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Grau de Química

Treball Final de Grau

Study of the currently electroless plating industrial process for ABS plastic and improvement proposal of this process to achieve the replacement of chromium etching.

Estudi del procés industrial de metal·lització del plàstic ABS i proposta de millora per a la substitució del Crom en el mordentat

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A en Ricard Tomás,

REPORT

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1. SUMMARY

The process of metallization of non-conductive materials is a generalized technique and for commercial use in sectors such as cosmetics, electronics and automotive. The material used par excellence is acrylonitrile-butadiene-styrene (ABS) plastic. In order to carry out this metallisation, this material is subjected to a line of chemical baths at certain temperatures and immersion time. The first part of the line is where the chemical stage is carried out, its plastic surface is prepared by etching it with a chromium sulfuric solution and then, is activated by a palladium solution. After the activation is done, there is the first deposited coating using a chemical nickel solution. The second part of the line, is where the electrochemical part begins and where the rest of needed metals are deposited.

In this report, an initial study of an alternative to the current etching process is carried out where it is possible to prepare the surface without the presence of chrome in etching solution since, this component, in the working conditions where it is used, has a high carcinogenic risk for some users, and causes genetic defects and decreases fertility among others. The European Commission has banned its industrial use since 2011 but due to the lack of alternative solutions, they have repealed the law until new European Community revisions which are estimated to take action in 2020-2021. In order to carry out this new proposal, a complete study of the surface metallisation process in ABS is carried out. To carry out the study of surface roughness at each stage, both the Confocal microscope and the scanning electron microscopy(SEM) are used. Finally, a comparison of the adherence of chemical nickel in etched surfaces between surfaces prepared with chromium etching and surfaces prepared with the new chromium-free etching was carried out with the use of the Crosscut as a qualitative method of industrial use, the Nano scratch technique, and the Calowear test in order to contribute to previous studies as a potential feasible proposal for this global demand within the industry.

Keywords: ABS Surface, hexavalent Chromium, Electroless plating, chromium-free, etching.

2. RESUM

El procés de metal·lització de materials no conductors és una tècnica generalitzada i d'ús comercial en sectors com la cosmètica, electrònica i automoció. El material emprat per excel·lència és el plàstic l' acrilonitril-butadiè-estirè (ABS). Per tal de realitzar aquesta metal·lització es sotmet aquest material a una línia de banys químics a certes temperatures i temps d'immersió. La primera part de la línia és on es du a terme la part química, es mordenta amb una solució de Crom sulfúric i s'activa la superfície plàstica per ser conductora, i la segona part de la línia, és la part electroquímica on es dipositen els metalls.

En aquest treball es realitza un estudi inicial d'una alternativa al mordentat actual on s'aconsegueixi realitzar la preparació de la superfície sense la presencia de Crom, ja que aquest component en les condiciones de treball que s'utilitza, hi ha un alt risc cancerigen per als usuaris, provocant defectes genètics i disminuint la fertilitat entre d'altres. El Reach va prohibir el seu ús industrial des del 2011 però degut a la manca de solucions alternatives, han derogat la llei fins a noves revisions de la Comunitat Europea que s'estimen pel 2020-2021. Per tal de realitzar aquesta nova proposta, es realitza un estudi complet del procés de metal·lització de superfícies en ABS. S'explica detalladament la línia química actual, on veurem les principals reaccions i deposicions en superfícies plàstiques d'ABS. el procés de mordentació, l'activació de la superfície la deposició de níquel a partir del estudi de les seves rugositats amb el microscopi Confocal i utilitzant l' Scanning electron miscroscopy (SEM) entre d'altres tècniques. Finalment, s'ha realitzat una comparativa utilitzant el Crosscut com a mètode qualitatiu i d'ús industrial, la tècnica nanoidentificator i el test Calowear per evaluar les adherències del níquel químic de les superfícies mordentades amb Crom i mordentades amb el nou procés estudiat, anomenat Chromium-free etching (sense la precència de Crom), per així contribuir a estudis posteriors com a possible proposta viable per a aquesta demanda mundial del sector.

Paraules clau: ABS, Crom hexavalent, procés químic de metal·lització, eliminació crom, mordentació.

3. INTRODUCTION

3.1. RAW MATERIAL. ACRYLONITRILE BUTADIENE STYRENE (ABS) AND POLYCARBONATE (PC)

In this report, Acrylonitrile butadiene styrene (ABS) and Polycarbonate (PC) will be properly studied. ABS will be the main material used for the most of experiments done. Abs is a terpolymer based on a mixture of Acrylonitrile butadiene styrene. Exists a wide range of compositions which are depending of the final requisites for that material. The components give to the that material a good quality to be choose for metallization. For example, acrylonitrile provides chemical resistance, rigidity, hardness from nitrile polar groups that guarantees good stability for the nitrile charges. Styrene also provides rigidity, fluency, and brightness.

Finally, polybutadiene provides the capacity of metallization. For that reason, is one of the most used materials for electroplating industries, attractive for sanitary, cosmetic, decorative and automotive field. At present, it is also used polycarbonate for bimaterial samples when the final requirement is metallizing only selective parts. Because PC is a non-metalizing material.

3.2. CONVENTIONAL METALLIZATION PROCESS.

Plating on plastics has two differentiated stage, electroless stage and electrolytic stage. At present, the industrial process is according to Kuzmik J. Pattent [1], and showed in Plating on Plastics reactions [2] and in Macdermid technical Technical Release Package [3]. The samples are immersed in these different solutions showed in figure 1 and 2 to get metalized. It is required an adequate immersion times and working temperature for each solution that are being described properly in this report.

The metallization conventional procedure is: Initially, samples should be washed in a solution. This first stage is optional and it is used to clean the surface of dirt, oil and grease, which manipulation may has caused. It is important to note that there are washing solution (mixtures of acids) indispensables to reduce the risk of solution contamination between stages.

Figure 1. Electroless chemical part

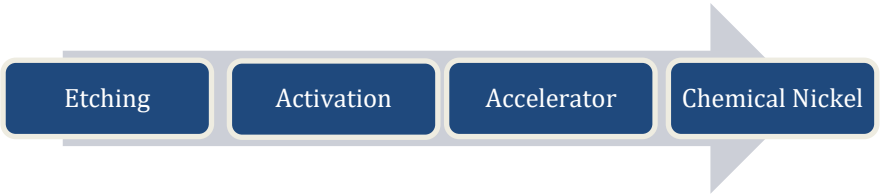
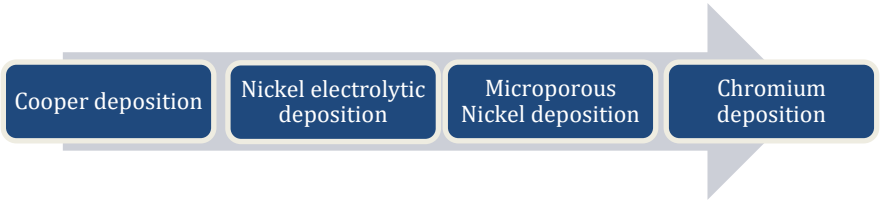


Figure 2. Electrolytic chemical part.



The first electroless chemical part it is described by Brenner and Riddell mentioned in [4] study. Etching is the first stage needed. Etching solution is a mixture of chromium hexavalent, sulfuric acid and some additives that remove some part of plastic surface to increase the area. And, making that part turn from a hydrophilic material. The etching role is creating some micro holes in the ABS surface by the reduction of chromium hexavalent. Then, the following solution is activation solution, it is also known as palladium solution. Activation solution is a mixture of palladium and tin complex in chloride acid and additives. The palladium solution feature is being deposited as palladium metal in these micro holes created in the ABS surface and become a catalyst agent for the chemical nickel deposition. Therefore, the following stage is accelerator solution. The accelerator is a mixture of hydrochloric acid base solution. It has the role of remove the excess of hydrolysed tin hydroxide. The excess tin hydroxide must be removed from the micro holes. Then, palladium can act as a catalyst. The next step is the chemical nickel deposition. The last stage in this electroless chemical part is chemical nickel solution. This solution is a mixture of ammonium, nickel complexes and some additives. The chemical nickel role is being deposited in the surface catalysed by palladium. It is the first metal coating in all the ABS surface deposited. Then, the ABS surface is completely ready to move on electrolytic chemical part.

In this electrolytic stage, it is deposited the needed metals to get a properly coating by electrolytic method. These solutions are formed by its metal complex, acids mixtures and

additives required. The first metal deposited is brilliant electrolytic nickel, then semi brilliant and finally microporous electrolytic nickel. This coating gives to the ABS surface the corrosion resistance needed. In order to complete the expected corrosion resistance, chromium metal has to be deposited. The chromium solution is the last stage to complete the metallization process.

3.2. HEALTHY AND ENVIRONMENTAL NEED FOR A CHANGE

The currently metallization process need the presence of chromium in electroless and electrolytic stage. It is well-known that chrome (III) and chrome (VI) are hazardous chemicals and toxics. It is also known for to be a human carcinogen. The waste produced are hazardous pollutants for environment too.

All healthy damages for humans who works in this kind of industry are mentioned by The Agency for Toxic Substances and Disease Registry (ATSDR) and The International Agency for Research on Cancer (IARC) and ECHA article [5-6]. Moreover, the Occupational Safety and Health Administration (OSHA) established the levels in the air of the work [7]; 0.005 mg/m3 for chrome (VI), 0.5 mg/m3 for chrome (III) and 1.0 mg/m3 for chrome (0), as averages during a daily day of 8 hours. Take account that in the electroless stage, the chromium is the main compound in etching solution and it is also present in the electrolytic stage for the final refurbishment. The concentration of chromium in electroless solution is almost double than in chromium solution in the electrolytic stage. There is a compelling need to sort chromium presence in this process out.

For the moment, European Commission has indicated in the attached letter that the supply and use of trioxide chromium or mixtures prepared, which contain trioxide chromium their use shall be temporary and the Commission shall specify a date by which their use is to be phased out or renewed. Nevertheless, this only is applied to the uses for those that has requested an authorization. The letter of the European commission for the derogation of the uses of chrome in the Galvanoplastic industry and a copy of the part mentioned of the final Opinion and Periods of Review recommended by the solicitors of Chromium Trioxide Authorisation Consortium (CTACsub) for the Authorization of chrome can be found in Appendix 1.

4. OBJECTIVES

The main objective for this research is obtaining a new eco-friendly chromium-free etching which could substitute the hexavalent and trivalent chromium during etching in the electroplating industry to avoid health problems in existing workplaces and reduce the toxicity of generated waste.

To achieve this goal there are three specific steps which will be crucial to define the success of this research:

- The study of the conventional electroless process;
- The design of the new electroless chromium-free etching procedure;
- The comparison of chemical nickel's adherence using the conventional electroless process and the new electroless chromium-free etching procedure.

5. EXPERIMENTAL SECTION

The first part of this section material includes the study of the conventional electroless process. Then, it will be described the design of the new electroless chromium etching procedure and reagents chosen.

5.1. ASSETS FOR CONVENTIONAL ELECTROLESS PROCESS: RAW MATERIALS AND REAGENT SOLUTIONS

The raw material samples used in this report, which will be characterized are ABS and PC taken directly from an existing electroplating company.

All solutions come directly from a currently electroplating company which is why some compounds cannot be disclosed and the concentrations are expressed as intervals. Take account that some of that solutions are mixtures of different additives, acids that are also not mentioned in table 1-3. Note that the volume of each of these solutions is:

- 250mL of etching solution
- 250mL of Palladium solution
- 250mL of Accelerator solution
- 250mL of Chemical Nickel

Table 1. Etching bath compositions based on external analysis [8]

Composition	$[Cr^{3+}]$	H_2CrO_4	Normality	Work Temperature
Etching 1	10.65 g/L	300-450 g/L	3-6N	65-75ºC
Etching 2	32.9 g/L	300-450 g/L	3-6N	65-75ºC

Table 2. Palladium Solution, Accelerator solution composition based on external analysis [8]

Composition	Pd Metal	Normality	Tin points	Mixture of Activator	Work Temperature
Palladium	0.1-2%	1.8-5N	2-9 points	-	20-35ºC
Accelerator	-	-	-	100%	20-35ºC

Table 3. Chemical Nickel solution composition based on external analysis [8]

Composition	Nickel Metal	pH	$HNaHPO_3$	Work Temperature
Chemical Nickel	10-20%	7-10	<150	25-40ºC

5.2. SAMPLE METALLIZATION USING THE CONVENTIONAL PROCESS

This sample metallization experiment consists in the immersion of ABS samples in the previously mentioned solutions according to Kuzmik J. method described in [2] method and following the instructions of an electroplating company.

In order to design the new etching procedure, it is needed to understand how etching attack the ABS surface. For that reason, there are two experiments described. First, it is carried out the butadiene hypothesis according to the use of the Electroless Method by Brenner and Riddel [4]. Then, it is evaluated the rugosity created in the surface by etchings using Confocal m. in different conditions.

5.2.1. Study of Chromium Etching solution

5.2.1.1. Experiment 1. Etching Attack. Butadiene hypothesis.

The purpose is evaluating the butadiene hypothesis and to get it, it is used the ABS material and PC. The experiment consists in immerse both materials in etching solution using the same condition. Then, surface characterization is carried out to compare the structure and composition before and after the etching attack conditions showed in Table 4.

Table 4. Work conditions to evaluate the butadiene hypothesis using standard conditions [3]

Etching bath	Temperature [ºC]	Immersion time [min]	Characterization
ABS sample	70	12	SEM, IR, Raman, Confocal m.
Polycarbonate sample	70	12	SEM, IR, Raman, Confocal m.

5.2.1.2. Experiment 2. Etching Attack. Trivalent Chromium effect hypothesis, Temperature, Soak time.

Two different etching baths are available. The concentration of trivalent chromium is the main difference between them, num1 is 10.65g/L of Cr^{3+} and the num2 is 32.90g/L of Cr^{3+}.

It has proceeded to analyse the effect of trivalent Chromium using the same conditions for Etching 1 and Etching 2. At the same time, the effect of temperature and soak time for these two-etching solutions, was evaluated using 3 samples for each experiment, as shown in table 5.

Table 5. Working conditions for Trivalent chromium effect, temperature, and soak time

Etching bath	Temperature [ºC]	Immersion time [min]	Characterization
1	25, 60, 80	12	Confocal m.
1	70	4, 12, 20	Confocal m.
2	25, 60, 80	12	Confocal m.
2	70	4, 12, 20	Confocal m.

Extra samples which have been attacked in etching 1 for more than 24h were also analysed (table 6).

Table 6. Conditions of samples from Electroplating plant. Samples have been more than 24h soaked in Etching 1.

Etching bath	Temperature [ºC]	time [min]	Characterization
1	70	1440	SEM, Confocal m.

5.2.1.3. Samples to metallization complete process

It is needed to prepare samples to successfully continue the metallization process.

Etching 1 is used for the followings experiments seen in table 7.

Table 7. Conditions of samples for following samples using standards conditions [3]

Etching bath	Temperature [ºC]	Immersion time [min]	Characterization
1	70	12	SEM, Confocal m.

5.2.2. Study of palladium solution

The following stage is palladium deposition. It is proceeded to analyse how palladium attack works. It is immersed 3 samples for this experiment, after being immersed in etching 1 that can be seen in the table 8.

Table 8. Work conditions to Palladium Attack using standards conditions [3]

Palladium bath	Temperature [ºC]	Soak time [min]	Characterization
1	31	4	SEM, Confocal m.

5.2.3. Study of accelerator solution

The following factor to consider is the refurbishment of the surface after palladium deposition. It is proceeded to analyse how accelerator works using 3 samples for this experiment, note that this three samples used for the experiment, had been immersed in etching, then

palladium solution and to complete this stage in accelerator solution. Working conditions can be seen in the table 9.

Table 9. Work conditions to Activator solution using standards conditions [3]

Accelerator solution	**Temperature [ºC]**	**Immersion time [min]**	**Characterization**
1	25	2	SEM, Confocal m.

5.2.4. Study of chemical nickel solution

Last step is electroless chemical nickel deposition. It is proceeded to analyse the chemical nickel deposition. Therefore, 3 samples are used for this experiment, that it had been immersed in etching, then palladium solution, accelerator solution and then in chemical nickel to complete the first metal deposition, as it is seen in the table 10.

Table 10. Work conditions to nickel deposition using standards conditions [3]

Chemical Nickel	**Temperature [ºC]**	**Immersion time [min]**	**Characterization**
1	31	9	SEM, SEM (EDS), Confocal m.

5.3. RESEARCH OF A NEW CHROMIUM-FREE ETCHING

5.3.1. Assets for chromium-free etching: Raw materials and reagent solutions

In order to develop this study, the same ABS material is used. Reagents used for this proposal are denominated using letters and numbers to maintain confidentiality as seen in table 11. Note that 250mL is the volume used for this research for each solution.

Table 11. Chemical Reagents used for new chemical attack in ABS surfaces.

Chemical Reagents	Name of Solution	Principal Compound	Medium
A1	Solvent 1	x	Neutral
A2	Solvent 2	Mechanical solvent	neutral
B1	New Etching 1	KM_nO_4	H3PO4
B2	New Etching 2	KM_nO_4	Acid
B3	New Etching 3	KM_nO_4	H2SO4
C	Pre-Pd	Mixture of acids	Acid
D	Palladium	Described in 5.2.2	X
E	New Accelerator	Mixture of acids	Acid
F	Chemical Nickel	Described in 5.2.4	X

5.3.2. Experimental procedures

The samples are being immersed in the solutions mentioned changing the temperature values, immersion values and the kind of solvent and new etching in every experiment. The work is carried out laboratory level. This means creating the right initial procedure conditions shown in table [12-13] that allows the different approaches and decisions openly discuss the accumulated problems, comprehensively analysing them and jointly developing well thought-out decisions made during the research development. This is a forerunner scientific research in electroplating industry. In the followings experiments the evolution of chromium-etching free research can be investigated. Below are some of the most representative experiments.

Table 12. Initial experiments 1. Immersion time [min] and Temperature of solution [ºC]

Sample	**1**		**2**		**3**		**4**	
Reagents	t [min]	T [ºC]	t [min]	T [ºC]	t [min]	T [ºC]	t [min]	T [ºC]
A1	-	-	-	-	-	-	-	-
A2	-	-	-	-	-	-	-	-
B1	12	70	6	70	6	30	-	-
B2	-	-	-	-	-	-	6	30
B3	-	-	-	-	-	-	-	-
C	-	-	-	-	-	-	6	25
D	-	-	-	-	-	-	4	35
E	-	-	-	-	-	-	2	30
F	-	-	-	-	-	-	10	35

Table 13. Initial Experiments 2. Immersion time [min] and Temperature of solution [ºC]

Sample	**5**		**6**		**7**		**8**	
Reagents	t [min]	T [ºC]	t [min]	T [ºC]	t [min]	T [ºC]	t [min]	T [ºC]
A1	5	25	-	-	-	-	-	-
A2	-	-	6	25	3	25	3	25
B1	-	-	-	-	-	-	-	-
B2	-	-	6	30	3	40	-	-
B3	-	-	-	-	-	-	6	30
C	-	-	4	35	4	35	4	35
D	-	-	3	35	3	35	3	35
E	-	-	2	30	2	30	2	30
F	-	-	10	35	10	35	10	35

5.3.2.1. *Working conditions for a new chromium-free etching*

Table 14 shows the suitable the working conditions for a chromium-free etching procedure.

Table 14. Work conditions for free-chromium electroless process

Sample	**1**		**Characterization**
	t [min]	T [ºC]	
A2	4	30	Confocal
B3	3	25	Confocal, SEM
C	3	25	Confocal
D	4	25	Confocal, SEM
F	10	35	Confocal

5.4. EVALUATION OF THE NICKEL COATINGS ADHERENCE

The nickel coating adherence is an important factor to consider. This aspect of a process is critical from the customer point of view. Because having a poor adherence in the final sample is a major non-conformity for this industrial sector.

Adherence is mainly depending on etching process according to [8-10] articles publicated. The table 15 shows the samples that are being tested. The adherence of the coatings is evaluated in a quality perspective using Crosscut test and it is also evaluated in a quantity perspective using Nano scratch and Calowear process described in [11-12] information.

Table 15. Samples tested to analyses the adherence.

Sample	Etching Temperature of [ºC]	Etching Soak time [min]	Characterization
1 (chromium etching)	70	12	Crosscut, Nanoscratch, Calowear
2 (chromium etching)	20	12	Crosscut, Calowear
3 (chromium etching)	70	4	Crosscut, Calowear
4(Chromium-free etching)	-	-	Crosscut, Nanoscratch, Calowear

5.6. CHARACTERIZATION

Basically, M. Confocal help to understand the deposition using the roughness and how hard is the attack of our initial etching. To understand the chemical part. SEM, IR, RAMAN is used to determinate the composition, and if the metals or some structure has been changed during the process.

5.6.1. SEM-DS/SEM-FE characterization

Two scanning electron microscopes (SEM) were used: a Fei Quanta 200 and the Jeol JSM-7100F, both operating at 20 kV, along with their respective energy-dispersive X-ray spectroscopy detectors (EDS), Edax Genesis EDS and Oxford Instruments Inca 250.

5.6.2. IR characterization

Thermo SCIENTIFIC NICOLET iZ10 / ATR diamant / detector DTGS. It is used about 32 scans. Spectral resolution 4cm^{-1}. Spectral range: 4000-525 cm^{-1}. Correction ATR.

5.6.3. RAMAN characterization

Labram HR HORIBA JOBN is used for the characterization. Excited laser: 532nm, Power 5mW.

5.6.4. Confocal microscopy characterization

It is used a SENSOFAR microscopy confocal to performance every measure. Conditions of measurement: M. Confocal, 212.07*212.07 nm, EPI 20x-N, Confocal Z-Scan 80micras, threshold 3%. Medium deviation: 5%

The Roughness Average, Ra, is the arithmetical mean deviation of all points roughness profile from a mean line over the evaluation length. N is the total number of samples and it is the distance from the average height. It is the most common parameter used to measure rugosity.

The Root Mean Square, Rq or Rms, is the average of the measured height deviations taken within the evaluation length and measured from the mean line.

5.6.6. Adherence characterization

5.6.6.1. *Crosscut*

Crosscut test is described by ISO 2409:2007; is a test method for assessing the resistance of paint coatings to separation from substrates when a right-angle lattice pattern is cut into the coating, penetrating through to the substrate. It is a quality test.

5.6.6.2 *Calowear and Nanoscratching*

One equipment of Calowear is used to measure the nickel deposited and evaluate the good adherence of that coating in differ Immersion time [min] and Temperature of solution [ºC]ents etching conditions. Then it is used an Optic microscopy to measure the spheres created. The ball used was 20mm of diameter. During the test the ball have done 473 going in circle around the point fixed in every sample.

Nanoindenter XP from MTS (Oak Ridge, TN) is used for nano scratching test to read the value when the coating could be scratched or cracked. Then it is also used an Optic microscopy to have images how nickel coating is after being tested. For nano scratch, a progressive increasing load is used, starting with 0 mN and increasing in a linear mode until 500 mN, having thus a total length of 500μm (plus 100 μm) per sample, the velocity was 10μ/s.

6. RESULTS AND DISCUSSION

6.1. STRUCTURE OF THE RAW MATERIALS USING CHROMIUM ETCHING SOLUTION. CHROMIUM ETCHING CHEMICAL REACTION.

6.1.1. Results obtained before etching immersion

ABS and PC has been characterized after and before etching immersion. Despite of the results obtained by Raman and SEM not providing any additional information (which is the reason why there aren't showed in the report), in the IR characterization the main structural difference between the two materials can be noticed. ABS spectrum is observed which presents 4 characteristic bands; 700-760cm^{-1} characteristics of substituted benzene rings in the styrene compound. Then, in 970 cm^{-1} belongs to the CH trans- deformation in polybutadiene compound and in 2240cm^{-1} can find the signals for nitrile groups vibrations in acrylonitrile. It should emphasise that there is no polybutadiene peak in Polycarbonate spectrum.

The results of the characterization before the etching attack confirmed that the raw materials taken directly from an electroplating industry were PC and ABS.

6.1.2. Results obtained after etching immersion. Butadiene hypothesis.

The results obtained by RAMAN and IR after etching attack for ABS and PC has not difference between the results before the attack. It means that there still the compounds found in spectres after the attack. The results obtained by SEM are the followings:

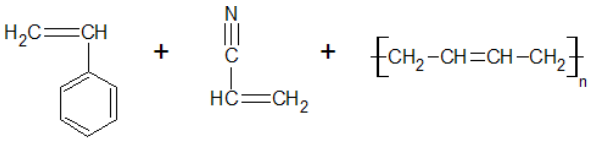
For Polycarbonate, these spectrums and images provided by SEM are equals before and after being attacked, which means that there are not changes in the structure.

For ABS, as seen in image 1, there are asymmetric holes about 0.5-1µm after etching attack. It seems that there is one compound of the Acrylonitrile-Butadiene-Styrene that has a reaction with Chromium hexavalent. Butadiene is the suitable compound because of his oxidation reaction. Highly likely etching solution oxide the butadiene chains in the surface of ABS during

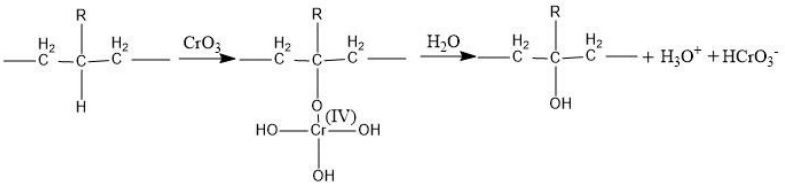
the immersion. Therefore, it is created microscopic holes, thus providing the bonding sites for the metallic coating. Then, it is concluded that ABS material can be metalized thank to the presence of Butadiene in the material as butadiene hypothesis as seen in image 1 and according to [2,4,13].

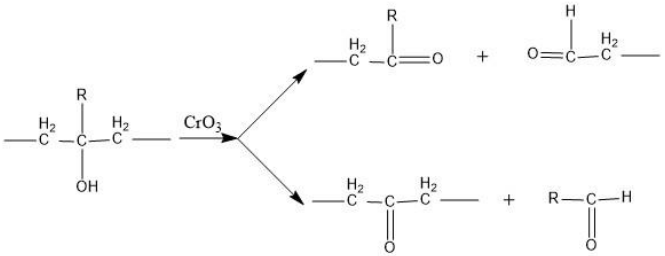
Image 1. Equation and reaction of ABS and Etching solution by Chemdraw.

ABS structure compounds:



The reaction of the selecty removal of butadiene eation proposed for ABS surface in etching solution:



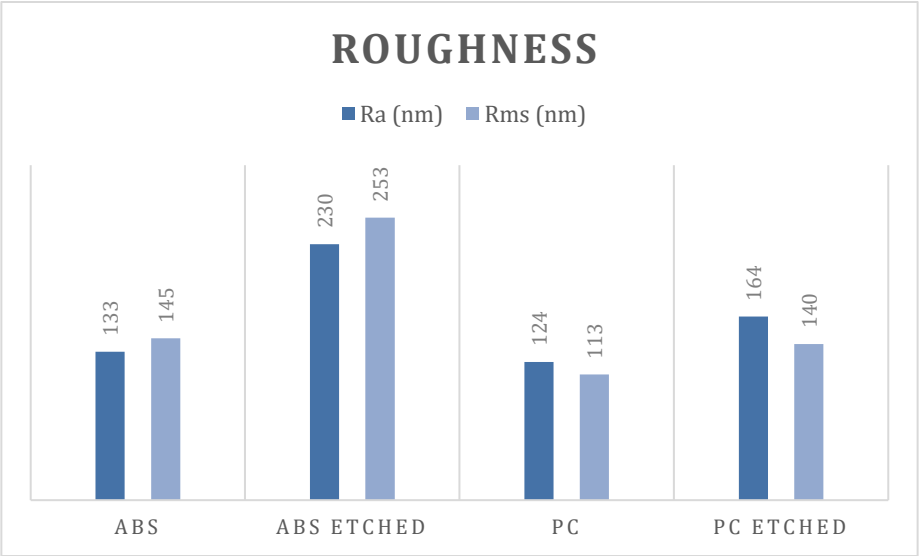


The results of M. Confocal for the ABS and PC samples immersed in etching using the same working conditions are the followings:

It is confirmed by roughness parameter that the ABS surface has been attacked by the chromium in the etching and PC has not been attacked as seen in table 16. There is an increase

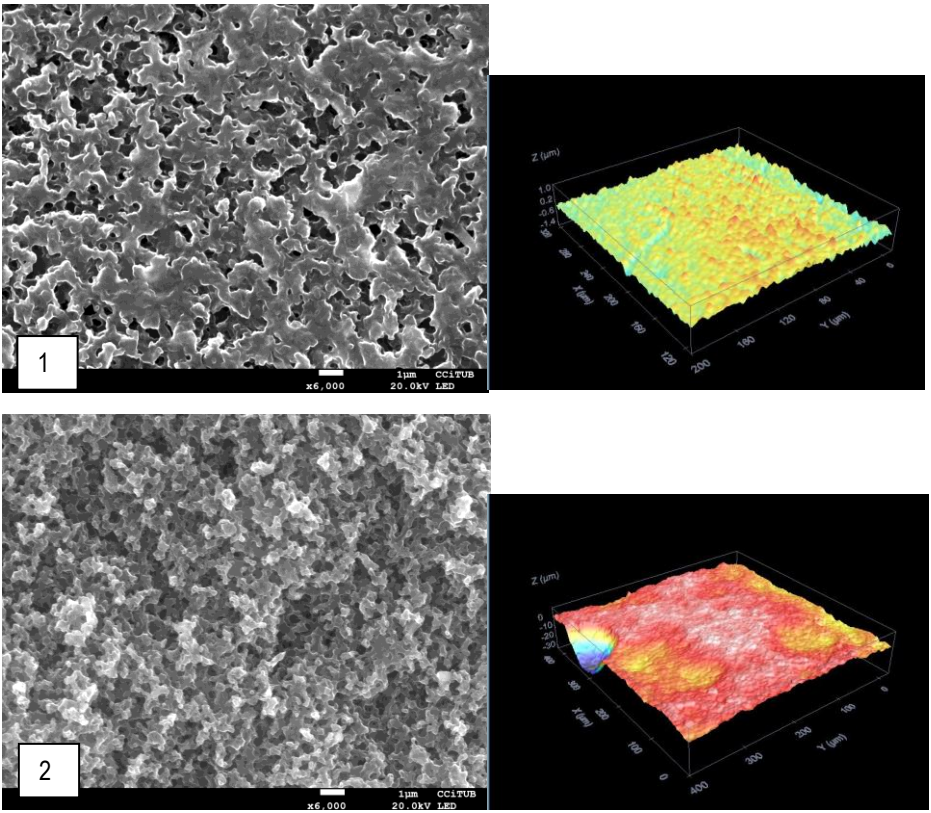
of roughness in ABS material immersed in etching solution, instead of Polycarbonate that there is apparently only a little increase of roughness. To ensure that the small difference in Polycarbonate material before and after etching is not relevant, these samples has been analysed by SEM. It is obtained the expected results; no changes in the surface of our material.

Table 16. Roughness of the raw materials surfaces. Conditions of measurement: M. Confocal, 212.07*212.07 nm, EPI 20x-N, Confocal Z-Scan 80micras, threshold 3%. Medium deviation: 5%



The results of M. Confocal for the ABS samples which had being in etching solution for more than 24h shows that samples suffered a stronger attack by etching. It was really difficult get a measure of the roughness. In the surface, there are holes with more different asymmetric measures and geometries than in ABS attacked using working conditions as seen in image 2. The Ra value is approximately 3.14µm. This roughness value shows that it is created a lever surface when the sample is immersed in etching solution during an excess of time. Then, it may be concluded that chromium etching can oxidase/degrade all the surface in this extreme condition as seen in image 2.

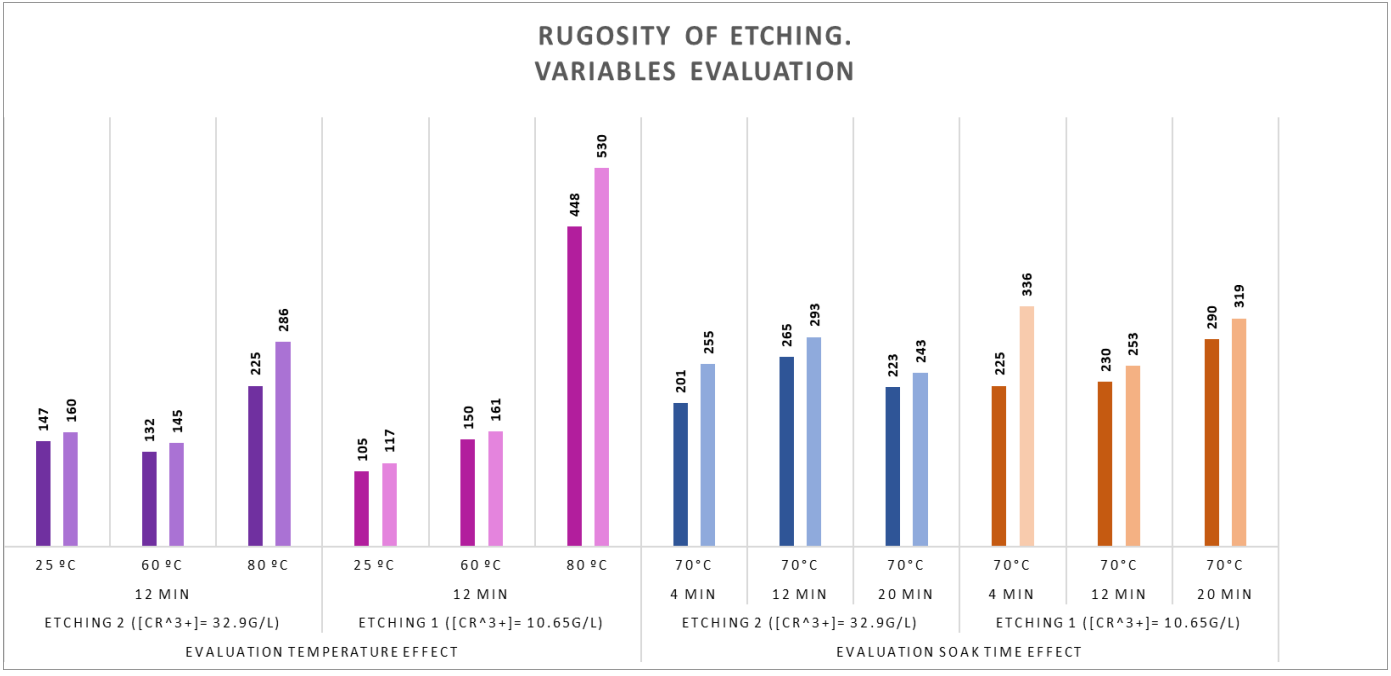
Image 2. ABS attacked by etching solution using working conditions. In this confocal image, the axis Z is 1µm to 1.4µm (1) ABS attacked by etching solution during 24h. In this confocal image, the axis Z is 0µm to 30µm (2).



6.2. CHROMIUM ETCHING EXPERIMENTS RESULTS. MAPPING OF ROUGHNESS.

The following experiment part is focused on the etching attack in ABS material evaluating the main variables using the table 17.

Table 17. Rugosity of Chromium etching attack evaluating trivalent chromium effect, temperature, and soak time. Conditions of measurement: Confocal m., 212.07*212.07 nm, EPI 20x-N, Confocal Z-Scan 80micras, threshold 3%. Medium Deviation 10%. Ra value is in the first column of each experiment (left one) Rms value is in the second column of each experiment (right one)



On the one hand, it is possible to confirm that there is a relevant difference between both trivalent chromium concentration tested using table 17. The samples with higher roughness than the other is 10.65g/L of trivalent chromium immerse in etching solution about 80ºC during 12min. The samples exhibiting lower roughness is 30.65g/L of trivalent chromium immerse in etching solution about 25ºC during 12min. That means that there is a relation between how etching attacks could be depending on the quantity of Trivalent chromium in the solution. According to Macdermid Technical release package [3], an increase of the quantity of trivalent Chromium above more than 40g/L etchant starts to lose its ability to perform properly. This effect is not exactly showed in the table 17. For etching 2, it could be more complicated to etch the surface than etching 1 using the same conditions, that this effect is only appreciated when is evaluating the temperature effect at 80ºC. Take note that, this increase of trivalent chromium is happening in every sample metallization. For that reasons, it is an advantage use porous vessels (Single pot System) also according to Macdermid Technical release package [3] to electrolytically regenerated the excess of trivalent chromium to fix it.

On the other hand, Temperature has an effect in the chemical etching samples. In the table 17, shows that the higher temperature used, the higher roughness. It seems that there is an important different between working at lower temperatures than higher temperatures for etching. In values about 20-60ºC there is no strong increase of roughness for both solution. Instead of that, the roughness is clearly higher when the temperature is about 70-80ºC.

Finally, immersion time has also an effect on surface roughness. In the same way as temperature, a decrease of that immersion time is a decrease of surface roughness. However, the extent of that difference is lower than the same magnitude given by the temperature.

6.3. METALLIZATION TO COMPLETE THE CONVENTIONAL PROCESS RESULTS

The standard conditions for a metallization process tables 7-10 have been used. Ra and Rms measured by the microscopy confocal are the parameter used for that study as seen in table 18. It is also attached images of the surface sample attacked for each solution in image 3.

Table 18. Roughness of Palladium, Activator and Chemical nickel roughness

Sample	Ra (nm)	Rms (nm)	Deviation	Characterization
Etching 1	230	298	13%	SEM, Confocal m.
Palladium	194	220	2.5%	SEM, SEM (EDS), Confocal m.
Accelerator	211	230	3.5%	Confocal m.
Chemical Nickel	143	156	4%	SEM, SEM (EDS), Confocal m.

The first samples analysed are being attacked by etching 1. There is a 13% of deviation, it means that there is more variability than in the others measures.

The second samples analysed has been attacked by etching 1 and immersed in palladium solution. Palladium solution is a mixture of palladium and tin complex in chloride acid and additives. The palladium solution feature is being deposited as palladium metal in these micro holes created in the ABS surface and become a catalyst agent for the chemical nickel deposition. It was achieved an unexpected result, it could be impossible detected palladium using SEM characterization. Probably, because there is only 20 to 100ppm of palladium in solution according to theoretical values in Plating on plastics by Kuzmik J.[3]. It is a very important step for the metallization process. Palladium metal deposed in micro holes, catalyse the chemical nickel reaction. Undoubtedly, exist a reaction in the surface because of the changed colour sample surface after being immersed in it. The surface became soft brown. And, the suitable chemical reaction probably is that according to the comments described by Kuzmik J. in [3]:

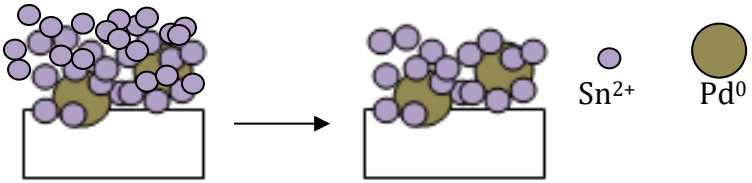
$Sn^{+2} \rightarrow Sn^{+4}$ $E^0 = +0.150$ V

$Pd^{+2} \rightarrow Pd^{(0)}$ $E^0 = +0.987$ V

$\Delta G^0 = -nFE^0$, $\Delta G<0$

The following step is the immersion in accelerator. The third samples analysed are being attacked by etching 1, being immersed in Palladium solution and then immersed in Accelerator solution. Therefore, the following stage is accelerator solution. The accelerator is a mixture of hydrochloric acid base solution. It has the role of remove the excess of hydrolysed tin hydroxide.

The excess tin hydroxide must be removed from the micro holes. Then, palladium can act as a catalyst. As it can be seen in table 18, there are an increase of rugosity, it probably means that the accelerator has remove the excess of hydrolysed tin hydroxide surrounded in the surface. The probably reaction is showed in figure 3 according to Kuzmik J. described in [2].



$Sn_aPd_b \rightarrow Pd_x + Sn_y^{4+} + Sn_{b-y}Pd_{a-x}$

Figure 3. Representation of Accelerator removing overload and its equation.

The images got it for the SEM can't should any difference between etching attack, palladium deposition with some tin complex, and after activator removed. Probably, this process is done using low quantities to be properly measured by SEM.

The last step is chemical nickel deposition. This solution is a mixture of ammonium, nickel complexes and some additives. The forth samples analysed are being attacked by etching 1, immersed in palladium solution in accelerator solution, then immersed in chemical nickel. As it can check in image 3 and 4, chemical nickel is deposited on butadiene holes reaction catalysed by palladium.

The probably chemical reaction in chemical nickel is according to Cavalloti and Salvago [14]:

$[Ni(NH_3)_6]^{+2} + 2e^- \rightarrow Ni^o + 6NH_{3\,(aq)}$ E^0=-0.49V (Pd catallized)

$H_2PO_2^- + 3OH^- \rightarrow 2H_2O + HPO_3^{2-} + 2e^-$ E^0=1.57V

$H_2PO_2^- + H_2O \leftrightarrow H_2 + H_2PO_3^-$

$\Delta G^0 = -nFE^0$, $\Delta G<0$

The speed of deposition of the chemical nickel is a function of a constant k1 depending on hypophosphite of sodium, on the concentration of nickel metal, on the value of the pH, on the concentration of the orthophosphite of sodium and on the energy of activation according to

Mallory G. in [14] argumentations. The thickness of nickel coating is an interesting parameter for adherence. Therefore, the sample is ready to pass to the next step in the industrial process, (the electrolytic stage), but this second process is not explained in this report.

Image 3. Metallization process. Conditions of measurement: M. Confocal, 212.07*212.07 nm, EPI 20x-N, Confocal Z-Scan 80micras, threshold 3% In this after palladium solution confocal image, the axis Z is 10µm to -2µm and the other axis Z is aprox, 1.5µm to -1.5µm

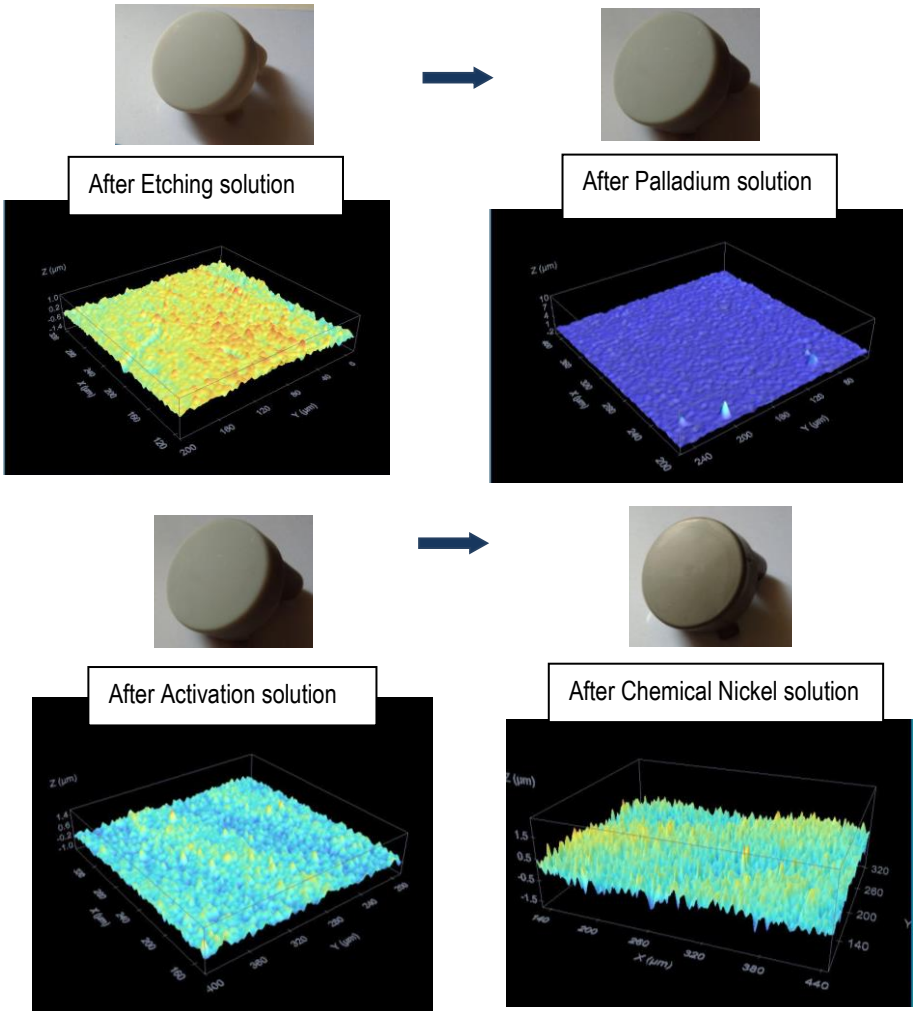
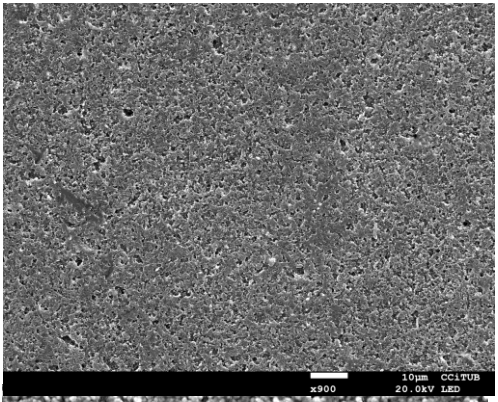
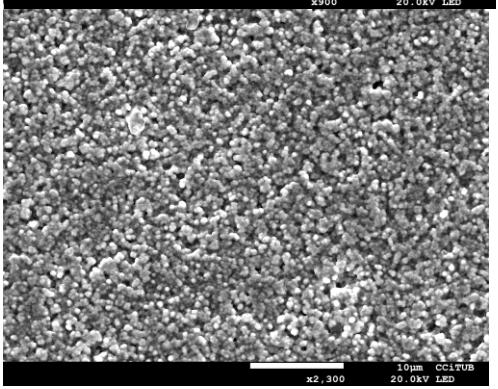


Image 4. Metallization process. SEM images

1. After Etching solution

2. After Chemical Nickel





6.4. RESULTS OF NEW CHROMIUM-FREE ETCHING PROPOSAL

It is showed in the image 5 the most representative visual images of the surfaces etched. The immersion sample have been done according to the number order of precedence referred to Table 12-13 in Experimental part.

Image 5. Images of Initial experiments and image of final sample using work conditions.

In the first three experiments in image 5 (num1-2-3) there was not any solvent in the process and the sample surface was totally attacked by $KMnO_4$ solution. Then, it is decided to reduce the force of reaction changing the immersion time and temperatures as in image 5 (num2). But there is no good appearance enough in the surface. And, it is also tried to reduce the concentrations of the reagents to 50% less concentrate and it is observed a little improvement on the surface. As it can be seen in image 5 (num4), the metallization can be done but there are lot of imperfections in the surface due to the several $KMnO_4$ solution attack.

Next step, it is deciding which the solvent is better. Two different solvents are available. After some test in the samples in image 5 (num5), A1 is removed from the experiment because it has been wet too much the sample surface and it was impossible to move on $KMnO_4$ solution. Then, it is used the second solvent, A2. Image 5 (num6), the metallization has been done but the solvent was so concentrate and nickel deposed has no adherence.

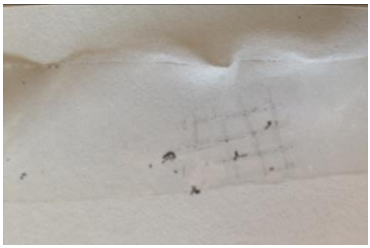
In image5 (num7) it has been realize that the $KMnO_4$ solution was correct but the immerse time for solvent has not appropriated. Also, it has been notice that the acid used for that solution was not the properly one. So, it has changed the acid in the $KMnO_4$ solution. In the last two steps, it has been changing immersion time and concentration in order to find the suitable parameters for the solvent. Finally, the sample has been metalized with a good appearance, homogenous surface but with no good adhesion checked using the crosscut test, image 5 (num8). After the last changes (elimination of the post-pd solution) the sample surface has good appearance and good adherence by Crosscut.

As It could be read in the experimental part, chromium-free etching could be added to the conventional process. There are only two changes in the stages, Chromium etching is replaced by Chromium-free etching plus the acid mixture, then it is possible to use the same following solutions that in the conventional process. So, after that, palladium solution is the following one, then accelerator solution and chemical nickel solution. The samples have been tested and studied by Confocal and SEM technique. The results obtained were interesting. When it is compared the roughness of both etchings, chromium-free etching surface is less roughness than chromium etching. Moreover, the surface analysed by SEM it was quite different. It has micro holes but the disposition, the geometry is more variable than in etching chromium. Although the quite different results when it is analysed chemical nickel deposed its structure is totally identic for both etchings used using different values of roughness [15].

6.5. EVALUATING THE ADHERENCE OF THE COATINGS

Crosscut test results show that both coatings have a good adherence from a quality perspective as it can be seen in this image 6. The only significant difference between both nickel coating is the colour. In nickel deposed using chromium etching is grey instead of the nickel using chromium free etching that is bright.

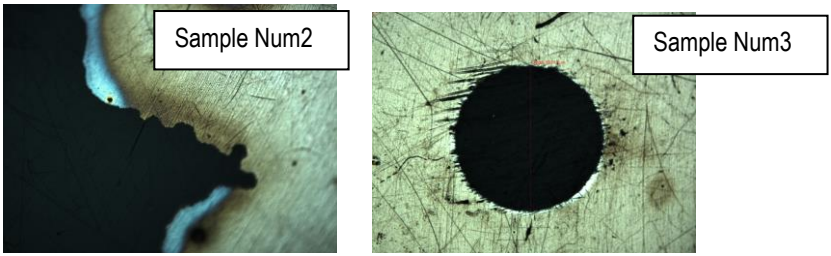
Image 6. Crosscut results for table 15 sample num4.



On the one hand, the results obtained by Nano indenter do not provide any direct conclusions. There was a scratch in both coatings as it was looking for. It means that the chemical nickel deposited using the different etching has adherence for a progressing load 0-500mN applied. Then, it is needed to apply more force to the surfaces to get more valuable inputs as coefficient of friction between the surface and ABS material, and know in which value occurs the first crack. Using the hardness (H) and the elastic modulus (E) in function of the penetration depth (h) given by the instrument.

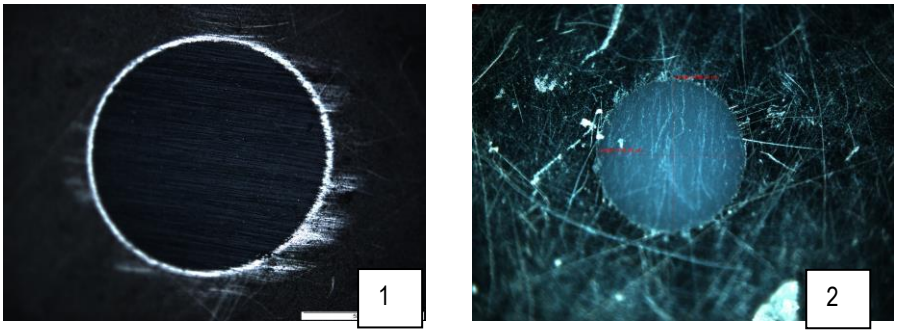
On the other hand, Calowear results provided a first idea how is the surface for the 4 samples showed in table 15. Sample 1 (70ºC, 12min) Sample 2 (20ºC 12min), Sample (70ºC 4min) and Sample 4 (etched by the new chromium-free etching). It could be not possible read the thickness value for sample 2, and sample 3 (samples which has been in etching solution in a not properly working conditions) because the spheres were scratched and the thickness were not uniformly deposited as it seen in image 7. The images are taking using the same conditions, there is only a light changing.

Image 7. Chemical nickel thickness measurement for sample num2 and num3



The nickel thickness of sample num1 treated by current working conditions could be measured. The value is 0.54 μm. Comparing the samples with the nickel deposited using chromium etching, it can conclude that when it is used the not properly working conditions in etching solution, the chemical nickel cannot be deposited with a good adherence. A poor adherence is related of the quantity of nickel was deposed.

Image 8. Chemical nickel thickness measurement for sample 1 (1) White sphere is the thickness of Chemical Nickel deposited. Inside of the white sphere can be found the ABS surface previous treated by etching, palladium solution and accelerator solution. Chemical nickel thickness measurement for sample 4. (2)



Finally, when it is compared with the new free-chromium etching a not expected results are achieved. The nickel thickness for sample num4 cannot be measured. It means that the adherence of the chemical nickel in the surface prepared by chromium-free etching it seems not to be good enough (image 8 (2)). The coating has not resisted the ball scratch. Moreover, the rest of nickel surface that appears in (image 8 (2)), it is also little scratched surrounding. Maybe, the manipulation during the transport and the test created that little scratches, but both kinds of samples have been manipulated par equal. By contrast, the nickel deposed using chromium conditions its surrounding surfaces is complete clean of little scratched in (image 8 (1). Then, current metallization procedure has better results and appears to have greater adherence and nickel thickness than the new metallization procedure.

7. CONCLUSIONS

The current electroless metallization process is complete described from the beginning. The forth main steps are completely explained using roughness and SEM images. The role of accelerator and palladium, and nickel was evaluated and contrasted to the chemical theories available. It cannot be possible to find the palladium deposited in the micro holes, but it has realized its importance as a catalyst of chemical nickel.

It could possible realize how etching work in the surfaces and understand and confirm the hypothesis of butadiene in ABS plastics. It was carried out a mapping of roughness for this etching using the variables temperature, trivalent chromium and immersion time to evaluate how new etching could be defined. Then, it is known that temperature is the critical parameter for control de roughness in etchings.

An improvement proposal of this process to achieve the replacement of chromium etching have been achieved. After some initial experiments, it can be found the ideal reagents used for and the working conditions for that new etching called chromium-free etching in this report. Then, a chromium-free etching samples have been metalized for the first time.

The comparison of the adherence for chemical nickel deposed using chromium-free etching and chemical nickel deposed using chromium etching has been carried out. Finally, current electroless metallization procedure has better results and seems have greater adherence and nickel thickness than the new metallization procedure using these adherence techniques.

8. REFERENCES AND NOTES

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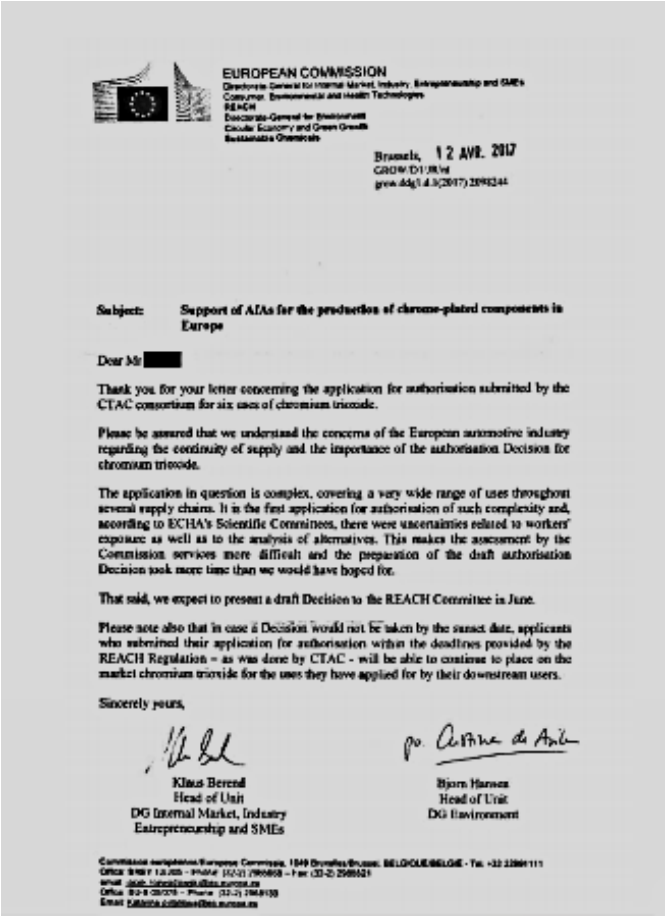
9. ACRONYMS

ABS	Acrylonitrile butadiene styrene
PC	Polycarbonate
ATSDR	The Agency for toxic substances and disease registry
IARC	The International Agency for Research on Cancer
OSHA	Occupational Safety and Health Administration
CTACsub	Chromium trioxide authorisation consortium
Confocal m.	Confocal microscopy
IR	Infrared spectroscopy
SEM	Scanning electron microscopy

APPENDICES

APPENDIX 1: COPY OF EUROPEAN COMISSION LETTER



EUROPEAN COMMISSION
Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs
Consumer, Environmental and Health Technologies
REACH
Directorate-General for Environment
Circular Economy and Green Growth
Sustainable Chemicals

Brussels, 12 AVR. 2017
GROW/D1/JR/rd
grow.ddg1.d.3(2017)2093244

Subject: **Support of AIAs for the production of chrome-plated components in Europe**

Dear Mr [redacted]

Thank you for your letter concerning the application for authorisation submitted by the CTAC consortium for six uses of chromium trioxide.

Please be assured that we understand the concerns of the European automotive industry regarding the continuity of supply and the importance of the authorisation Decision for chromium trioxide.

The application in question is complex, covering a very wide range of uses throughout several supply chains. It is the first application for authorisation of such complexity and, according to ECHA's Scientific Committees, there were uncertainties related to workers' exposure as well as to the analysis of alternatives. This makes the assessment by the Commission services more difficult and the preparation of the draft authorisation Decision took more time than we would have hoped for.

That said, we expect to present a draft Decision to the REACH Committee in June.

Please note also that in case a Decision would not be taken by the sunset date, applicants who submitted their application for authorisation within the deadlines provided by the REACH Regulation – as was done by CTAC - will be able to continue to place on the market chromium trioxide for the uses they have applied for by their downstream users.

Sincerely yours,

Klaus Berend
Head of Unit
DG Internal Market, Industry
Entrepreneurship and SMEs

p.o. Arthur de Azila

Bjorn Hansen
Head of Unit
DG Environment

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Email [redacted]

Table x. Copy of the part mentioned of the final Opinion and Periods of Review recommended by the solicitors of Chromium Trioxide Authorisation Consortium (CTACsub) for the Authorization of chrome.

Functional chrome with decorative character incl. Etching of plastic (from the deadline 21.09.2017)

- Periods of review proposed by the solicitors: 7 years
- Periods of review recommended by RAC/SEAC 4 years
- Beginning recommended for the update of documents, assuming that are necessary 2.5 years: 21.09.2017
- Presentation recommended of review of documents 2 months before term 21.03.2020
- Deadline fot the first review 21.09.2021

APPENDIX 2: IR CHARACTERIZATION OF RAW MATERIALS

Table X. Characterization of raw materials ABS and PC.