so far as the present author's knowledge goes, it has not been translated into English and (probably in consequence) has received comparatively little attention in this country.

Brunner investigated (*inter alia*) the influence of current density, potassium cyanide, and metallic silver content, on the efficiency of silver cyanide electrolytes, and the physical characteristics of resulting deposits.

The practical value of his work must be the apology for including some of his results in the present paper, as in the accompanying Tables.

Tables I, II, III, XI, XII, are of experiments carried out in an atmosphere of hydrogen, while those of IV, V, VI, VII, VIII, IX, X, XIII, XIV, XV and XVI are in air.

The scientific conclusions which have been based on these experiments, particularly on the comparisons of the results in hydrogen and air respectively, have been discussed fully by Brunner himself, as also by Schlotter.¹ They show clearly that even with a solution of very low silver content there is little tendency to hydrogen liberation, except at very high current densities, and that the small loss in cathode efficiency is largely due to the depolarisation of hydrogen ions (on discharge) by dissolved air.

From the point of view of the practical silver plater, these figures reveal the extraordinary latitude allowable in the relationship of the three main factors of practice, *viz.*: "current density," "metal concentration," and "free cyanide," and yet indicate unmistakably what may be termed "the path of safety".

With regard to these factors it may be observed—

- (1) As to current density—how significant is the figure of 0.003 amperes per sq. cm. (approx. 2.75 amps. per sq. ft.). In each of the experimental series, in spite of solutions widely different in composition, a C.D. of this value gives not only a very high (in many cases 100 per cent.) efficiency but—with the exception of the extreme conditions in Tables XIV, XV, and XVI—a satisfactory deposit.

It must, however, be noted that these are laboratory experiments.

- (2) As to metal concentration and free cyanide, it will be seen that the best results are obtained when the relationship between the double salt $KAg(CN)_2$ to free KCN content is practically a molecular ratio of 1 : 2.
- (3) The value of agitation in working silver-plating baths is shown throughout the series, but remarkably emphasised by the results embodied in Tables XV and XVI as also VIII, IX, and X.

This work of Brunner (as also Foerster²) has placed our knowledge of the foregoing factors of silver-plating practice on a sound foundation which cumulative practical experience has on the whole amply confirmed.

PART II.

In 1904 it fell to the lot of the present author to attempt the co-ordination of the working of two electro-silver plating plants of widely different origin and different working conditions.

The difficulties encountered led him to undertake on a practical scale a careful comparison of the working of silver vats, with widely varying proportions of both "silver" and "free cyanide" content.

¹ *Galvanostogie I Teil über Elektrolytische Metallniederschläge*, 1910, pp. 142-48.

² *Zeits. Elektrochem.*, 13, 561 (1907).

In the two plants referred to were vats with a silver content from as low as 20 or 22 dwt. per gallon (6 to 7 grams per litre) to as high as between 5 and 6 oz. per gallon (30 to 35 grams per litre). The free cyanide content also varied from 14 per cent. to approximately 100 per cent. of the combined cyanide.¹

Some of these solutions were upwards of forty years old, while others were less than five years old.

Observations of the behaviour of these were carried on over a period of approximately three years, and the general conclusions arrived at may be summarised as follows:—

The best results were obtained—

- (a) In general, from old solutions.
- (b) From solutions containing over 2 oz. but not more than 4½ oz. silver per gallon.
- (c) From solutions where the percentage of “free” KCN to “combined” KCN was from 75 per cent. to 100 per cent.
- (d) From solutions in regular use rather than from those intermittently used.

(e) Where the temperature of the vats was not less than 17° C.

Since the exact data on which these conclusions were based cannot— for obvious reasons—be given, some further explanation is necessary, but first the question must be discussed.

“What constitutes a good result in commercial silver plating?”

The main factors, leaving out “adhesion” which is largely a matter of basis metal and preparation—are undoubtedly

- (1) A perfectly smooth, finely grained, and lustrous deposit, relatively soft and capable of being readily burnished and polished.
- (2) Rapid deposition, *i.e.* high electrolytic conductivity.
- (3) A high anodic and cathodic efficiency.

Now with regard to the conclusions outlined above, it will be observed (leaving (a) for the moment) that (b) is in accordance with recent general investigations into the subject of the electro-deposition of metals, which have shown that a high metallic concentration is an essential to rapid deposition and thick deposits.² On the other hand the experience not only of the author but many practical platers has shown that when the silver content of a vat appreciably exceeds 4 to 5 oz. the solution becomes sluggish and difficult to work, and is very liable to yield irregular deposits (probably owing to an aptitude to settle into layers of varying density).

In any event such solutions are financially uneconomic.

(c) is confirmed very closely by the laboratory experiments of Brunner, and is still further endorsed by the experience of many Sheffield electro-platers, who have been good enough to furnish the author with the results of their own work.

Some explanation may be necessary as to this method of calculating free cyanide as a ratio of the combined cyanide. From a practical point of view it is distinctly advisable to correlate these factors, but it must be pointed out that the necessity for definite proportions of free cyanide is influenced by the factor of C.D., inasmuch as one of the chief functions

¹ These percentage figures are based on the percentage of “free” to “combined” cyanide, the latter being calculated on the equation. $Agx + 2KCN$, x being, of course, an univalent radicle.

² See, *e.g.*, Pring and Tainton on Zinc, *Trans. Chem. Soc.*, 1914, vol. cv., p. 710; Kalmus, Harper, and Savell on Cobalt, *Four. Ind. and Eng. Chem.*, 1915, 7, p. 379; Watts on Nickel, *Trans. Amer. Electrochem. Soc.*, 1916, vol. xxix., p. 395.

of free cyanide is to dissolve the AgCN formed at the anode as the result of the decomposition of the complex anion $\text{Ag}(\text{CN})_2^-$ —which is obviously quantitatively determined by the C.D. employed.

From a purely theoretical point of view conclusion (d) is a little difficult to understand, and the author hesitates to advance any explanation, though his experience is confirmed by other workers. It is indeed a truism in silver-plating practice that "the more a solution is worked the better it becomes".

This subject has been investigated by Jordis and Stramer¹ who conclude (*inter alia*) that the content of carbonates increased more rapidly in used baths than in similar baths not regularly used. These authors also found that ammonia, ammonium cyanide, and potassium formate are present in old and used baths.

This point is, however, somewhat akin to conclusion (a) which must now be dealt with more fully. Not only in the particular observations now referred to, but from many sources evidence is forthcoming of the undoubted superiority of old solutions over new ones.

Most writers on electroplating who have referred to this point (notably Langbein and McMillan) have attributed the improvement to the gradual accumulation of organic matter which undoubtedly occurs.

That it is a question of the presence of substances other than $\text{KAg}(\text{CN})_2$ and KCN is evident when vats of almost identical silver and free cyanide content are compared under conditions of equal temperature and current densities. The older vats in general show a higher conductivity and yield a more lustrous and consequently more easily polished deposit. Practical experience, however, has demonstrated that this explanation is not fully adequate.

Chemical examination of a number of these old solutions (forty to sixty years) reveals the presence of surprisingly large amounts of potassium or sodium salts other than cyanide.

The author has previously published² an analysis of such a solution which may be regarded as typical, and through the kindness of Mr. Arthur Bowker he has recently had the opportunity of examining another old Sheffield solution, which has been in regular use for approximately sixty years.

In this instance the total solid matter present was very high indeed, being approximately 179 grams per litre of which an appreciable proportion appeared to be organic.

Time and facilities have not admitted of a complete analysis being carried out, but the following have been determined:—

Potassium Silver Cyanide ($\text{KAg}(\text{Cn})_2$)	. . .	26.63	grams per litre
Potassium Cyanide (KCN)	. . .	16.04	" "
Carbonates (as K_2CO_3)	. . .	21.37	" "
Chlorides (as KCl)	. . .	20.8	" "

It will be noted that the content of chloride is an important item in the composition of this solution, and is undoubtedly due to the practice of some of the older platers of making up their baths from silver chloride.

The question of the presence of potassium salts, other than cyanide, in silver-plating vats has been the subject of comment (usually adverse) by most writers on electrodeposition. Particularly has the presence of

¹ *Zeits. Elektrochem.*, 1903, 9, s. 572.

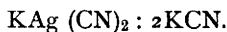
² Barclay and Hainsworth, "Electroplating". Arnold, 1912, p. 193.

potassium chloride been condemned by such authorities as Sprague,¹ Gore,² McMillan,³ and others. One of the very few exceptions is Langbein who quite properly points out, what the others apparently ignore, that its presence increases the conductivity of the bath. This would be expected from purely theoretical considerations, but the point is established beyond question by the work of Frary and Porter,⁴ who found that both the "chloride and hydroxide have a decided effect in increasing the conductivity," both having apparently the same value as an equivalent "free cyanide" content. This paper (by Frary and Porter) is of great interest as representing a systematic attack on the problems of this subject of the complex composition of commercial silver-plating baths. These workers investigated mainly the influence of the presence of potassium chloride or potassium hydroxide on the simple potentials of various metals usually used as cathodes in silver plating, *e.g.* mercury, silver, copper, brass, iron, and zinc. As previously indicated the specific conductivity of the various electrolytes was also determined. The investigations show clearly that no appreciable difference results from the presence of KCl or KOH on the electrode potentials, and that therefore no adverse effects in adhesion of deposits need be feared. The interesting statement is made "that the specific gravity of the solution may be regarded as a rough measure of its conductivity". This is in general accord with the author's practical experience.

The general conclusions which the author has reached as the result of co-ordinating his own experience with that of many other workers in the same field, may be summarised as follows:—

(1) That the most suitable silver content of an electrolyte for commercial silver plating, having regard not only to technical efficiency but to economic considerations, is approximately 3 troy oz. per gallon (22 to 25 grams per litre).

(2) That the proportion of free potassium cyanide in such a solution should follow the molecular ratio—



Thus the composition of the electrolyte recommended would be—

Potassium Silver Cyanide, KAg (CN) ₂	. 5½ troy oz. or 38 grams
Potassium Cyanide, KCN	. . . 3½ " " 24 "
Water	. . . 1 gallon or 1 litre.

(3) That the presence of such potassium salts as the hydrate, carbonate, chloride, and cyanate are advantageous, at least within such limits as obtain in normal silver-plating practice in the case of solutions in regular use for relatively long periods of time (thirty to forty years); and that therefore new solutions may be made from the corresponding silver salts without fear of untoward results.

(4) That a factor of vital importance in commercial practice is *current density*, it being essential that this factor be correlated to the metallic strength of the solution and the proportion of free cyanide employed. Thus, for example, a low current density yielding good results from a solution of silver and potassium cyanide of, say, 1 oz. per gallon, would be too low for such a bath as recommended above. Not only would the work be slower in operation, but the physical quality of the deposit would

¹ "Electricity," 2nd ed. Spon, 1884, p. 420.

² "Art of Electro-Metallurgy." Longmans, 1887, p. 159.

³ "Treatise on Electro-Metallurgy," 2nd ed. Griffin, 1890, p. 198.

⁴ *Trans. Amer. Electrochem. Soc.*, 1916, vol. xxviii, p. 323.

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suffer. A current density of $2\frac{3}{4}$ to 3 amperes per square foot is, however, suitable over a very wide range of bath compositions.

(5) That the working temperature of silver-plating baths is also important and should vary within limits not greater than 17° C. to 23° C.

(6) That a regular addition of potassium cyanide should be made weekly to a bath in regular use, the exact amount being regulated to that just sufficient to keep the free cyanide content to the standard given above. In vats containing 150 gallons, this will probably amount to not more than 1 lb. per week.

(7) That commercial plating baths should be used regularly (and not intermittently), under the same conditions of current density.

Finally it may be pointed out that while the present technical position of the art has reached a high level of efficiency, and a number of important problems have been satisfactorily solved, a considerable field of research is still open on such questions as—

(a) The exact influence of organic matter on the physical structure of the deposit.

(b) The chemical and electrochemical reactions occurring during the electrolysis of industrial silver-plating baths, and particularly of those complex solutions of considerable age which are found in practice to give such excellent results.

The author desires to acknowledge his indebtedness to Mr. R. G. Johnstone of the Midland Laboratory Guild for valued assistance in chemical analysis, etc., also to Dr. Schlotter's "Galvanostogie über Elektrolytische Niederschläge," from which he has extracted the figures relating to Brunner's experiments, p.

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Table.	Condition of Atmosphere.	Composition, grams per litre.		Current Density, per sq. cm.	Cathode Efficiency, per cent.	Mean Bath Tension, volts.	Character of the Silver Deposit and Observations.
		AgCN.	KCN.				
I	Hydrogen with stirring	13.4	8.125	0.001	99.66	0.44	Unsatisfactory deposit.
				0.002	{ 99.33 } { 98.26 }	irregular	Unequal stirring.
				0.003	99.66	0.83	Separation of AgCN on anode.
				0.004	{ 94.07 } { 96.13 }	2.3	
				0.005	95.18	3.8-4.5	
II	Hydrogen with stirring	13.4	19.5	0.001	{ 99.68 } { 99.28 } { 99.41 }	0.14-0.26	Matt, white, somewhat lustrous.
				0.002	{ 99.31 } { 99.85 }	0.29-0.35 0.4	Lustrous.
				0.003	100	0.37-0.45	Partially lustrous.
				0.005	{ 100 } { 99.9 }	0.5-0.8	" "
				0.01	98.1	1.5-1.6	Matt, powdery on edges.
III	Hydrogen with stirring	13.4	65	0.001	99.8	0.12-0.14	Very fine deposit.
				0.002	99.8	0.24	Very fine deposit, somewhat lustrous.
				0.003	100	0.35-0.32	Very fine deposit, somewhat lustrous.
				0.004	99.67	0.4	Very fine deposit, somewhat lustrous.
				0.005	{ 99.64 } { 99.52 }	0.48-0.5	Very fine deposit, somewhat lustrous.
IV	Air with stirring	13.4	8.125	0.001	83.09	0.4	Matt, white.
				0.002	89.01	1.1-1.6	AgCN on anode.
				0.003	92.64	0.8	
				0.004	93.5	over 5	
V	" " "	13.4	19.5	0.001	{ 81.86 } { 96.88 }	0.1-0.14	Matt, white, a little spongy in layers.
				0.002	{ 89.1 } { 97.59 }	0.24-0.28	Fine matt, steel white, somewhat lustrous.
				0.003	{ 94.78 } { 98.28 }	0.35 0.34	Very fine.
				0.005	97.17	0.58	Very fine, slightly lustrous.
				0.01	95.6	1.2	Matt on edge.
				0.02	94.25	2.2	Lustrous in centre.
VI	" " "	13.4	65	0.001	90.35	0.14	Slightly lustrous.
				0.002	91.67	0.25-0.3	" "
				0.003	95.8	0.32	" "
				0.004	98.36	0.4	Fine matt.
				0.005	97.2	0.4-0.47	" "
VII	" " "	13.4	260	0.001	100	0.08-0.1	Lustrous.
				0.002	99.6	0.1	" " steely white.
				0.003	100	0.12	" " lustrous.
				0.005	100	0.15	Slightly lustrous.
				0.01	100.3	0.26	Very fine matt.
				0.02	100.4	1.0	Powdery.
0.04	76.03	1.2-1.4	Deposit not weighable.				

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Table.	Condition of Atmosphere.	Composition, grams per litre.		Current Density, per sq. cm.	Cathode Efficiency per cent.	Mean Bath Tension, volts.	Character of the Silver Deposit and Observations.
		AgCN.	KCN.				
VIII	Air without stirring	13.4	19.5	0.001	97.45	0.15-0.2	Very fine, slight lustre.
				0.002	99.21	0.3-0.4	
				0.003	100	0.54-0.6	Fine matt, somewhat lustrous.
				0.005	97.15		
IX	Air without stirring	13.4	65	0.001	97.33	0.03-0.1	Matt, greyish.
				0.002	99.67	0.14-0.18	„ white.
				0.003	{99.10 97.37}	0.2	„ „
				0.005	{90.13 94.81}	0.8-1	Powdery grey.
				0.01	84.84	1-1.2	„ „
				0.02	62.7	1.5-1.6	Loose deposit.
X	Air without stirring	13.4	260	0.001	97.88	0.14-0.4	Lustrous.
				0.002	97.77	0.26-0.5	„
				0.003	99.27	0.38-0.46	„
				0.005	91.89	0.8-0.88	Matt; gas evolved.
				0.01	87.4	1.0-1.4	Spongy; gas evolved.
				0.02	73.31	1.2	„ „ „
XI	Hydrogen with stirring	4.5	19.5	0.001	100	0.12-0.2	Matt.
				0.002	100.14	0.37	„
				0.003	99.66	0.44-0.5	„
				0.005	99.63	0.76-1.0	„
				0.01	99.2	1.26-1.34	Matt; somewhat spongy.
				0.02	83.2	2.7	Spongy.
XII	Hydrogen with stirring	1.34	19.5	0.001	97.87	0.15-0.2	White.
				0.002	{98.83 97.76}	0.5-0.62	„
				0.003	91.12	0.6-0.7	„
				0.005	57.99	1.2	Spongy; gas evolved.
XIII	Air with stirring	4.5	19.5	0.001	92.44	0.13	Slightly lustrous.
				0.002	94.21	0.2	„ „
				0.003	94.54	0.42	Matt.
				0.005	{95.55 93.83}	0.6-0.68	„
				0.01	95.93	1.2-1.5	Somewhat spongy.
				0.02	90.69	2.2	Spongy; gas evolved.
XIV	„ „ „	1.34	19.5	0.001	89.47	0.15-0.23	Slightly lustrous.
				0.002	93.58	0.35-0.6	„ „
				0.003	81.00	0.8-0.84	Grey, matt; gas evolved.
				0.005	61.17	1.5	Spongy; „ „
XV	Air without stirring	4.5	19.5	0.001	97.06	0.2-0.4	Matt.
				0.002	85.42	0.88	Grey; slight evolution of gas.
				0.003	76.50	0.96	Grey; slight evolution of gas.
XVI	Air without stirring	1.34	19.5	0.001	82.29	0.68-0.7	Grey; gas evolved.
				0.002	79.97	0.8-0.9	Somewhat spongy; gas evolved slightly.
				0.003	71.15	1.8	Very spongy; gas evolved.