

## A NEW MAXIMUM CURRENT DENSITY IN COMMERCIAL SILVER-PLATING.

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During extensive researches on the physical structures of electro-silver deposits, which are at present being carried out at the University of Sheffield, the author observed that in certain instances exceedingly fine deposits of silver were obtained at an extraordinarily rapid rate.

In view of the enormous cost of plant for electroplating purposes, and the urgent need for increased output, the discovery was further investigated with surprising results.

It is well known that the maximum current densities used in the electro deposition of various metals from their respective solutions have been increased enormously by the introduction of moving electrodes. Cowper Coles' production of copper tubes is perhaps the classical example of this method, in which the current density was raised to over 200 amps. per square foot. Again, the deposition of nickel, tin, and zinc has been considerably accelerated by barrelling and similar processes.

None of these mechanical devices, however, are as yet available for production on a commercial scale of thick deposits of silver, such as are to be found on restaurant, hotel, and ships' outfits, and in fact all the best quality of electroplate.

It is also conceivable that flowing electrolytes would be conducive to higher current densities being used, in fact the author's experience of this, particularly in the laboratory, suggests great possibilities in this direction.

The disadvantages, further revealed as a result of experiments conducted on a commercial scale, altogether outweigh the benefits derived, from the resultant higher maximum current density. The difficulty of obtaining a fine reguline deposit of silver with a changing electrolyte, when treating large numbers of articles varying both in size and shape, is very great.

In criticising the quality of a deposit from the commercial standpoint, it is essential that it be judged with a view to subsequent processes to be operated on that deposit, and the final result obtained as the finished product.

It is admitted by all electroplate manufacturers that the deposits should be such that the characteristic mirror-like finish be obtained with least expenditure in labour after plating.

Microscopic examination of these silver structures enable one to make the following generalisation, that this ideal condition is to a large extent governed by the size and position of the crystals of the deposit. It is also clearly understood that other factors influence the labour involved in the process technically termed "finishing" but as these obtain, whatever the deposit may be, these factors will be ignored in this discussion.

It will be conceded that under normal and usual condition of commercial electroplating, *i.e.* an electrolyte composed of the double cyanide

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of silver and potassium with a percentage of free potassium cyanide, varying from approximately 40 per cent. to 70 per cent., the higher the current density used, the larger is the crystal obtained, until the crystalline structure is such that "finishing" is impossible, and the deposit is said to be "burnt".

This characteristic of ordinary silver-plating solutions has naturally set a maximum current density permissible which most authorities give as 3 to 4 amps. per square foot. Even at this rate the current density is considered in some cases to be too high, and results in what is technically termed a "hard" deposit.

In this connection the author may be pardoned in making some reference to a paper given before the members of the Sheffield Society of Applied Metallurgy in December, 1913, on "The Adhesion of Silver-deposits to High-grade Nickel Alloys," wherein the use of a small percentage of potassium carbonate was suggested in freshly-made silver-plating solutions as a means of improving the deposits. The excellent results obtained from old plating solutions naturally prompted this inclusion.

During the investigation referred to at the commencement of the paper, the electrolytes from which abnormal silver deposits were obtained always contained potassium carbonate. The metal from these was precipitated in a fine reguline condition, until the percentage of the latter compound reached the neighbourhood of 10 per cent., and the current conditions were normal. Any further increase produced large crystalline structures, very difficult to burnish or polish, and a current density of 6 amps. per square foot of cathode surface brought down a deposit from which the desired final "finish" could not satisfactorily be produced.

It was observed, however, that the solutions containing a higher percentage of potassium cyanide in conjunction with potassium carbonate, somewhat counteracted this undesired effect. On further investigation it was found that with a free cyanide content far in excess of that usually advised, and with potassium carbonate in very large quantities, not only could the current density be increased enormously, but that the deposit was of a finer texture altogether.

In order to present this matter in as useful and as practical a manner as possible, the author had the process installed on a commercial scale with most satisfactory results both as to rate of deposit and character of deposit. After depositing upwards of 8000 oz. of silver, an analysis of the electrolyte gave the following result:—

Silver . . . .	26·14 grammes per litre.
Free KCN . . . .	47·25    "    "    "
Potassium Carbonate . .	165·00    "    "    "

The deposit from which the photomicrograph No. 1 was taken, was recently obtained from the foregoing bath, and under ordinary working conditions, but with a current density as high as 8 amps. per square foot of cathode surface, and was one of over 150 articles plated during the same period, and in the same bath. The deposit as illustrated in the micrograph No. 2 was obtained under commercial conditions as operated to-day, and not those forming the subject matter of this paper, and the current density of  $3\frac{1}{2}$  amps. per square foot used. The period of immersion in the depositing bath was the same in each case.

The difficulty of showing quite clearly the size, shape, and position of the crystals of a deposited metal by means of a photograph, is no small one. Thanks to the valuable assistance rendered by Dr. Thompson, the

author is able to do this, and it will be noted that the micro-structure of No. 1 is almost identical with that exhibited in No. 2 micrograph.

The economy effected, when the maximum current density is increased over 100 per cent. as suggested in this paper, will be obvious to all. The



FIG. 1. ( $\times 100$  diams.)

reduction of time in deposition resulting in double the output, should be of considerable value, and the enormous saving in capital outlay in materials and plant, amounting in large establishments to many thousands

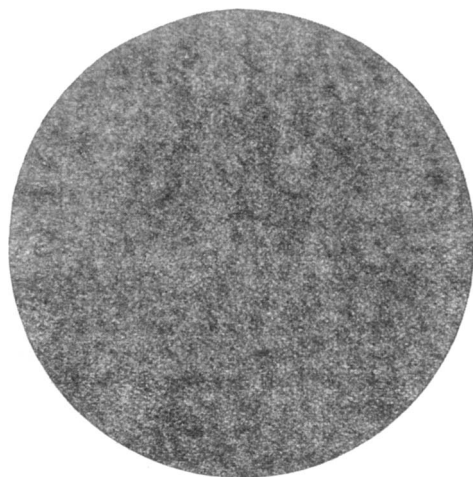


FIG. 2. ( $\times 100$  diams.)

of pounds, will doubtless be fully appreciated by the electroplate manufacturers of this country.

The author realises that this investigation is by no means complete, but is of the opinion that the publication of the results obtained at this early stage is fully justified because of the important bearing they have on the electroplate industry.

The author acknowledges the enormous amount of work done on this and cognate subjects, in which investigators obtained good deposits of silver with a current density as high as 16 to 18 amps. per sq. foot experimentally. Commercially, the current density used is about 4 amps. per sq. foot. As the author is unaware of any publication dealing with *commercial* electro-silver-plating where deposits are produced as stated in the foregoing, it is claimed for this paper to be the first published process in commercial electro-silver-plating, wherein such a large current density is used, resulting in deposits of very fine crystalline structure.

In conclusion, the author begs to acknowledge his indebtedness, and to tender his sincere thanks to Dr. F. C. Thompson, for his valuable assistance in preparing the microphotographs.