Electrochemical Formation of Phosphate Coatings with Superior Corrosion Resistance by Application of Bi-polar (DC+AC) Pulses

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Since the formation of phosphate conversion coatings can be considered an artificially induced corrosion process, the polarization of the anodic and cathodic reactions are the major rate controlling factors. Owing to high polarization of the reaction of hydrogen ions discharging, the zinc phosphating tends to be slow at ambient temperatures. For these reasons, the process of phosphate coating formation takes place, in reality, at relatively high bath temperatures. The higher temperatures, however, are related to generation and precipitation of a large quantity of sludge which results in a greater consumption of energy and materials.

The basic idea of this work is to drastically reduce the polarization of the zinc phosphating reaction by combining conventional accelerators in the bath with the application of bi-polar (DC +AC) voltage pulses. As a result, phosphate coatings will be obtained at ambient temperature, and the sludge generation will be eliminated as well. Moreover, the use of this pulse/reverse technique favours the formation of zinc phosphate coatings with homogeneous and fine-grained structure which increases corrosion protection.The comparative corrosion investigations show that the corrosion resistance of zinc phosphate coatings obtained electrochemically at ambient temperature is considerably higher than that of conventionally formed coatings.

One of the most important applications of phosphate coatings is as pre-treatment for painting of ferrous metal. The microcavities and capillaries, fissures and undercuts of the coating provide a relatively large surface area and paint adhesion is greatly improved over that of a clean, untreated metal surface. In addition, the insulating effect of the phosphate coating on local corrosion cells on the metal surface helps prevent the spread of corrosion from regions where the paint has been damaged from chipping or scratching.

The paint-base phosphate coatings for ferrous metals are of the iron or zinc phosphate types. Amorphous or noncrystalline iron phosphate coatings are used to promote the bonding of power coatings to a clean ferrous substrate. These coatings are a mixture of iron oxides and iron phosphate. The beneficial characteristics of iron phosphate include relatively low operating coast, simple equipment requirements, low sludge formation, and moderate control requirements. The iron phosphate coatings, however, offer poor corrosion protection.

Zinc phosphating is the type of coating formation commonly used in the automotive and appliance industries and in other applications where the higher cost is justified by the improvement in performance. The crystalline coatings are extremely adherent to the substrate. The formation of a fine, dense crystal pattern of zinc phosphate noticeably improves corrosion resistance and paint adhesion. Steel parts that have been properly coated with zinc phosphate and painted are superior in resistance to under-coat corrosion than those coated with iron phosphate. Zinc phosphating baths, however, can operate at higher temperatures - most of them are maintained at about 60^0 C. The increased demand of heat forms excessive sludge which leads to a higher consumption of energy and materials.

This paper focuses on the electrochemical aspects of the zinc phosphating processes in order to develop an efficient method of phosphating at ambient temperature by application of bi-polar (DC+AC) voltage pulses. This method will eliminate sludge generation as well as increase considerably the corrosion resistance of phosphate coatings.

The Electrochemical Aspects of the Phosphate Coating's Formation[1,2,3,4]

The phosphate coatings are formed by chemical reaction during immersion of the metal in an aqueous solution of a primary phosphate $Me^{II}(H_2PO_4)_2$ containing a certain amount of free phosphoric acid (Me^{II} stands for ions Fe^{2+}, Zn^{2+} or Mn^{2+}). According to Machu, the formation of insoluble phosphate coatings can be considered an artificially induced and controlled process of electrochemical corrosion, involving two mutually linked reactions: anodic and cathodic.

The greater part of the surface area functions at first as an anode, whereas the cathodic regions are restricted to grain boundaries, residual oxides, etc. The anodic current is linked to the formation of soluble iron (II) ions in the near-surface solution layer around the local anodic regions:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

Simultaneously, equivalent amounts of hydrogen ions are discharged at local cathodic areas.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

As the reaction (2) proceeds, a reduction of the hydrogen ion concentration (alkalization) at the metal-solution interface occurs. Thus, the chemical reaction of phophating is displaced towards the formation of insoluble secondary and tertiary heavy metal phosphates:

$$4Me^{2+} + 3\,H_2PO_4^- \rightarrow MeHPO_4\downarrow + Me_3(PO_4)_2\downarrow + 5H^+ \qquad (3)$$

In the case of iron phosphating of steel, the ferrous cations obtained during the anodic dissolution reaction (1), are the only metal ions which are incorporated into phosphate coating, whereas in zinc phosphating, zinc ions and other heavy metal ions come into the conversion coating from a phosphating bath. The coating process is complete when the surface of the metal is so fully covered by the crystalline phosphate that no significant further neutralization of the near-surface liquid layer can take place. Obviously, the rate of the chemical reaction (3) depends on the velocity of the both electrochemical reactions (1) and (2) of a metal corrosion in acidic aqueous solutions. Therefore, this rate will be related to the corrosion current, I_{corr} - the abscise of the point of intersection between the anodic and cathodic polarization curves in an Evans' corrosion diagram shown in Figure 1.

It is well known that the corrosion rate of metals in acidic aqueous electrolytes is strongly influenced by the cathodic polarization of the reaction of hydrogen ion reduction. It is exactly because of the great hydrogen over-voltage on a zinc substrate, that the phosphating process tends to slow down especially at a lower temperature. In practice, several chemical and physical methods are applied in order to accelerate the zinc phosphate coating formation.[5] In what follows, we consider the most important of them and give an electrochemical interpretation of their beneficial depolarization effect.

1. *Acceleration by oxidizing agents*

The accelerating effects (depolarization) of the oxidising agents result from them preventing the metal surface from being physically blocked by hydrogen bubbles. The hydrogen evolution reaction (2) has been replaced by easier and faster processes in which water is produced:

$$\textit{accelerator}\ XO + 2H^+ + e^- \rightarrow H_2O + \textit{reduction form of}\ XO \qquad (4)$$

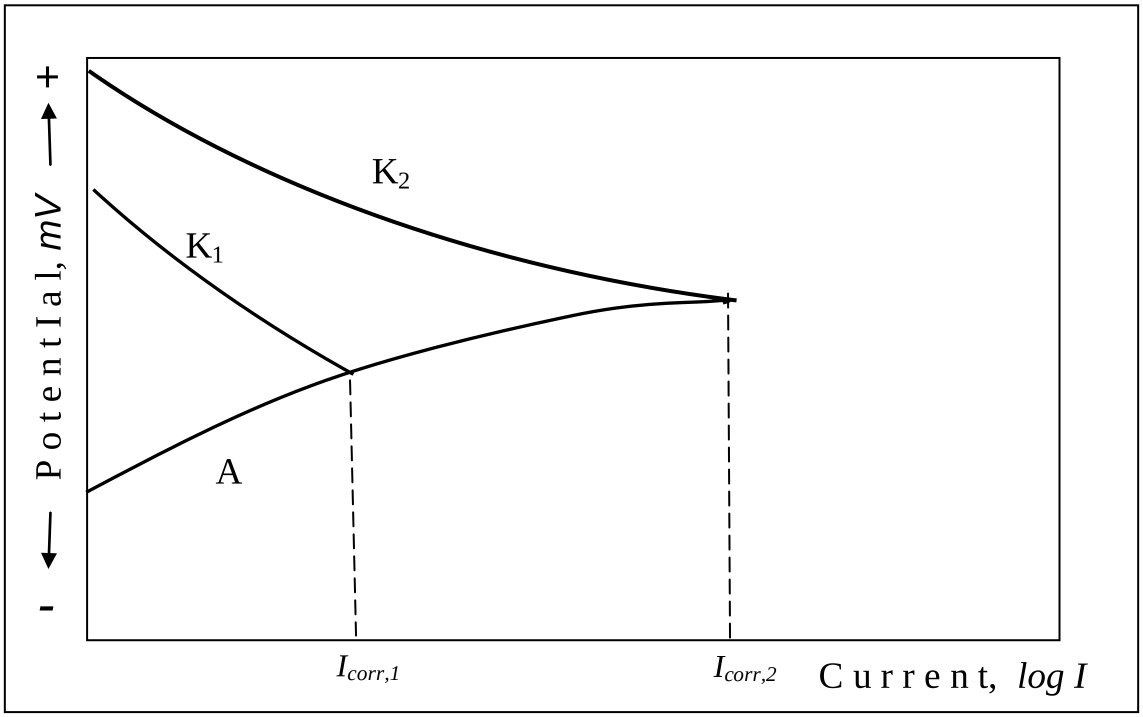

Fig. 1 *Schematic corrosion diagram showing increased values of current by adding the oxidizing agents in phosphating solutions*

Cathodic processes: *curve* **K**$_1$ $2H^+ + 2e^- = H_2$

curve **K**$_2$ $Ox_{(acc.)} + H^+ + 2e^- = Red_{(acc.)} + H_2O$

Anodic process: *curve* **A** $Me - ne^- = Me^{n+}$

The rate of the phosphating processes can be graphically determined by the corrosion currents $I_{corr,1}$ and $I_{corr,2}$ corresponding to the velocity of phosphating without and with accelerators respectively (Fig. 1). One can see that in order to function as efficient accelerator, the redox equilibrium potential, E^{0}_{0x} of the oxidizing agent has to be much more positive than that of the hydrogen, E^{0}_{H}. Such chemical substances are nitrate, nitrite and chlorate ions

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O; \quad E^0 = +0.94\ V \quad (5)$$

$$NO_2^- + 2H^+ + 2e^- \rightarrow NO + H_2O; \quad E^0 = +0.99\ V \quad (6)$$

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \quad E^0 = +1.40\ V \quad (7)$$

Usually these reactions promote the conventional zinc phosphating process when the treatment bath is heated to over 60-70^{0}C. Such combination of both chemical and physical (heat energy) accelerating factors, however, disturbs the state of equilibrium in the bulk and the reaction sites are not already restricted to the treated metal surface. This affects the entire treatment bath, causing inevitably an extraneous reaction (3) to occur in addition to the phosphate film formation, e.g. sludge generation.

2. *Acceleration by metals more noble than iron*

A certain degree of acceleration can be obtained by introducing into phosphating bath ions of metals more noble than iron, such as nickel, copper, cobalt, or silver. The metals are deposited electrochemically over the iron surface undergoing treatment, thereby providing more active cathodic centers. According to the Tafel equation, the over-voltage (polarization) of the cathodic reaction of the hydrogen evolution is strongly dependent on the values of exchange current density $i_{0,H}$:

$$\eta_c = b_c \log (i_c / i_{o,H}) \quad (8)$$

where b_c is constant ca. -0.12V per tenfold current change. One immediate consequence of this equation is that the larger the exchange current $i_{o,H}$ the smaller is η_c and vise versa. This means that to the higher values of $i_{0,H}$ for hydrogen evolution on some cathodic substrates (Ni, Cu, Co, Mo) the greater process' velocity.[6] Consequently, zinc phosphating will be accelerated in accordance with the increasing corrosion currents $I_1 < I_2 < I_3$, as it is shown in Figure 2.

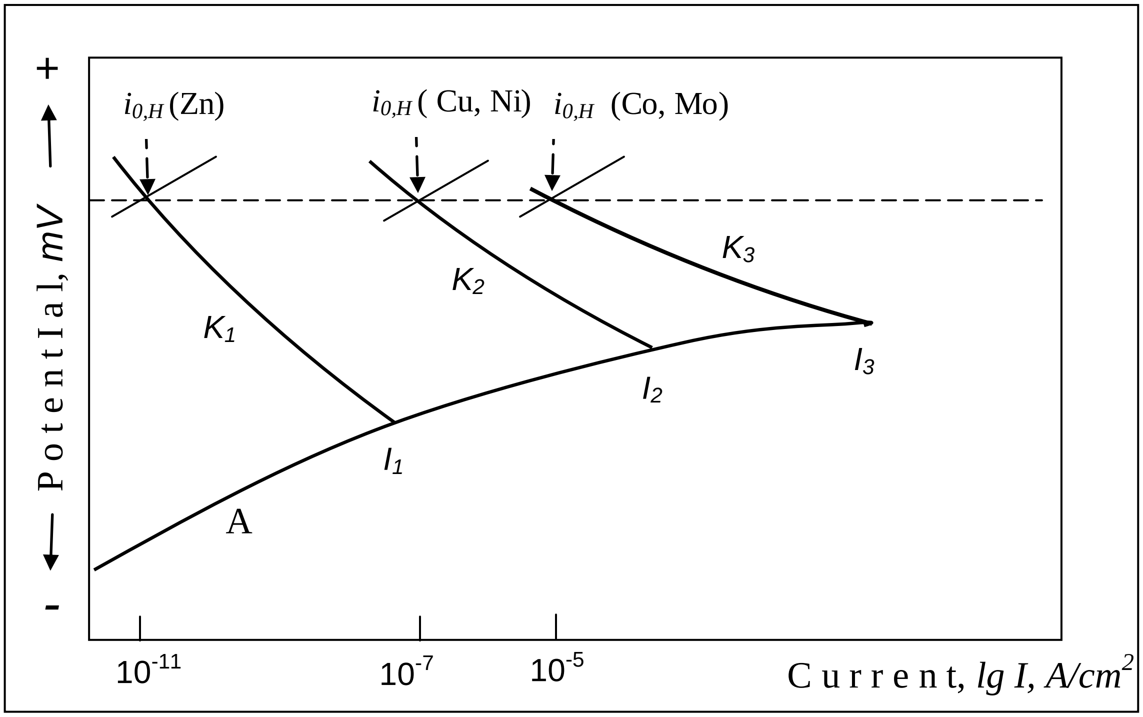

Fig. 2 *Schematic corrosion diagram showing the increasing corrosion rate in relation to the rising of exchange current of hydrogen evolution,* $i_{0,H}$ *on different metal substrates;*

Cathodic processes: curves ***K_1, K_2, K_3:*** $2H^+ + 2e^- = H_2$

Anodic process: curve ***A:*** $Me - 2e^- = Me^{2+}$

3. Acceleration by using cathodic current

This mechanism of acceleration is similar to the cathodic protection of metals.[7] As it can be seen from the Fig. 3 the shifting of the potential of protected metal in negative direction from E_{corr} to E_c, reduces the anodic current from corrosion current I_0 to zero, and increases the cathodic current from I_0 to I_{DC}. During the cathodic polarization, the reaction (4) takes place and the liquid layer adjacent to the substrate is neutralized. In this case the oxidizing agents (accelerator XO) consume electrons that are supplied not by an etching reaction (1), but by an external source of electrons – the cathode, and therefore, the accelerating effect can be related to the increased cathodic current I_{DC}. The cathodic DC polarization, however, can slow down or totally eliminate the phosphoric acid pickling reaction of metal substrate. This means that there is no dissolving and incorporation of ferrous ions into the phosphate coating, which has a negative effect on the good protective properties of phosphate coatings. In order to prevent this elimination of the pickling step, some investigators electrochemically accelerate the zinc phosphating process by using forward-reverse pulse techniques[8,9] or by applying an alternating current (AC).[10] Moreover, because of depolarization action of the later, displayed graphically as a diminishing slope of cathodic curve, the acceleration is even greater and reaches the value of I_{AC} (Fig.3).

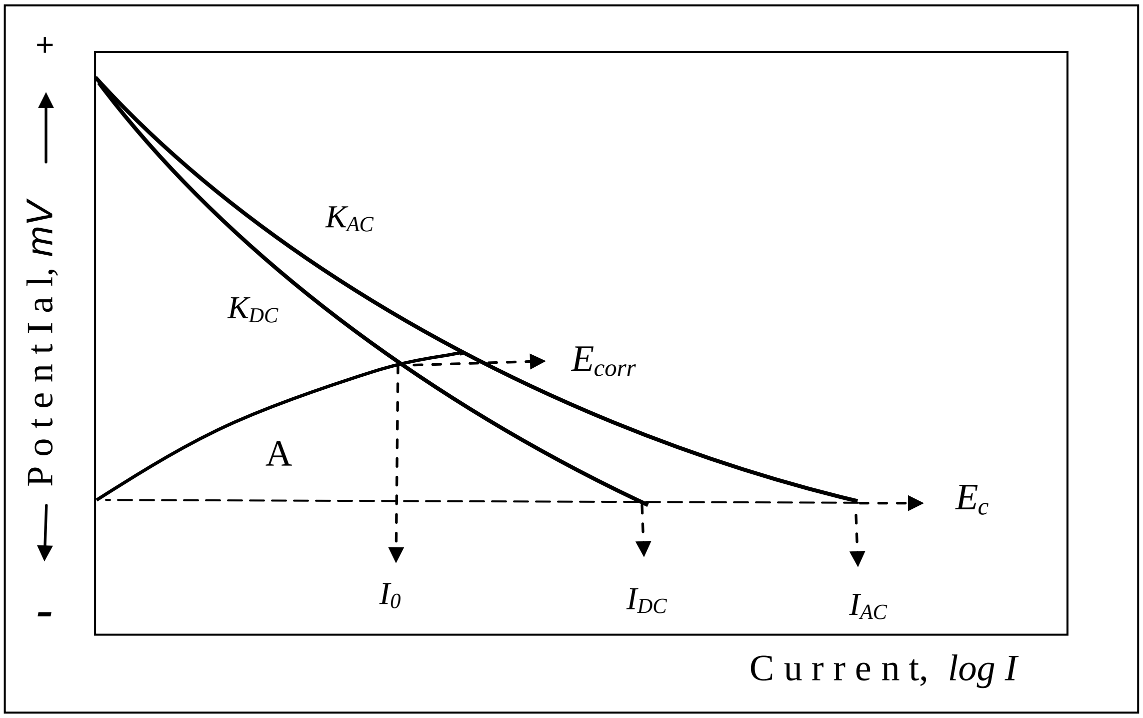

Fig. 3 *Schematic corrosion diagram showing the acceleration of phosphating by using direct current (DC) or alternating current (AC)*

The basic idea of this work is to reduce drastically the great polarization of phosphating reactions by combined use of the three above considered accelerating means. In addition, the electrochemical acceleration is to be performed by using bipolar (DC +AC) pulses. This approach of acceleration enables us to produce zinc phosphate coatings at ambient temperature, and hence to reduce or totally eliminate the sludge generation.

Acceleration by the Application of Bipolar (DC + AC) Voltage Pulses[11]

As it was already mentioned, the heterogeneous process of phosphating of ferrous metals at ambient temperatures proceeds very slowly because of high polarization (over-voltage) of both electrochemical reactions of reduction and oxidation. Consequently, every attempt to accelerate the phosphating processes at lower temperature by physical means should compensate the shortage of heat energy in the system. Thus, the application of bipolar (DC + AC) voltage pulses appears to be an especially suitable and efficient method of electrochemical the acceleration of cathodic and anodic phosphating reactions because of the following characteristic features and advantages.

- *Bipolarity of (DC+AC) pulses enables the control of both the cathodic and anodic reactions of the phosphating process*

As a type of treatment, the application of bipolar pulses is closely related to the electrochemical mechanism of spontaneous phosphate coating formation, described above. Since the formation of conversion coatings can be considered an artificially induced corrosion process, involving two mutually linked and simultaneously proceeding reactions – anodic and cathodic – one can infer that the application of bipolar (DC +AC) pulses can be successfully used for controlled formation of phosphate coatings.

Table 1

PARAMETERS OF (DC + AC) BIPOLAR PULSES	
FORWARD *(Cathodic)*	REVERSE *(Anodic)*
Peak of Cathodic Voltage, U_c, *V*	Peak of Anodic Voltage, U_a,*V*
Pulse Duration, T_{on}, *ms*	
Pulse Frequency, f *Hz*	
Frequency of Alternating Sinusoidal Voltage, f_{AV} *kHz*	

The parameters and waveform of bipolar (DC + AC) voltage pulses are shown in Table 1 and Figure 5. As it can be seen from the Figure 5, the superimposing of high-frequency alternating voltage (AV) on DC-voltage pulses results in cathodic (I_c) and anodic (I_a) current pulses simultaneously. By varying the pulse voltage peaks we are able to find the optimal coordination of both processes of reduction and oxidation and thus to obtain phosphate coatings with the best properties.

- *The off-time between two (DC+AC) pulses improves phosphate coatings' properties*

The off-time, T_{off}, directly influences the structure of the deposits and their properties as it provides a relaxation time for 1) the recovery of ions taking place in electrode reactions in the depleted diffusion layer and 2) the adsorption and diffusion of adatoms as well as the crystallization of phosphate species on the treated metal surface.

One of the stages of electrocrystallization is taken up by the time consuming process of surface diffusion and incorporation of adatoms into the crystal lattice. We have described elsewhere[12] the leveling mechanism and focused on the relationship between the rates of adsorption and diffusion of adatoms during T_{off} on the one hand, and the pulse frequency on the other. It was established that coatings deposited at a pulse frequency that guarantees maximum leveling should exhibit superb qualities because of the high degree of structural homogeneity. By varying the pulse frequency, at constant pulse duration, T_{on}, we can find the exact off-time, T_{off} that yields a maximum value of leveling power and thus creates the optimal pulse conditions for formation of high quality phosphate coatings.

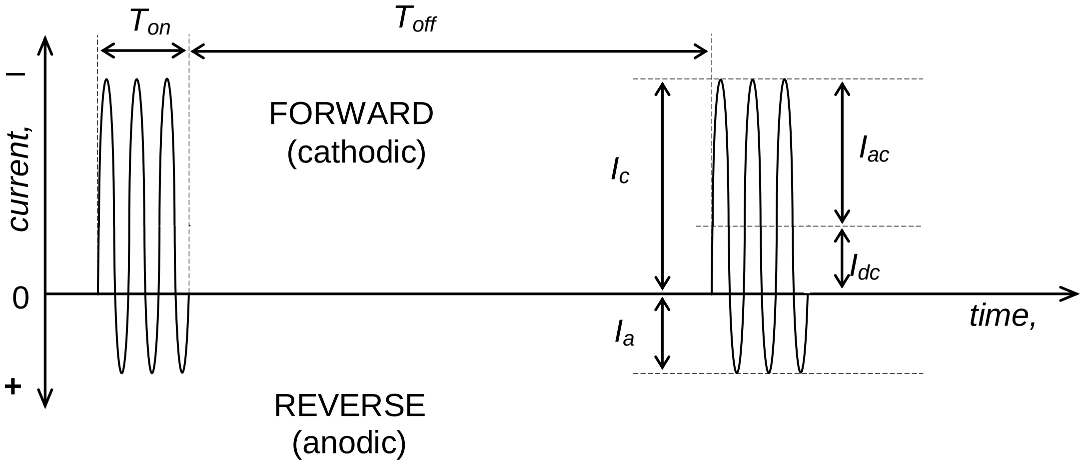

Fig. 5 *The asymmetric waveform of (DC+AC) bipolar pulses*

- *It is possible to apply very high pulse current densities, which promotes the formation of fine-grained phosphate coatings*

When the sinusoidal alternating voltage U_{av} is applied on a two-electrode electrochemical system the resulting current through the working interfaces is the sum of distinct contributions from the faradaic current i_f and double-layer charging current i_c.[13] The rate of the net electrochemical process, i_f ,is in inverse proportion to the faradaic impedance Z_f . The later can be presented as a combination of the series resistance R_s and the pseudocapacity C_s according the formulae $Z_f = R_s(\varpi) + \frac{1}{\omega C_s}$. From the frequency dependencies of R_s and C_s it follows that there exists a frequency of the applied voltage U_{av} at which the faradaic impedance $Z_f = R_s(\varpi) + \frac{1}{\omega C_s}$ is minimal and, correspondingly, the faradaic current i_f is at its maximum. Therefore, we can use this experimentally determined frequency of alternating voltage to apply maximum pulse current peaks, and hence, considerably to accelerate the formation of phosphate coatings. As it was already demonstrated in our previous work,[11] the comparison on the basis of the same average current densities shows that the current peaks of the (DC+AC) pulses are nearly three times greater than the ones of the ordinary DC pulses and many times greater than continuous direct current. This means that if the peaks of pulse current are higher, the grain structure of the obtained coatings is finer.

The above characteristic features and advantages of the bipolar (DC + AC) pulse technique present an incentive to develop an environmentally friendly and effective pulse technology for electrochemical formation of zinc phosphate coatings with excellent protective properties.

Experimental Techniques and Results

The device used for electrochemical pulse phosphating is schematically shown in Figure 6. It consists of a generator, **G**, for potentiostatic application of bipolar (DC+AC) pulses, an electrolytic cell and an oscilloscope, **Osc**. With the help of the latter, the cathodic and anodic pulse current peaks are measured, whereas the average cathodic current is measured by an ammeter, **A**. The sample to be treated is a plate of mild steel (20x50mm), and the counter electrode is the bathtub of stainless steel containing 400 cm^3 the phosphating solution. A conventional "low zinc" phosphating bath containing small quantities of heavy metal ions is used. The parameters of the generator, **G** can be varied within the following ranges:

Anodic Peak of the Sinusoidal Voltage U_a,	0 - 40V
Cathodic Peak of the Sinusoidal Voltage U_c	0 - 40V
Pulse Duration, $\boldsymbol{T_{on}}$	1 - 99 ms
Pulse Frequency, $\boldsymbol{f_p}$	1 - 20 Hz;
Frequency of Alternating Sinusoidal Voltage $\boldsymbol{f_{AV}}$ **,**	0,5 - 5 kHz

The optimal values of the parameters are established experimentally through leveling power measurements. From the relationship between leveling power, *LP%* and pulse frequency f_p it can be determined the maximum values of leveling power of 6Hz. The other pulse parameters of leveling maximum include: pulse duration T_{on}= 10 *ms,* and frequency of alternating voltage, $f_{a\text{-}v}$ = 3.0 *kHz.*

During the process of electrochemical phosphating with a duration of 8 minutes, bipolar (DC+AC) voltage pulses are applied on the samples of mild steel which results in cathodic and anodic pulse current density of 15 A/dm^2 and of 7 A/dm^2 respectively. The temperature of the phosphating bath is maintained at about 30 ±1 ^{0}C. The average thickness, expressed as a coating weight per unit area, of the obtained zinc phosphate coatings (*samples* ***A***) is about 1.9 g/m^2. The other set of samples (*samples* ***B***) are conventionally phosphated (without external electrical polarization) in the same phosphating bath at 70±1^{0}C, in the course of 3 minutes.

The comparative evaluation of corrosion resistance of the samples ***A*** and ***B*** was performed by salt spray test. The neutral saline solution (pH=7) which is periodically sprayed over the samples contains 50 g/l NaCl. In order to accelerate the test procedure, a relatively high temperature of 55^{0}C is maintained.

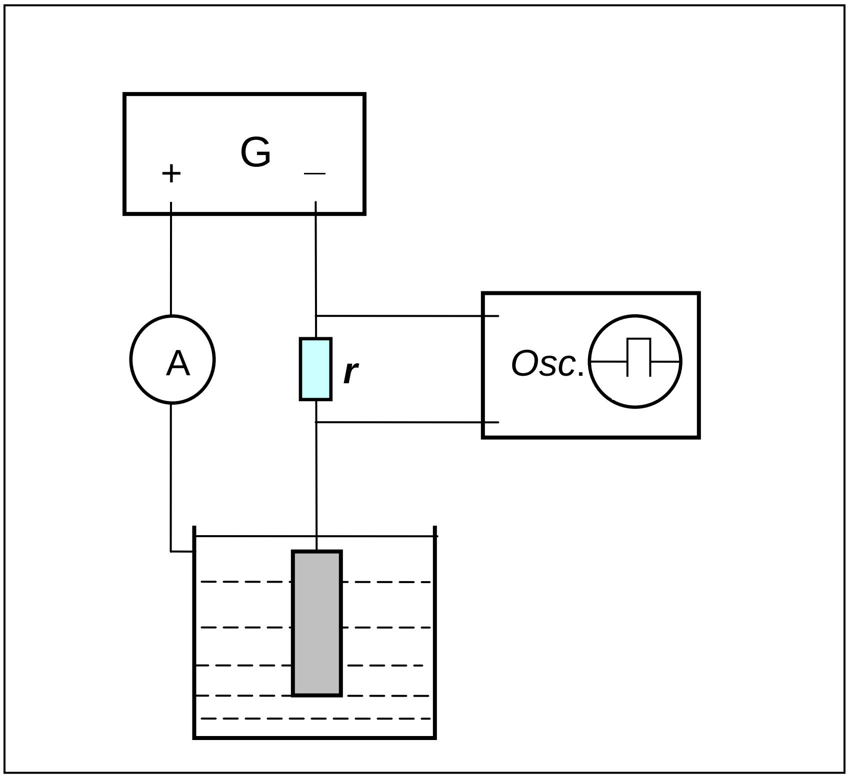

Fig. 6 *Schematic diagram of the apparatus for electrochemical phosphating by application of bipolar (DC+AC) voltage pulses*

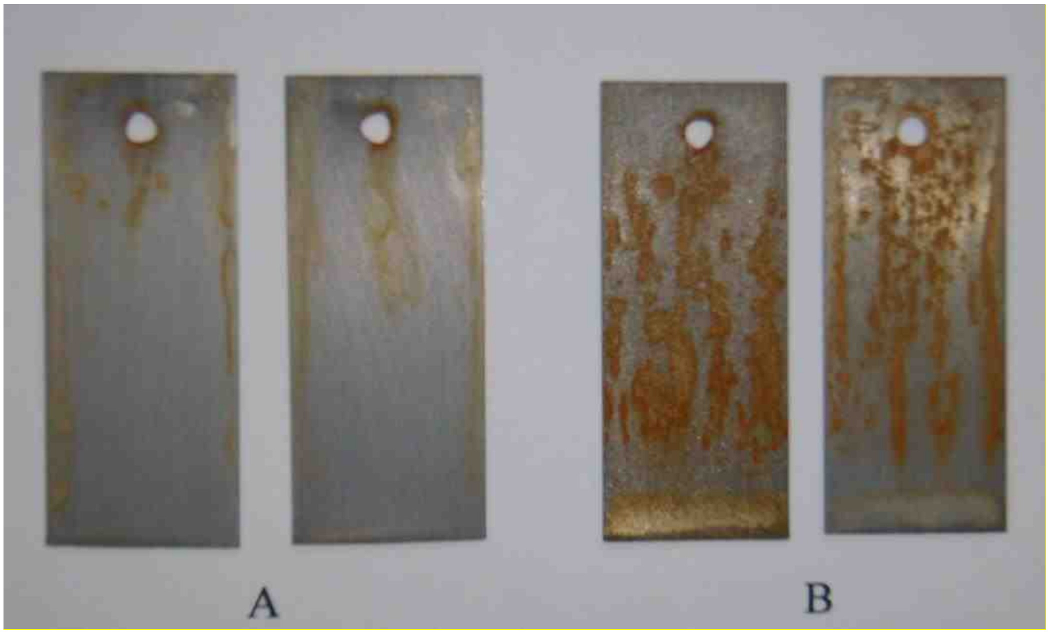

Fig.7 *View of the electrochemically phosphated samples (***A***) and of the conventionally phosphated samples (***B***) after 80 min. of salt spray testing*

Figure 7 presents the results from a great number of corrosion tests. Compared are the appearances of the samples ***A*** and ***B*** after 80 minutes salt spray treatment. This picture presents solid evidence that the electrochemically obtained phosphate coatings have very high corrosion resistance in comparison to the conventionally obtained coatings. At the same time, the thickness of the conventionally obtained coatings is twice as big. It is to be noted also that the excellent corrosion resistance of electrochemically formed phosphate coatings is obtained at ambient temperature of the phosphating bath, at which the possibility for sludge generation is practically eliminated.

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