ANNALS of the ORADEA UNIVERSITY.
Fascicle of Management and Technological Engineering, Volume IX (XIX), 2010, NR2

RESEARCHES ABOUT THE REALIZATION OF THE MOULDS BY ELECTROCHEMICAL TECHNOLOGIES

LUCA Cornelia[1], CHIRILÃ Elena[2]
[1]Technical University “Gheorghe Asachi” of Iasi-Romania
email: cionescu@tex.tuiasi.ro
[2]Technical University “Gheorghe Asachi” of Iasi-Romania
email: cornelialuca@yahoo.com

Keywords: footwear, sole, mould, electro-deposing technology

Abstract. The paper presents researches about the elaboration of some electrochemical technologies for the manufacturing of moulds used in the footwear soles obtaining. There are presented a few methods in the obtaining of the moulds using in electro-deposit process. The paper presents the stages in the obtaining and preparing of the electrodes (including the compatibility properties), in the preparing of the electrolysis equipments and in the obtaining of the metallic dies which will be fitted into the proper mould.

1. INTRODUCTION

The field of the electrochemical technologies includes the technologies used in the obtaining of certain working parts of the moulds, under the current action, into the aqueous of metallic salts. These technologies may be electro-deposit once or electro-chemical corrosion once. Both kinds may be applied in the obtaining and varying of the moulds used in the footwear industry.

The paper presents solutions for the obtaining of certain working parts of the moulds for soles, considering the electro-deposit technologies.

2. EXPOSITION

The electro-deposit technology is used, in the manufacturing of the moulds for soles, in two variants: the electroplating and the electroforming. Using the electroplating, it will settle down thin layers of high-oxidizable metals on the surfaces of usual metals objects, as a protection against their oxidization under the action of the environment or chemical agents. The electroforming technology is used for the thicker deposits, over 1 mm, on the surfaces of certain shapes, for the obtaining of the assemblies with high mechanic strength. The so obtained layers will, usually, appear from the surface and then, they will be used in this state or after a previous consolidation.

In the case of electro-deposit technologies, the surface which receives the metal in an ionic state represents one of the electrodes of the electrolysis equipment, the other one being a metallic bar (which has the same material as the deposit one, or another kind of metal, but an inert one, from the electrolytic leaching point of view). In this process, it is very important the quantity of metal which is deposed on the cathode, both in the electroplating case and in the electroforming one, too. [1,2,3]. This quantity is in proportion to the current quantity which passes by the electrolyte and to the electrochemical equivalent of the certain material. This statement, which is the sum of the two electrolysis laws enunciated by Faraday, allows a quantitative estimation of a certain metal deposits, depending on the current quantity which passes by electrolyte. So, a current quantity, equal to 1 coulomb (one ampere per second), will release different quantities of metal from cathode. These quantities are adequate to the electric energy unit passes by and they are called the electrochemical equivalent of the certain metal. Making a ratio between the chemical equivalent of the metal, the molecular mass/valence and the electrochemical equivalent, it will obtain a number which is constant for all metals, the so called Faraday number, whose value is 96500 coulombs, more exact, 96487,3±0,5 coulombs.

In these conditions, the metal quantity which is deposed on the cathode is given by relation (1):

$$m = K \cdot q \text{ , [g]} \tag{1}$$

where: m-mass of the metal deposed on the cathode, in gram; K-factor of proportionality, respective, the electrochemical equivalent of each metal which were electrolyzed; q-electricity quantity which passes by the solution, in ampere seconds, which is given by relation (2):

$$q = i \cdot t \text{ , [A.s]} \tag{2}$$

where: i-amperage, in ampere; t-time, in second.

The electrochemical equivalent, K, may be calculated for each metal, knowing the Faraday number and using the relation (3):

$$K = \frac{M}{v \cdot 96500} \tag{3}$$

where: M-atomic mass of the metal; v-valence of the metal; 96500-Faraday number.

The metal deposits by electrolysis are realized during the some currents (which have small voltage, 2-6 V, and big amperage) passing through the electrolyte solution. The value of the voltage is specific to each metal. The amperage, in ampere, is variable, but it provides a current density which value is about 10 A/dm^2. Knowing the surface on which the electro-deposits will take place, in dm^2, it will choose the source of direct current [4].

The protection covering with thin layers, electroplating and the protection covering with thick layers, electroforming, take place, as a rule, in the same way for each metal but the realizing conditions are different.

The paper presents a method which was used in the obtaining of the certain mould working parts, of the certain cavities which, ulterior, were fixed into the proper moulds used in the soles manufacturing.

3. EXPERIMENTAL PART

3.1. Preparing of the non-metallic electrodes

The moulds for soles, which are obtained by electro-deposit, are realized using the electrolysis equipments. This kind of equipments has an electrolytic tank made from a material which does not react with electrolyte solutions. Into its interior, there are placed two electrodes, between them being a certain distance. The electrodes are connected with a source of direct current. The cathode is the electrode which receives the metallic deposits resulted by electrolysis. In the case of the electroplating process, the cathode is the metallic object which will be covered with a protective layer. In the case of the electroforming process, the cathode may be a metallic object but a non-metallic one, too, (its surface is made conductive through a metallic layer which has a small thickness). The anode may be a soluble or an inert one. In the interior of the tank, there is the electrolyte which is an aqueous of a salt of the metal which will be deposed.

Before the realizing of the electro-deposit processes, the preparing of the electrodes was necessary. The paper presents the preparing of the non-metallic electrodes, only.

The non-metallic electrodes are, usually, bodies which have complex spatial shapes and were obtained from non-metallic materials by copying processes as processes of mould of certain waxes, resins or thermoplastics plastics on real objects. The obtained moulds are made conductive by superficial metallization; when they become good conductors of electricity, they may be used as cathodes into the ionic baths. In these conditions, using the electroforming processes, it can obtain moulds in entire or parts of moulds. The concrete technologies know two classes of operations, previous to the electro-deposit operation: the operations for the realization of the moulds and the operations for making the moulds to be conductive [4,5].

3.1.1. Moulds realization

Alter they are made conductive, the casts will be used for the metallic electro-deposing, which will be a mould or a working part of the mould. The metallic layer obtained by electro-deposing must be interlinked to the object which was obtained into the mould. Having this purpose, starting with a real object, the ways to arrive to the object produced into the mould could be the following:

1. primary model (+)→plastics cast (-)→ plastic electrode (+)→conductive proprieties by superficial metallization (+)→electro-deposing for the obtaining of the mould or of the mould element (-)→forming of the plastics finished product (+);
2. primary model (+)→ covering of the model with a wax film (+)→conductive proprieties by superficial metallization (+)→electro-deposing for the obtaining of the mould or of the mould element (-)→forming of the plastics finished product (+).

In both situations, “(+)” means the primary model and the finished product and some intermediate stages which have identical forms with these, too, and “(-)” means the interlinked forms. Interlinked form means the shape which was obtained by casting or by electro-deposing on a primary model or on an object identical with this.

The first way is longer because it needs intermediate operations. In the same time, it allows the realization of more identical electrodes; this situation provides a continuity of the moulds obtaining activities, without the remaking of the primary model, every time. The second way, the shorter and simpler one, is used in the prototypes case, especially in all activities which prepare the new collections of products.

From now on, the paper will present, in shortly, the two ways in the realization of the moulds used in the obtaining of certain polyurethanes rubber soles [4,5].

For the casts obtaining it is necessary, in the beginning, the realization of the primary model of the sole, the shape of sole, which it will be obtained into the mould. The primary model will be made by wood, using a mechanical or manual shaping process, for the medium number of size. The entire series of sizes will be obtained by multiplication using a machine for the shoe-lasts copying. The primary model of the sole will not include the sole model, in the beginning. So, its dimensions will be decreased respectively to the size of the non-skid relief. These primary models, made from wood, will be completed, using various procedures, with the model of the non-skid relief, for example, the covering with textures, meshes, natural or artificial leathers, the confectioning by hands of some models, etc. The primary models of the soles are represented in figure 1.

For the cast obtaining, the following steps must take place: The primary model of the sole completed with model of the future sole (+) will be fixed on a wood or burnt plaster base; the assembly will be fixed into a drain box; on the entire surface of the primary model and of the base will be sprayed an anti-adhesive lacquer and then, it will cast the mixture used for the cast forming, (-). All these operations are showed in figure 2. For the casts obtaining, it may use easy forming materials and which may copy all surface details of the covered primary model. So, it can use silicone rubber, unsaturated polyester resins, epoxy resins, burnt plaster.

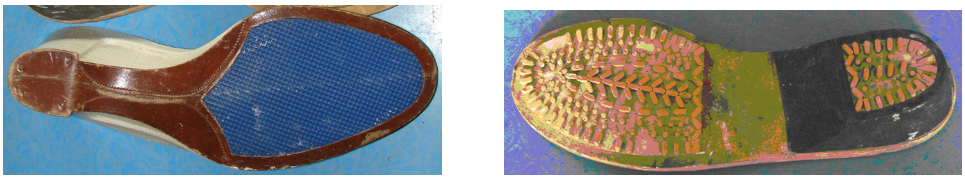

Figure 1. Primary models of the soles

Figure 3 represent a cast made from burnt plaster. When the mould is obtained using the second way, it will not use the intermediate model. So, the primary model of the sole will not be fixed on a wood base but on a burnt plaster one.

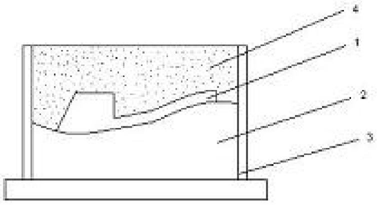

Figure 2. Cast obtaining
1-primary model of the sole; 2-base; 3-drain box; 4- cast

Figure 3. Burnt plaster cast

Preparing a mixture of three parts of water and one part of burnt plaster, it will be obtained a fluid pulp which can easy take the shape of the drain box and of the object whose shape is the cast one. For the resistance increase, the burnt plaster casts may be reinforced with glass fibers, asbestos fibers,, textile fibers,, etc. In this way, the burnt plaster casts may be used in repetitive casting of the electrodes. From this point, the obtaining process of the mould takes place as in the first method case.

3.1.2. Realization of the waxes or plastics electrodes

The object which is identical to the covered primary model and will be used as electrode, will be obtain [4,5] into casts, manufactured as paragraph “a” shows. Following this aspect, into these casts, it may be cast waxes, acrylic resins, polyamide resins, epoxy resins, polystyrene, etc.

The waxes are the easiest material to be used; it binds and coalesces easily and, in a melting state, it takes easily the shape of the object which covers by casting. To reproduce exactly every detail of the cast, before the casting, the waxes will be heated at 50-60^{0}C. The wax is a mixture which may or may not contain graphite for conductibility proprieties.

The acrylic resins are obtained by entire polymerization of the methyl methacrylate. Following this aspect, the monomer will be blended together with 5-15% plasticizer and with 1-3% dibenzoyl peroxide (lucidol), as initiating agent, 30-60 minutes. In this way, it avoids the air checks generation before the casting into the silicone rubber cast. To avoid the adherence of the polymer to the silicone rubber cast, it will spray a solution of paraffin into benzene. Knowing that the polymerization process introduces constrictions, the casting may be made in steps, for the shapes which have bigger thickness. After the casting, for the polymerization, the shapes may be heated in steps, until 125 ^{0}C. The thermal condition is pointed when the monomer and the initiating agent are delivered. The so obtained product is firm and it may be corrected by ulterior machine works.

The polyester resins are used for the non-metallic electrodes obtaining by using a casting technology which is similar to the technology of the acrylic resins casting.

The epoxy resins are used in a fluid state, completed with active filler, such as different amines and other substances and with some fillmasses. The so obtained products have a high mechanical resistance.

The thermoplastic polyamides are used for the non-metallic electrodes obtaining, too. They are obtained by casting, in a melting state, into a cast which was heated over 80^0C, to realize the copying of all details of the cast.

The polystyrene may be used for the electrodes obtaining, too. In this case, it will use shock-absorbent polystyrene foils which have 0,8-1,5 mm thickness and which are obtained in vacuum, after a previous heating with a infrared source. The using of the vacuum forming process is applied when the primary model does not have very fine surface details.

The technology of the non-metallic electrode obtaining is showed in figure 4 and it consists in the following operations: the fixing of the cast, obtained as paragraph “a” showed, into the drain box; the greasing of the cast, using a petrolatum; the casting of the one of the anterior presented mixture. Figure 5 represents an electrode which was obtained using wax as a material.

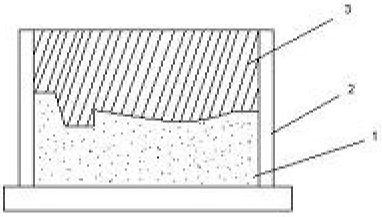

Figure 4. Obtaining of the non-metallic electrode: 1-cast; 2-drain box; 3-non-metallic electrode

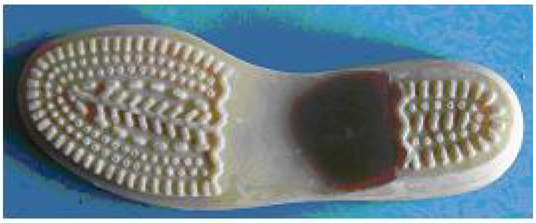

Figure 5. Wax electrode

3.1.3. Obtaining of the conductive electrodes

Excepting the wax electrodes, which content graphite, the rest of the electrodes are not electric conductive. Wanting their using as conductors, their surface must be covered with a metallic film. This operation may be realized using one of the following two methods.

The first method in the obtaining of the conductive electrodes is based on the realization of a mixture between phenol formic aldehyde, soluble in alcohol, blended together with a copper colloidal powder and its layers, in a thin film, on the surface of the electrode. This film is applied, with good results, on the surfaces of the wax electrodes which do not contain graphite in their mixture. The presence of the alcohol into the solution, allows the superficial solubilization of the wax and the anchorage of copper powder. This method has a version which consists of the spraying a slurry of powder of copper, silver or graphite in polymers diluated solution.

In the other kind of electrodes case, but in the case of those made from wax, too, it may apply a special method of conductive proprieties obtaining, which consists of the reduction of some copper, silver, nickel, cobalt salts at the metal state.

Before the covering, in some cases, it is necessary to excite the surface of the polymer. So, the objects made from polystyrene or some other polymers, which are used as electrodes, are degreased with organic solvents and then, they are kept 3-5 minutes into a solution NaOH 10% at 50-60^0C. After the washing with water, the object will be introduced into a stannous chloride and hydrochloric acid solution (10g $SnCl_2$+40 cm^3HCl per liter) and will be kept 3-4 minutes at 25^0C. The tin will be reduced and so, it fixes on the surface of the object. After the washing with water, the process goes on by treating the part with a silver ammonia solution, 10g/l $AgNO_3$ and 50 ml/l NH_3.

The object coating will be made by its immersion into a solution or by its spraying. In the coating with copper deposition it may be used different solutions versions [4,5], consisting of a copper soluble salt, complexing salts and reduction agents. Following these aspects, the compositions of these solutions are given in table 1.

Table *1. Solutions versions for the coating of the non-metallic electrodes by immersion*

Chemical substance	Version		
	1	2	3
Coating by copper deposition			
Copper sulphate ($CuSO_4.5H_2O$)	7 g/l	10 g/l	5 g/l
Rochelle salt	22,5 g/l	-	25 g/l
Soda salt	2 g/l	10 g/l	25 g/l
Sodium hydroxide	4,5 g/l	100 g/l	7 g/l
Nickel chloride ($NiCl_2.6H_2O$)	2 g/l	-	-
Formic aldehyde (sol.40%)	26 ml/l	40 ml/l	10 ml/l
Glycerine	-	100 g/l	-
Coating by nickel deposition			
Nickel sulphate ($NiSO_4$).$7H_2O$)	25 g/l	-	-
Sodium hypophosphite (NaH_2PO_2 H_2O)	25 g/l	10 g/l	-
Sodium pyrophosphate($Na_4P_2O_7.10$ H_2O)	50 g/l	-	-
Aqueous ammonia (28%NH_3)	20-25 ml/l	-	-
Nickel chloride ($NiCl_2.6$ H_2O)	-	30 g/l	-
Sodium citrate ($Na_3C_6H_5O_7.2$ H_2O)	-	10 g/l	-
Coating by silver deposition			
Silver nitrate	20-30 g/l	-	-
Potassium hydroxide	10-15 g/l	-	-
Ammonia solution, 25%	60-80ml/l	-	-
Glucose	12-15 g/l	-	-

Table 2. Solutions versions for the coating of the non-metallic electrodes by spraying

Solution A		Solution B	
Chemical substance	Quantity	Chemical substance	Quantity
Coating by copper deposition, at 20^0C			
Copper acetate	30g/l	Hydrozin hydrate	75g/l
		Sodium hydroxide	15g/l
Coating by copper deposition, at 60^0C			
Formic aldehyde, 37%	80 ml/l	Copper sulphate ($CuSO_4.5H_2O$)	80ml/l
		Rochelle salt	80 g/l
		Sodium hydroxide	80 g/l
Coating by nickel deposition, at 20^0C			
Nickel sulphate ($NiSO_4.7H_2O$)	30g/l	Hydrozin sulphate	15g/l
		Sodium hydroxide	11 g/l
Coating by silver deposition, at 10^0C			
Silver nitrate	2-3 g/l	Pure glucose	2-3 g/l
Potassium hydroxide	2-3 g/l		
Aqueous ammonia, 25%	8-10 ml/l		

In all the cases, the solutions have a strong basic pH, (12). The reduction agent, the formic aldehyde, will be added into the solution, with a few minutes before the using. In the spray coating case there are used two kinds of solutions [4,5] which are sprayed, in the same time, on the surface of the object, using a pistol for each of them. The spraying solutions are given in table 2.

3.2. Obtaining of the metallic chills

The deposition of the metallic layers on the conductive non-metallic electrodes will realize by electroforming. Using this kind of galvanic deposition, it will obtain metallic chills whose thickness is 5-6 mm, with a certain mechanical resistance and which can be ulterior incorporated into the proper mould.

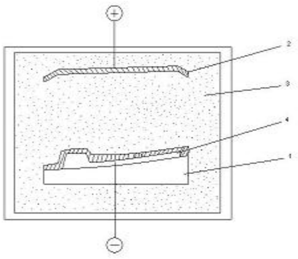

Figure 6. Electrolysis installation
1-non-metallic electrode; 2-anode;
3-electrolyte; 4 metallic chill

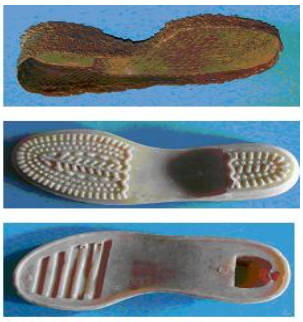

Figure 7. Metallic chill, sole

These chills are the cavities of the future moulds. For the metallic chills obtaining [4,5], the coated non-metallic electrode is placed into electrolysis installation, in a cathode position, as figure 6 shows.

The metal deposing will be made by anode solubilization or, when anode is non-soluble, by reducing of a certain salt of electrolyte solution which contains the metallic ion. The metal deposing will be made slowly, sometimes over 72 hours. It depends on the concentration of the metallic ions into the solution, on the current density and on the presence of some epilamens. At the beginning the current density has a small value 1-2 A/dm^2, and then, it will be raised to 10 A/dm^2. So, the surface of the electrode will be uniformly, by metallic deposits which will complete the discontinuances of the coating layer. The deposing, which is more irregular in the beginning, becomes more regular and, in the end, it will produce a regular, compact texture which obey the geometrical system of the crystal lattice. This kind of metallic chill is presented in figure 7.

Table 3. Solutions of the electrolytes used for nickel chills obtainingl

Chemical substance, parameters	Quantity		
Nickel sulphate ($NiSO_4.7H_2O$)	280-300 g/l	400-420 g/l	220 g/l
Natrium sulphate ($Na_2SO_4.10\ H_2O$)	-	140-160 g/l	-
Magnesium sulphate ($MgSo_4$-7H_2O)	50-60 g/l	-	-
Sodium chloride	5-10 g/l	-	8-10g/l
Sodium fluoride	-	2-3 g/l	-
Nickel chloride ($NiCl_2.\ 6H_2O$)	-	25-30 g/l	-
Fumarole acid (H_3BO_3)	25-30 g/l	25-30 g/l	25-30 g/l
Temperature	30-40 ^{0}C	55-60 ^{0}C	50-60 ^{0}C
Current density	2-4 A/dm^2	8-12 A/dm^2	1,2-1,5 A/dm^2
pH	3,0-5,0	3,5-4,5	4,2-4,6

For the obtaining of the copper metallic chills, it will use the electrolyte solutions 150-300g/l copper sulphate ($CuSO_4.5H_2O$), 7-15 g/l sulphuric acid and 30-50 ml/l ethanol. The value of the current density is 1-3 A/dm^2.
In the case of the nickel deposing it will use solutions which have compositions as like as in the case of the nickel protection. [4,5]. This kind of solutions are presented in table 3.
The metallic chills obtained by electro-deposit will be incorporated, by different casting technologies, mechanical working, into the proper moulds used for the soles obtaining. A sole obtained into this kind of mould is represented in figure 7.

CONCLUSIONS

- The moulds for soles or parts of them, which are obtained by electro-deposit are realized using electrolysis equipments.
- The using of these technologies is an advantage, especially in the designing and quick realizing of certain new soles collections stadium. The moulds for soles obtained by electro-deposit technologies will be realized with low costs, in a short time, in the experimental phases (for the marketing tests), before of the proper mould realization for the mass production.
- The casts used for the non-metallic electrodes realization will be made with classic technologies.
- The conductive properties of the electrodes will be obtained by a process of metallic coating on the non-metallic electrode. The coating of the object will be made by its immersion into an electrolyte solution or by spraying. When the immersion process is applied, it will use many kinds of electrolyte solutions, which may be a copper, silver, nickel, cobalt, aluminum soluble salt. When the spraying process is applied, it will use two kinds of solutions, one of them contains the metal which will be deposed, copper, nickel, silver salts, and the other one which is the reduction agent applied, in the same time, on the electrode surface; for each of these substances, it will use another pistol.
- The metallic chills which will generate the cavities of the moulds, the sole proper models, will be obtained by galvanic deposits using characteristic electrolysis installations. After that, these chills will be fitted into the proper moulds which will be parts on the injection equipments.

Acknowledgements. The paper is a part of an extended research undertaken under the Project no. 134124-LLP 2007-RO-LMP Education, Audiovisual and Culture Executive Agency, Brussels, Belgium and Project no. 2007-3111/001-001 LE3-MULPRO.

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