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## PROCESS FOR OBTAINING PRODUCTS OF GREAT VALUE, EASILY AND RAPIDLY, BY ELECTROLYTIC MEANS

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The object of the present invention is a new process which makes it possible to obtain products of irreproachable quality with great facility and under particularly advantageous conditions.

It applies more particularly, but not exclusively, to the obtainment of entirely polished metals, alloys and metallic deposits, the characteristics of which are far superior in every respect to those of the products obtained by the processes at present known.

The new process is based on the fact, as ascertained by the petitioners, that the tension applied to electrolytes not only exerts a considerable influence on the behavior of the electrolyte but also brings about a profound modification in the very nature of the electrolyte.

In usual practice the tension applied to the electrolytes is only slightly greater than the tension of decomposition, said tension of decomposition being determined on the one hand by the resistivity of the electrolyte under consideration and on the other hand by the counterelectromotive force of polarization.

According to the recognized principles the amount of the tension to be employed is particularly well defined in the work published in France in 1930 under the title "L'électro déposition des métaux" by Dr. W. Pfanhauser, translated by A. Alleman, N. Gourot and J. Fregier.

In this work which is one of the most carefully studied and most complete on the subject, the author indicates, as regards the relation between density and tension (page 94 and following pages), how one can determine said tension in practice and he adds (page 117) that the fact of raising this tension would be detrimental since, as the density increases at the same time, maximum density would be exceeded.

It is not therefore only through reasons of economy that only tensions reduced to a minimum have been employed up to the present but also because of material impossibility.

Indeed the increase in tension, consequently the increase in the density of the current, causes considerable disadvantages which professionals in the science have seemed to consider as an impassable barrier up to the present.

Now the petitioners have established the surprising and unexpected fact that if one persistently increases the tension a moment arrives where the known disadvantages are not only reduced but actually disappear completely over a certain period in the course of which the results obtained are better. It next happens that the disadvantages reappear then disappear again if the tension is further increased and so on.

After a number of tests the petitioners noticed that this periodicity in the recurrence of the disadvantages was due to the fact that, as the temperature increases considerably, said temperature is no longer in normal relation to the tension and to the density of the current in respect of the composition of the electrolyte.

Therefore, in order to benefit by the advantages obtainable, it was necessary to endeavor to remain within a period of favorable operation.

It was then that the petitioners established a second fact: after having increased the tension to the suitable point if it be then diminished down to a point where the temperature remains stable it so happens, automatically and without any intervention, that the density of the current tends to reach a maximum while the tension tends to reach a minimum. These two new values would appear to depend only on the composition of the electrolyte.

The density of the current will then be far greater than normal and the tension will be greater than normal tension to the extent of some volts.

This indicates that the nature of the electrolyte has become completely modified during the period of increased tension to which it has been submitted temporarily.

Indeed the fact may be very easily ascertained in certain cases. For instance if one watches a solution of copper sulphate to which the aforementioned treatment is applied one will observe the appearance of a particular phenomenon commencing at a certain tension.

A circulation, syrupy in appearance, will be set up and will at first commence to flow along the anode or anodes, it will then form, at the bottom of the vat, sheets possessed of an alternating movement from the bottom upwards and vice versa, it will then tend to flow upward along the cathode or to turn with said cathode. It is from this moment onward that the density of the current increases and that the tension tends to drop.

There is therefore reason to assume that this circulation constitutes a particularly conductive path along which move extremely minute metallic particles. Moreover one notices that, notwithstanding the high density of the current, variations in the distance between the electrodes have no appreciable effect on the tension.

It is remarkable to note that that portion of the liquid which is thus caused to circulate pos-

sesses interesting properties. It seems to oppose, in a perfect manner, the gaseous discharge which so frequently sets up the formation of spots and irregularities on the cathode. Moreover the oscillating sheets remain at a constant level if the working conditions of the electrolyte remain stable.

If the horizontally rotating cathode be replaced by a cathode of a diameter less than that of the former one will notice, between the new cathode and the oscillating sheets, a clearer layer which does not oppose the gaseous discharge.

By operating as at the commencement the level of the oscillating sheets will rise, the clear layer will disappear and the normal process will be resumed as soon as the level of the sheets reaches the new cathode.

A similar phenomenon occurs after a prolonged stop in working, the level of the sheets drops, the sheets may indeed disappear completely.

They can be caused to reappear by proceeding in the same manner as previously.

It has been noted also that different metals can be deposited at the same time without having to modify the composition of the original bath.

In the case of copper for instance if, after treating the electrolyte according to the process of the invention, chromium anodes are positioned alongside the copper anodes it will be noticed at once that the electrolyte changes color, passing from blue to green, and an alloy of copper and chromium is obtained at the cathode without any difficulty and without having to change the working of the electrolysis.

In order to apply the process which forms the subject matter of the invention it should however be borne in mind that it is necessary to obtain absolute automaticity and that, under these conditions, separate excitation generators should be employed, the regulating of the tension being obtained by acting on the excitation and not by means of a bath rheostat which has, so far, been considered as indispensable.

Control instruments should be placed on the excitation circuit for, in actual practice, the indications supplied by said instruments will make it possible to regulate working conditions with certainty.

It is of course understood that, under the conditions of the operation, the size of the vats must be determined by taking into account the density of the current it is possible to obtain and taking into account also the differences in temperature due to outside influences (surrounding temperature, temperature of premises heated in winter, etc.).

The putting into practice of the process as set forth hereinabove is effected as follows: whatever the composition of the electrolyte may be, the tension is progressively increased to 2, 3, 4, 5, 6, 8, 10 . . . etc., volts and this is done until the moment when it is ascertained that the resulting intensity of the electrode circuit continues to increase whereas the tension itself tends to drop.

As this coincides with a marked elevation in the temperature of the electrolyte, the tension is then progressively reduced until the temperature of the electrolyte remains stable.

After a short while the tension will have reached its minimum and the density of the current will have reached its maximum. The electrolytic process will then be perfectly established and the products obtained will be of remarkable quality in respect of outside aspect, structure, purity and mechanical characteristics.

This process is particularly efficient when it is utilized in conjunction with smoothing devices acting in the manner described in German Patent No. 480,420 delivered May 18, 1926 and corresponding French Patent No. 628,300 of November 4, 1926.

As an example this is the application of the process for the purpose of obtaining an electrolytic copper pipe of about 125 square decimeters in lateral surface in a bath comprising no substance other than water with 24% of copper sulphate and preferably very little acid, at an initial temperature of 15° centigrade. By acting on the excitation the tension of the generator is brought up successively to 2, 4, 6, 8, 10, 12, 14 volts. Total corresponding intensities of 100—200—300—500—800 amperes are obtained.

When 14 volts is reached, the tension will show a tendency to drop and the intensity will rise, the temperature will increase rapidly.

The excitation will then be acted upon in the reverse way to drop the tension progressively and to maintain the temperature until the moment when said temperature increases no further, which will occur in the neighborhood of 45° to 50° centigrade.

The tension will thus have been stabilized at 6 or 8 volts and the intensity at 1100 or 1200 amperes which will remain the stable working conditions under which it will be possible to obtain without any inconvenience a faultless deposit, polished, very fine in grain, and it will be possible, if it is so desired, to compose an alloy by adding anodes of the metal selected.

The supplementary expenditure in energy owing to the tension employed is amply compensated by the quality and the value of the product obtained as well as by the economy effected, on the other hand, by the absence of special products, the absence of auxiliary heating and the absence of devices for stirring the electrolyte.

The micrographic examination of a thick tube obtained by the process which forms the subject matter of the invention reveals extraordinary fineness of the grain.

In addition the mechanical characteristics of the metal constituting such a tube show the coexistence of great hardness and high resistance to breakage and great elongation as well as very great malleability. Chemical analysis shows its purity.

This clearly indicates the great value of the product obtained. It should be noted, in addition, that the tube has emerged from the electrolytic bath completely finished and polished without having to undergo any treatment or subsequent mechanical polishing. In the case of plates or cylinders intended for heliographic engraving or similar purposes, a light coal polishing may be effected if necessary.

It has been possible to obtain, in the same manner and with equal facility, deposits of iron, zinc and aluminum as well as alloys of handsome outside appearance, the physical and mechanical properties of which are distinctly superior to those of the products known to date.

What we claim is:

1. In the process of depositing from a copper-containing electrolytic bath, comprising progressively raising the voltage and consequently the current density in the electrode circuit until a condition is reached where the current density continues to increase of its own accord whereas

the voltage tends to decrease, progressively decreasing the tension down to a point where the temperature of the electrolyte is stabilized, and thereafter operating the electrolytic bath during the deposition process at the voltage and current density thus established.

2. In the process of depositing from a copper-containing electrolytic bath, comprising progressively raising the voltage and consequently the current density in the electrode circuit until a condition is reached where the current density continues to increase of its own accord whereas the voltage tends to decrease, progressively decreasing the tension down to a point where the temperature of the electrolyte is stabilized, thereafter operating the electrolytic bath during the deposition process at the voltage and current density thus established, and maintaining the temperature of the electrolyte substantially constant throughout the process.

3. An electrolytic process for the deposition of copper from a copper-containing solution, including the step of raising the electromotive force at the electrodes so as to increase the current intensity therebetween until the said intensity tends to rise automatically simultaneously with decrease of electromotive force, and then progressively decreasing the electromotive force to a point at which the temperature of the electrolyte becomes stabilized.

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