## THEORETICAL PRECONDITIONS TO USE THE RESONANT PHENOMENA AT SEDIMENTATION OF WEARPROOF GALVANIC COVERINGS ON THE PERIODIC CURRENT WITH THE RETURN ADJUSTABLE PULSE

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The application of new forms of organization of repair of machines, and the creation of specialized sites and shops on restoration and hardening of machine parts do not remove from the agenda a problem of developing new ways of productivity increase of escalating and producing coverings with increased physical-mechanical and antifriction properties.

To solve these problems, for last 10-15 years, has been increased the volume of researches on using of nonconventional electrolysis conditions (new forms of polarizing current) [1,2,5,7,8,9] and on developing new electrolyte structures, allowing to build up coverings with properties of self greasing [10, 11].

The increase of speed plating (with the use of direct current) due to the increase of output on current is the major trend of works on improving the process of chromium plating, which, is known to be characterized by low [1], values of the output of current. At the same time, in draw plating iron and iron based alloys the current output is, as a rule, more than 85 % [1] and, therefore, because of this to (achieve) essential increase of sedimentation speed, is practically, impossible [1]. Therefore, the basic way of sharp increase of productivity of plating processes of is the rise of cathodic current density, by applying non-stationary electrolysis conditions.

Due to works of [2, 3, 4, 6, 8, 9] and those of other scientists it was shown, that the application of non-stationary electrolysis modes allows to affect essentially the productivity of the process and properties of coverings, due to the use of new forms of polarizing current that has on occasion resulted in the replacement of electrolytes complex (difficult) by structure and not easily controllable under production conditions.

In works [2, 3-9] rather extensive material has been accumulated on sedimentation of galvanic coverings in conditions of non-stationary electrolysis which allows operating the process of building-up deposits with various structures and functional purposes. It does not, however, it the field of fully characterizes advantages and opportunities. According to the forecast [9], in a scope of non-application of non-stationary modes further development will be achieved by electrolysis with fixed parameters of polarizing pulses. In works of some authors [2, 3, 5, 6, 9 etc.] it is shown, that forms of polarizing currents (one-half-period, twohalf-period, reversive etc.) as well as the frequency of their research influence considerably the sedimentation kinetics. microstructure and physicomechanical properties of plating. Thus of the deposited coverings and the productivity of plating process [4, 5, 6] are essentially improved. In the literature there are various viewpoints on the mechanism of influence of a pulsing current on the formation of coverings [2, 4, 5, 6, 13, 14]. In the opinion of [2,4] this influence is due to concentration changes, current pulsation near the cathode which provide uniform sedimentation conditions, as compared to the use of direct current. The current pulsation helps reduce the concentration scarcity of nearby electrode space [2] and allows the alignment of concentration conditions along the whole surface of a specimen.

In the opinion of professor A.K. Krivtsov and of his pupils [6, 7, 15], the quality improvement of deposits with the use of a pulsing current occurs because of periodic surface passivation during a pause, high amplitude in a pulse, the formations of a cathodic film, the adsorption of impurities etc. Besides, the assumption [15] has been stated, that during the crystallization (of copper and gold) on the cathode a the leading role in the formation of this or that form of deposits (large-size crystal small-size crystal, hard, plastic etc.) is not for the nature of a complex, form in solution, the degree of dissociation, hydration, etc., but for the state of an electrode surface, i.e. passivity and activity of sides of a growing crystal, adsorption layers, barter films suboxide and hydroxide intermediate of connections.

On the other hand the assumption [14] is stated, that current density during following the pulse passage actually has smaller value as the part of a current goes for recharging the capacity of a double electric layer. During the pause the process of sedimentation proceeds owing to discharging the capacity of a double layer [14], i.e. at high current densities. Thus the density of a current can be raised as much as twice, in the relation to constant, unchanging quality of plated coverings. The author [2] explains this quantitative leap due to the shift of polarization in more positive side at similar densities of compared currents. The improvement of properties of electric coverings is attributed to the return part of the period [2] which proves is confirmed also by other researches [3, 5, 8, 16, 17].



**Figure 1.** The form of a curve of a periodic current with a return pulse (PCVRP)

Despite above advantages of a pulse way of plating in galvanic technique in recent years, the way of restoration of the worn out machine parts by means of wearproof platings, with the use of periodic current with a reversely adjustable pulse [4,8,12,14,17] has been accepted too.

Special attention, in this plan, deserves work [8] in which the conditions of iron sedimentation of were investigated in regulating a return pulse both in amplitude, and duration. Thus a smoother regulation of electrocrystallization process was provided, which is connected, in the opinion of the author [8], with the possibility to increase power equivalence of the augmented surface of an electrode as а result of dissolution of nonequilibrium crystals during an anodic part of a cycle (Fig. 1). Varying only the parameters, of return pulse, it is possible to change, the sizes of grains from 2 up to 4...5 microns [8]. Such coverings have more perfect structure and high physicomechanical properties [8]. By such parameters as microhardness, metal fatigue durability and wear resistance, they surpass the coverings of iron produced by direct current.

To achieve UPPIRM, the authors of work [19] developed and protected by the copyright certificate the device transforming a three-phase alternating current of industrial frequency into a periodic current with a return pulse adjustable in time and amplitude.

The principle of work, of the given device was described in detail in work [19]. It is necessary to note, that the device enables to receive one-halfperiod rectified current of two phases, and a return pulse is made due to a share of the one-half-period rectified current of the third phase. The duration of a return pulse during one period is regulated with the help of well known control systems. Thiristors with separate control systems may be used as rectifying elements [19].

However, the return component can be got as well as a result of imposing current on the direction alternating variable on constant. On this case the sedimentation process is essential by influenced by the frequency of the imposed alternating current which should be chosen depending on the nature of the plated metal and solution composition [5, 12, 20 etc.]. Thus, for example, in work [20] it is shown, that at the sedimentation of iron, with the increase of frequency of alternating current from 50 up to 5000 Hz, the appreciable change of structure of coverings occurred. The frequency rise above 5000 Hz did not result in considerable change of structure of iron. The majority of researchers [5,20,21 etc.], explain positive influence on properties of coverings, by from imposing an alternating current on a direct one by the elimination of concentration scarcity in nearelectrode space, and by the activation and passivation of a the cathode surface in the return part of a half-cycle. This effect of amplified even more, if the direct current is imposed by alternating one (of various frequency) in a resonant mode at a set of inductance with the accisent of differential capacity of the electrode [22], the most influence on the structure of coverings being rendered by the hydrogen absorbed on a surface [22]. The author [22] showed that the size and (amount) of large crystal (20...25  $\mu$ m), created at the frequency of an alternating current of 50...100 Hz, essentially exceeded the deposits made on a direct current by these parameters. It is supposed [22], that such a change of structure of coverings is connected with an increase of the (amount) of electricity in a pulse resonant condition) and a change (a of concentration of discharging ions at the surface of an electrode.

Problems of resonant phenomena in electrochemical reactions are deeply considered in works with the use of the theory quantum kinetics of electrochemical reactions [23] according to

which the speed of electrochemical process depends on the electrode condition of reagents and their intramolecular nuclear configuration, the change of solvent polarization close to reagents and the influence of the latter on the solvent structure, on the rapprochement of reagents with each other and exit of products from a reaction zone, on the change of configuration of ionic atmosphere around the reacting particles, as well as on the properties of an electrode and electrochemical field [23]. Various models were offered [23] for calculating certain non-uniformity reactions where of solvent polarization and its influence on Franc-Kondonov barrier in the reaction of resonant splitting of electronic energy levels, intramolecular fluctuation, and the of effect type of frequencies of polarization fluctuation on the energy of solvent reorganization were taken into account. Besides, were considered [23] frequency dispersion of dielectric permeability and the interaction of intramolecular fluctuations with fluctuations of solvent molecules, causing the frequency shift of intramolecular fluctuations. Resonant splitting of proton oscillatory levels was also taken into account. In this case it was shown [23], that at weak (connection) of reagents with the environment, the transition probability is essentially determined by a discrete character of oscillatory spectrum for the proton and is of resonant character.

Thus [22, 23], positive effect of the influence of imposing a resonant alternatingcurrent on the structure of coverings at the presence of this return component has been found. Another inspector [24] has developed al new of the accelerated charge of storage batteries based on the conditions of resonance asymmetric current.

efficiency The of using resonant phenomena was stated also in the realization of other processes as, for instance, in work [30] it is shown, that application of resonant phenomena in arc welding accelerates the process of the arc discharge and affects positively transfer and final structure of the welded metal. This process is based on the principle of discretion of phenomena of the arc discharge where the only system excitant is the object of welding (i.e. the arc discharge). The welding arc discharge in this case, is the subject of action of a number current components. By regulation they maybe divided into a constant and set of variable components and as it is underlined in [30], the final structure of the roelded metal is defined by a percentage (ratio) between the number of variable and constant components of the current.

In another work [31] it is shown, that due to a ferromagnetic resonance, the definition of a gradient of elastic tensions of crystal lattices of various materials has become possible. On reddening a resonant line, quantitative estimations of changing dislocation density in studied specimens haze been made.

Deep theoretical and experimental researches described in works [25,26], allowed to establish, that the electrodeposition metals, even at a direct current, is accompanied by the appearance action of "electrical noises" (variable and components of a current) the study of which allows to receive additional data on electrolytic processes occurring on the cathode. As a result of the research done [26] it was found out that the occurrence "electrical noises" in electrodepositing is connected with processes of ion discharge, diffusion phenomena, basic and accompanying reaction taking place on the cathode.

Bulgarian scientists [27-29] also stated the reasons of occurrence of variable current components. As, for example, in [28,29] it was established, that the occurrence of variable current components results from a non-uniform (discrete) course of processes on the cathode [28].

Irregular fluctuations of microcurrents (about  $\pm$  10% of a limiting current) were also found out by another researcher [14]. He drew characteristic oscillograms of above fluctuations at a limiting current of diffusion both at potentiostatic, and galvanostatic introduction of a cell. The author [14] sees the reason of the fluctuations in short-term changes of the thickness of a diffusion layer.

Non-uniformity of electrochemical processes on the cathode is also proved by authors [5, 32] who consider, that the most true explanation of favorable influence of a variable current component of a on the roughness of plating (in the process with strongly expressed a highly distingue wished concentration polarization) is related to non-stationary (discrete) character of near – electrode and electrode phenomena.

The increase of current flowing through the electrolyte, result in increasing the (amount) of ions which need to receive their charge. Therefore, the frequency of their discharge grows and around of the cathode the pulsing cloud of charged ions [33] is crated. Such a pulsing cloud of charged ions in discharging the category on the cathode leads to the occurrence of variable current components (VCC) by [26] it "electrical noises" which under are of irregular form have character by their form [14,27, 33]. The duration of such pluss is about  $1 \cdot 10^{-3}$ ) and even less [27]. Taking into account positive influence of a resonant method of imposing alternating current on the direct one [22] and nonstationary character of near - electrode and electrode processes [25-29, 31-33], one of the

authors of the given work [34] for the first time undertook the attempt of electrodepositing wearproof plating in a mode of the resonance of variable current components (VCC).

The researcher [34, 35] theoretically proved and confirmed experimentally a hypothesis about an opportunity of regulating variable current components (VCC) (fig.2, a), due to consecutive inclusion of oscillatory contour in a catholic electrolysis (fig.2, b), that allowed at



**Figure 2.** Oscillograms of a constant (a) and variable components current at series connection oscillatory contour (b) in an electrolysis circuit [36].

certain ratios of electrical R-L-C parameters of the contour to input VCC in the resonance [36] it was illustrated [31,35], that (coatings), plated with usage of VCC resonance posses an improved structure, high physic-mechanical, antifriction and antiscuff properties and with success may be success bully utilized for (strengthening) and restoring worn machine parts.

From the reasoning stated above, it should be noted that phenomena of oscillations and resonance are widely applied in different electrochemical processes. At the same time, the prospects of applying resonant phenomena in electrodepositing with the usage of different kinds of polarizing current present not only theoretical but also a large practical interest galvanotechnique as a whole.

Therefore, in the present work an attempt was undertaken to prove theoretically possibility of conducting of the process electroplating in the mode of a periodic current resonance with a reverse (UPPIRM).

Taking into account positive results of scientific research [2-9, 12, 14, 15, 19, 20, 22, 24, 29, 33-35], a hypothesis has been suggested by us of the opportunity of electroplating of wear proof covering in the mode of PCVRP by series connection in the cathode circuit of the electrolysis of oscillating circuit with "R,L and C" parameters (fig.3, posture.19).

In the given scheme (fig.3, a) a device described in work [19] is used as a source for

powering plating baths UPPIRM. This device enables to receive one half-wave rectified current of two phases (curve PC), and reverse (pulse) (VRP) – at the expense of a share of the half-ware rectified current of the third phase (fig.3,b). The duration of the reverse (impulse) in one period is adjusted with the help of known control systems. As rectifier cells Thyristors with separate control systems may be utilized as rectifying units.



Figure 3. The electric circuit UPPIRM device for, powering. Plating baths (a) UPPIRM and the (shape) of curves in a resonant mode of electrolysis (b): 1.2.3 – rectifier cells: 4-resistor: 5.6 – instruments controlling anodic and cathode currents; 7,8,12-secondary windings of the 9.11 transformer the anode bath and, correspondingly, the cathode bath; 10-bath; 13single-phase transformer; 14-thyristor; 15,16,17primary windings of the transformer; 18-voltage regulator of a three-phase current; 19-oscillaing circuit

The device wile work as follows (fig.3, a) the voltage of a three-phase alternating-current the of 50Hz, supplied from the circuit to the input terminals of the contact regulator of three-phase current (RTC), is adjusted by (smoothly) from zero up to 380V and is further supplied to primary windings 15,16 and 17 of the lowering transformer of a three-phase current.

The reduced voltage of demanded value from the secondary windings (for example 7 and 8) the transformer is supplied to thyristors 1 and 2 and the rectified half-wave current of two phase pawing in a the cathode direction through oscillating circuit 19 obtained from them, powers plating bath 10. Only for this time during period Tc (fig.3,b) metal plantings on the cathode 11 takes place. Turning the power on and off of thyristors 1 and 2 is provided, by their control systems. The accordingly, (voltages) from the system controlling thyristor 1 is supplied to electrodes band, and from thyristor 2-to electrodes band. The (voltage) of the third phase, is supplied to thyristors 3 and 14 through the single phase transformer.

Between the two series connections of thyristors 3 and 14 the reverse from the third phase

is generated during a certain part of period T, the reverse. Thus the current of a return pulse current flowing in the anodic direction. Resistor 4 serves for limiting current when it flows through thyristor 14.

In our performance, the electrochemical circuit "power source – electrolyze is considered as a closed dynamic system, i.e. the system is oscillatory. Thus, in our case, fuppirm acts an external exposure of this system. And, as is known [36], the external exposure sets initial actuation and initial velocity which, in their turn, determine an initial amplitude and an initial phase of oscillations. An oscillation frequency (f) and a decay coefficient  $(\delta)$  are determined only by properties of the system [36]. In this case we should consider oscillations in a system under the action of external periodic force - UPPIRM as so-called forced vibrations, and then their properties will depend not only on system parameters (f and  $\delta$ ), but also on amplitude and frequency of the external force.

As the form of UPPIRM has is of pulsating character with the frequency of FUPPIRM=50Hz and, at powering plating bath the current flows through oscillating circuit 19 (fig.3, a) it is apparent, that it is possible to use weld known classic methods of mathematical calculation of electrical parameters of the contour ( $r_L$ ,  $r_C$ , L and C) at which a parametric resonance of UPPIRM is possible. For this purpose it is possible to use known mathematical expression [30,35,36] from which one may calculate corresponding parameters.

$$f_{res}^{UPPIRM} = \frac{1}{2\pi\sqrt{L\cdot C}} \sqrt{\frac{r_L^2 - L/C}{r_C^2 - L/C}}, Hz \quad (1)$$

Where  $\rho 2 = L/C$  - a square of a wave drag of an oscillating circuit;

**rL** and **rC** - respectively, reactances in parallel branches of the oscillating circuit with inductance and capacitance.

Analyzing this equation it is possible to conclude, that at the known frequency of following UPPIRM  $(f_{res}^{UPPIRM})$  and fixed values **rL** and **rC**, varying a ratio between inductance (**L**) and capacitance (**C**) of the oscillatory circuit, the approximation to achieving resonant conditions of UPPIRM is possible, i.e. at  $r_L^2 = r_C^2 = L/C$ , the intrinsic part of the oscillating circuit ( $f_{OC}$ )will be equal to the frequency of UPPIRM  $(f^{UPPIRM})$ , following. In this case, according to the classic vibration theory [36] UPPIRM resonance will be achieved.

Under these conditions, the amplitude of periodic current will reach its maximum values

 $(I_{max}^{UPPIRM} = I_{res}^{UPPIRM})$  (fig.3, b). When changing the frequency of UPPIRM (f<sub>UPPIRM</sub>), following it is possible to (achieve)  $I_{res}^{UPPIRM}$  again. Thus, changing UPPIRM frequency and reaching resonant conditions of plating it is most likely, that it will be possible to influence the kinetics of the plating process, the microstructure, physical-mechanical ad antifriction properties of deposits produced.

Thus the qualitative analysis of data of theoretical concepts testifies to possibility of process control of the electrodeposition of metals on UPPIRM by changing electric parameters of the oscillating circuit.

For experimental verification of theoretical prerequisites mentioned above it is necessary to create a unit for powering plating. Baths UPPIRM in a resonant mode of following.

The development of such a device becomes the priority of our further research.

## References

**1. Batischev A.N.** The Prospects of development of the technology of restoring parts by galvanic coverings. Collection of scientific works; The state and prospects of restoring and strengthening machine parts. Central Russian House of Knowledge, M., 1994. - p.105-108.

**2.** Belonuchkin P.P. The study of affects of polarizing current forms on the iron-plating process and phyzico-mechanical properties of coverings applied to repair machine parts. Autosinopsis of the Phil. Doct., rechnical sciences, Chisinau, 1969.- 16p.

**3.** *Bibikov N.P.*, *Galvanic coverings deposited by meaks of the current of alternating polarity. Edition* 2, *M-L; Mashgiz, 1961-71p.* 

**4.** Vagramian A.T., Sutiagina A.A. The effect of alternating current on the process of nickel plating. Edition of the Academy of Sciences of USSR, series of chemistry Nr.3, 1952- p.409-414.

5. Gnusin N.P., Kovarsky N.I. The roughness of plated surfaces. Novosybirsk, Nauka, 1970-234p.

6. Krivtsov A.C. The production of galvanic coverings at the pulsating current. In collection: Chemistry and Technology of nonarganic substances; Works of Technological Institute from Ivanovo, Issue 7, 1958.- p.89-95.

7. Costin N.A., Krivtsov A.C. About the mechanism of lustre production of nickel deposits at the pulse electrolysis. Electrochemistry, vol.18, issue 2, 1982,

p.210-214. 8. Kosov V.P. Theoretical foundations and the development of technology of restoring wear-proof parts of iron plating at the periodic current. Auto

synopsis of the Phil. Doct. thesis, (Doctor of Technical Sciences), Chişinau, 1979, 33p.

**9.** Costin N.A. The Prospects of development of pulse electrolysis in galvanotechnique and surface processing, vol.1, Nr.1-2, M.1992, p.16-18.

10. Roscovan Gh.V. Restoring tractor parts by selfgreasing iron-nickel coverings. Autosinopsis of the Phil Doct.thesis (Technical sciences), Chisinau, 1992, 17p.

11. Stoicev P., Roscovan Gh., Toca A. Tribolegical behavior of galvanic iron-nickel alloy with self – greasing properties (a XVIII-a sesiune de comunicări științifice cu participare interațională (21-22 octombrie, Acadmia Militară Thnică), București, 1999.-197-204.

12. Petrov I.N., Kosov V.P., Stratulat M.P. The repair of tractor parts by means of galvanic coverings. Edition "Cartea Moldovenească", Chișinau, 1976.-150p.

*13. Molchanov F.V.* Accelerate chromium plating. *Kiev, Technica, 1965.- 45p.* 

*14. Fetter C. Electrochemical kinetics, M., Chimia, 1971.- 434p.* 

**15. Khamrayev V.A., Crivtsov A.C.** The effect of non-stationary electrolysis modes on structure formation and physical and mechanical properties of the deposits of copper and gold. - Ed. of Higher schools. Chemistry and chemical technology. Vol. 22. Issue 5, 1979.- p. 584-589.

16. Levin A.N. Theoretical foundations of electrochemistry. M.: Metallurgy, 1972-536 p.

17. Rapoport L.S. Studies of the influence of periodic current parameters on the efficiency of tractor parts restored by iron plating. Authorized Paper of the Thesis of Phil. Doctor (Technical Sciences), Chisinau, 1977- p. 19.

18. Shvetsov A.M. The research of antifriction properties of coverings produced by hard steeling. Authorized Paper of the thesis of Phil. Doctor (Technical Sciences). M., 1969. - p. 16.

**19.** Cosov V.P., Erlikh D.M. and Olkhovsky. E. N. Authorized Certificate N 387040 (USSR). A device for powering galvanic baths with periodic current of a reverse pulse. Published in Libr. Nr 27 of June 21, 1973.

**20.** Mamontov A. E. Studies of the mechanism of electroplating and physical and physical and mechanical properties of iron plating. Authorized Paper of the thesis the Doctor of chemical sciences. M.: I Ph. Ch. Academy of Sciences, USSR, 1969 - p 29.

**21. Kruchkov A.A., Levin A.I.** Theory and practice of electrodeposited coverings. Theses of reports at the regional conference, Riga, 1965. – 22 p.

22. Antonyan S.B. The effect of joint action of alternating and direct currents on the morphology, substructure and physical and mechanical properties of deposits of nickel and copper.

Authorized paper of the thesis of Phil. Doctor (Chemistry), Vilnius, 1979. – 10 p.

23. Frumkin A. N., Andreyev V.N., Boguslavsky L. I., etc. Dual layer and electrode kinetics. M.: Nauka, 1981. – 76 p.

**24. Filatov V.N.** The development of the method of accelerated accumulator charge by means of asymmetric current. // Electrochemical industry. Ser. Chemical and physical sources of current. Issue 3(72), 1980. p. 13-15.

**25. Tiagai V.A., Lukianchikova N.B.** Balanced fluctuations in electrochemical processes // Electrochemistry, Vol. 3, issue 3, 1967–p.316-322.

**26.** *Tiagai V.A. Theoretical analysis of Faraday's noise caused by diffusion and discharge. // Electrochemistry, Nr. 1, 1971. – p. 69-72.* 

**27.** *Bader M.G. The fatigue strength of repaired steel shafts. Metal and materials, 1967. - p. 300.* 

**28.** Budevski E.B. Some fundamental aspects of Progress in surface and membrane science, v. II, 1976. – p. 71-116.

**29. Kaischev R., Budevski R.** Contemporary Thysics. Nr. 8, 1967. - p. 489.

**30.** Svirchevsky A. M., Antoseac V.G. The efficiency of resonant phenomena in arc metal welding. Chishinau, Shtiinta, 1976. – p. 116.

**31. Garkunov D. N., Pinchuk V.G., Matushenko V. J.** The influence of watersmoking on processes of strengthening in friction. Theses of reports of scientific and technical conference: Theory of friction, wear and greasing. P. 1, Tashkent, 1975-p. 108-109.

**32. Kovarsky N.I., Gnusin N.P.** Polarizability and roughness of copper deposits produced from sulphate electrolytes, produced from sulphate electrolytes. *ЖПХ Vol. 3, issue 12, 1966, p. 2830-2832.* 

**33.** Lazarenko B.R., Lazarenko N.N. Processes occurring on electrodes during electric current flowing through an electrolyte. // Electronic material processing, Nr. 1, 1966. - p. 3-9.

**34.** Stoicev P.N. Restoring tractor parts by galvanic coverings with the use of resonant phenomena. Authorized Paper of the thesis of Phil. Doctor (technical sciences), Chishinau, 1983. - p. 18.

35. P. Stoicev Improving duration and restoring car parts by wear-proof coverings. Thesis of the Doctor hab. of technical sciences. Chisinau, 2001. – p. 381.
36. V.V. Migulin, V.I. Medvedev, E.P. Mustel and V.N. Parygin. Basics of the fluctuation theory. M.: Nauka, 1978. - p. 391.

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