The Impact Of The Use Of Nanotechnology In Surface Treatment In The Automotive Industry

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ABSTRACT

Nanotechnology is one of the most discussed topics in the 21st century in engineering - and with large investments - due to the revolution it brought to particles and interfaces comprised in the order of one hundred nanometers, as fast as nanoparticles. Its importance and study are based on the use of the best properties of these materials provided by their size and base, applying them strategically and technologically. The objective of the current work is to promote the use of nanotechnology, applied to the automotive sector, more specifically in surface treatment, corroborating it through a dense bibliographic material and real results caused by the replacement of phosphatizations.

The research was carried out in two stages (exploratory research and case study) being able to demonstrate at the end of this, its pre and post implementation impacts, conditions, benefits in the medium, short and long term and present its results in order to name its importance and supply in the technological and industrial market.

INTRODUCTION

Nanotechnology makes a crucial contribution to the necessary developments and production of innovative materials and processes in the automotive, aerospace, and waterborne transport sectors. Most nanotechnology-based research and development is in the automotive sector, as we depend on it more often than air or water transport. Nanotechnology is applied to body parts, emissions, chassis and tires, automobile interiors, electrical and electronics, engines, and powertrains [1].

Nanotechnology encompasses all kinds of technological development within the nanometer scale, usually between 0.1 and 100 nanometers. [2].

OBJECTIVES

GENERAL

The objective of this study is to improve the understanding of and defend the application of nanotechnology, in detriment to the use of phosphating, in surface treatment, basing its defense on the analysis of real data from the implementation of the technology implemented in a real production process in an automotive industry.

SPECIFIC:

- To study the implementation of green TTS (Surface Treatment) in the study industry;

- Identify the advantages and impacts of using nanotechnology in surface treatment;

- Measure the impacts with real data the results of the implementation.

JUSTIFICATION

Currently, companies in the automotive sector, the segment that is the object of this study, are resistant to the application of nanotechnology for surface treatment to replace phosphating. This surface treatment has been used in the market for more than 50 years and brings few advantages to the process, besides its balance that is shown to be more negative than positive, by means of cost data, process time, environment, quality, among other factors.

In this project, the objective is to counter corporate resistance with data from a real application.

LITERATURE REVIEW

Painting is a coating process that improves the cohesion of the material and the surface properties of the parts, besides acting as a barrier against corrosion, permeation or diffusion from the surface. Currently it is highlighted that robotics has been a great ally of the automotive industry [3].

A paint system is usually composed of a primary or base paint (primer); an intermediate paint (pigmented or solid) and a finishing paint (finishing varnish). Paints are not completely impermeable to air humidity. In this sense, dry film thickness becomes a highly important factor for a saturated humid environment. Complete paint systems should have maximum thickness and minimum porosity possible, preserving adhesion with the substrate and between coats, ensuring maximum paint impermeability [4].

The automotive painting process has two essential functions. The first of these is associated with the appearance of the product. The second is to protect the car's metal structure from corrosion. Along with the design of the car, the paint is inevitably present in the customer's first contact with the product. From the 1970s on customers began to become increasingly demanding about the appearance of their vehicles, and then the automotive paint industry had to adapt to a new demand [5].

SURFACE PREPARATION

Painting requires appropriate conditions for the material and surface on which the paint and other chemical components for its coating will be deposited. Polypropylene, for example, has some characteristics that make it complex to adapt to the painting process. The low surface tension of the polymer is one of them, which makes the material unsuitable for adhesion to coatings. For this reason, polypropylene depends on surface pre-treatment techniques to facilitate the adhesion of the coating to the material [6].

Cleaning

It is possible to directly associate the technical performance of the coating with the quality and preparation treatment of the surface to be painted. The surface treatment depends on the requirements for the appearance of the coating and the type of raw material of the part on which the paint will be applied. Surface preparation first involves methods for cleaning the area to be painted, which is important for eliminating irregularities such as dust, oil, cracks, and other contaminants. Surface cleaning can be divided into six categories [7].

Blasting: It is a surface cleaning process that can be done through abrasive means such as sand, steel grit, which are thrown towards the material by compressed air or water.

Degreasing: It is a surface cleaning process where low toxicity and flammability organic solvents are applied to remove oil, grease, and dust.

Manual mechanical cleaning: This is a low-efficiency surface cleaning process, where operators use tools such as sandpaper, scrapers, brushes, and spatulas to remove impurities or tricks from the surface. The process can be used on metallic or non-metallic surfaces.

Motorized mechanical cleaning: It is a surface cleaning process carried out by operators using tools such as sanders, motorized polishing machines, pneumatic hammers, etc. The process can be used on metallic or non-metallic surfaces.

Sanding: It is a process of cleaning and finishing the surface by roughening it using sandpaper.

Chemical cleaning: This is a surface cleaning process that makes use of chemical solutions. This process can be carried out by acid or alkaline solutions. The acid solutions have the function of chemically stripping the material through inorganic acids such as: sulfuric acid, hydrochloric acid, and nitric acid. Alkaline solutions are used to neutralize the pickling action by washing the surface. The alkaline compounds used for cleaning are: sodium hydroxide and sodium silicate. Plastic surfaces are more complex to achieve satisfactory adhesion of the coatings. Consequently, the proper preparation of the surface to be painted is paramount to maximize the performance of the coatings. Therefore, cleaning with organic solvent is the most indicated for plastic surfaces composed of polypropylene [8].

Eletrodeposition

It is a process of painting by immersion, water-based, and its main purpose is to protect the anticorrosive surface before receiving the paint. Before being applied, the bodywork receives a pre-treatment, with a total cleaning of its entire surface to remove irregularities, residues, dirt, grease, and other aspects, which prevents foreign particles present there from compromising the rest of the steps [9].

This layer has this name (electrodeposition), because an electrical effect ensures that the paint particles penetrate and fully cover the bodywork parts, both inside and outside. Its main purpose is to fully protect the bodywork against corrosion [10].

There are two types of electroplating. The first is anodic electrodeposition where the surface of the part is positively charged while the paint deposited during the process is negatively charged. The second type is cathodic electrodeposition, where the part is negatively charged (grounded) while the paint particles are positively charged, and this type of electrodeposition is more common among industrial painting processes [11].

PAINT COATING

The automotive painting process in the industries, described by [12] is one of the production stages of a complete vehicle and can be summarized in 12 stages:

-Surface Treatment , formed by ten tanks that have the purpose of cleaning the surface of the bodywork;

-Cataphoresis (KTL), which consists of a dip painting;

-Greenhouses, which dry and cure the KTL;

-Sealing Masks, which consists in applying the fixing holes and pins;

-Pre-curing oven for the sealing mass, used to dry the mass;

-Primer application, used to level out small surface irregularities on the parts;

-Curing oven, used to dry the primer coat;

-Color Selection System;

-Color Base application, which consists of applying a paint that provides the appearance relative to the vehicle's color;

-Pre-curing oven, used to dry the applied paint;

-Application of Varnish, which will provide the aspect related to the paint's shine on the vehicle;

-Varnish Curing Greenhouses - cure the layer of varnish applied.

SURFACE TREATMENT

The Surface Treatments play a key role in preventing corrosion, increasing the durability and life of metals and promote better adhesion of paint, which is the main means of protection against corrosion, forming not only a protective but also a decorative layer [13].

Surface treatment processes are divided into two categories: Conversion Layers and new trends. Conversion Layers are subdivided into: Phosphatization, Chromatization and Anodization. As for the new trends we can mention the Silanization and the Nanoceramics [14].

In the coating industry, phosphating is one of the main surface treatments used. The phosphatization is a process of metal conversion into an insoluble phosphate (salt) of the metal ion, most often zinc phosphate that deposits on the surface modifying the surface properties [15].

The Phosphating Process is mostly used to prepare the metal surface for good adhesion of the paint and protect the surface from the development of corrosion processes. The durability of the paint is directly linked to the effectiveness of the pre-treatment system on the substrate[13].

The treatment of metallic surfaces through phosphatization ensures better performance of the following processes of painting for corrosion protection, being necessary the processes of Ecoat (KTL), Surface and Base Coat application for effective protection against corrosion [13].

About 90% of the chemicals in Brazil that are used for surface treatments are of foreign origin. Brazilian companies make the final formulation of the mixture and adjustments according to the climate of the region where the products will be used [16].

Phosphate-Based Surface Treatment

The most widely used use of phosphating is the preparation of the metal surface in order to increase the adhesion of the paint and prevent the development of the corrosion process, prolonging the life of the treated part. The treatment of the surface of metals prior to painting is to turn this unstable surface into a stable surface, becoming an inert base to receive the paint [17].

Most automotive industries use the phosphatization process for the pre-treatment of the metallic surfaces of cars, this process can meet the market requirements for corrosion protection and adhesion of the paint film applied by electrodeposition [13].

A continuous automotive painting line basically consists of the following steps:

-Pre-treatment: phosphatization by aspersion or total immersion;

-Cathodic or cataphoretic electrophoretic painting (e-coat): cathodic application of a 25 µm to 30 µm thick film. The main purpose is to increase protection against corrosion.

-Surfacer: layer 25 µm to 30 µm thick.

-Finishing paint (base color coat): application of a 15 µm to 25 µm thick layer in the final color desired by the customer.

-Clear coat: application of a 35 µm to 50 µm layer to provide gloss and enhance the color [13].

To obtain a uniform phosphate layer it is necessary that the layer is not only free of impurities, but also to condition the surfaces to be phosphatized to obtain a uniform, dense and microcrystalline phosphate layer, avoiding flaws or imperfections of the deposited phosphate layer, so as not to compromise the quality of the process [13].

Phosphating can be carried out in 3 ways: phosphate 3 in 1, phosphate by immersion, phosphate by spray. The product resulting from the electrochemical reactions on the metal surface results in the formation of an insoluble, crystalline phosphate layer ranging from 2.8 g/m² to 3.2 g/m². The phosphate crystals that are formed on the surface have their morphology influenced by the agitation process in the immersion treatment and also differ if the process is by spray [13].

The morphology of the crystals formed determines the degree of porosity on the surface and consequently interferes in the results of the process, because where there is no crystal formed on the surface, the surface will be dirty to corrosion. The refining step is also important, because a high pH promotes the precipitation of phosphates, forming small crystals. If the acid pickling is too long and the surface is not well washed after this bath, long crystals may result, which is also not interesting for the painting process [18].

According to [19], the surface pretreatment cleaning steps performed before the phosphating step can also considerably affect the layer growth rate, layer thickness and phosphate crystal size.

To reduce the formation time of the phosphate layer are used additives such as Nickel, Zinc and Manganese dissolved in the phosphating solution, when we have a single system, called Tri-Cathionic phosphating, considered one of the most useful in the automotive industry. Nickel, among the metal ions that are used as additives in phosphatization, is the one that plays the best role, but it is very aggressive to human health and the environment [20].

Phosphating can be carried out in 3 ways: phosphate 3 in 1, phosphate by immersion, phosphate by spray [13].

The surface treatment, the object of this one, is zinc phosphate treatment, which can be by immersion or spray.

NANOTECHNOLOGY IN SURFACE TREATMENT

A new generation of nanotechnology surface treatment processes has recently been discovered to replace phosphate processes, with significant improvement in both ecological and economic terms. These processes are free of heavy metals such as nickel, manganese, zinc, phosphorus and chromium. These new coatings have as their main characteristic the thin layer formed, whose thickness of the film formed is on the nanometric scale [21].

For many years, phosphating methods have been widely used for the treatment of metallic surfaces, in particular amorphous phosphating, mainly due to the ease of use, ease of control of the different parameters and good corrosion resistance for multiple applications. Currently, there is research work to find alternative applications that provide competitive advantages in surface treatment, in order to minimize environmental impact and that meet, at the industrial level, the following main conditions [22].

1) Quality identical to or better than that obtained with phosphatizations at the defined parameters;

2) Ease of application (reducing or not increasing the number of steps required);

3) Robustness (that tolerates a certain degree of contamination from the baths);

4) Reduced environmental impact, either by reducing the volume of effluent or by reducing the phosphate content of the effluent;

5) Competitive (lower or identical) overall cost of operation.

When talking about nanotechnology we refer to the process capable of generating a layer of a few nanometers, compared to the thickness about micron, obtained with traditional methods, such as amorphous phosphating and other phosphatizations [23].

The metal surface treatment methods or processes under development, referred to as nanotechnology treatments, can be divided into two distinct groups: sol-gel or filmogen treatment and conversion treatment, which will be developed next [23].

NANOTECHNOLOGY SURFACE TREATMENT

Nanotechnology applied to surface treatment, the object of this study, concerns the process performed on the body before receiving the protective and beautifying layers, such as anticorrosion, primer, base, and varnish. This step is contained within the painting process which is subdivided into 3 blocks: cleaning, protection and characterization which are further subdivided into 6 main processes as shown in figure 01.

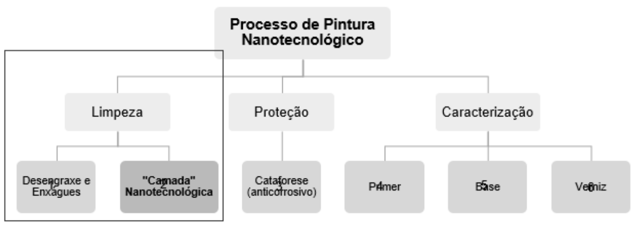

Figure 1 - Macro view of the nanotechnological painting process
Source: Jacinto, K; Costa, L. 2021.

CHARACTERISTICS AND IMPACTS

As seen throughout this study, nanotechnology surface treatment has distinct characteristics and implementation needs.

As To The Process

Green TSS is based on silanes that form aqueous solutions, through hydrolysis and condensation, polysiloxanes. During the coating process, the reactive silanol groups can be chemically bonded to the metal as well as to the paint coating. Heat treatment, for example, after cathodic electropainting (CEP), further crosslinks the polysiloxanes [24].

Figure 02 demonstrates the vital steps of a phosphatization-based TTS that is comprised of 6 processes:

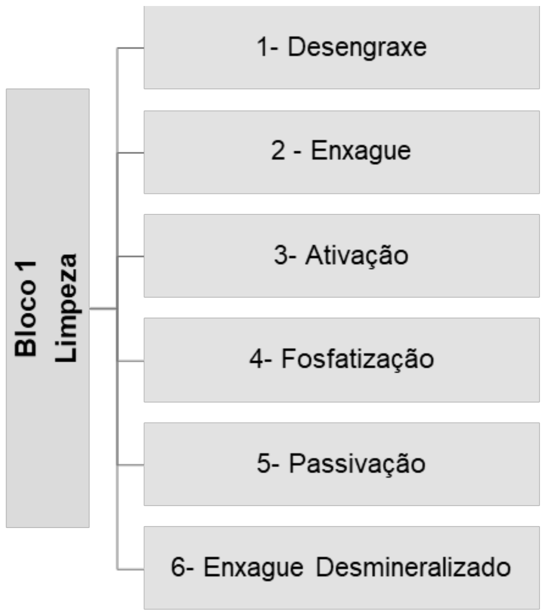

Figure 2 - Representative diagram of steps in a phosphate-based painting process
Source: Jacinto, K; Costa, L. 2021.

The nanotechnology surface treatment is more robust and has a simpler process with fewer steps. Its bath technology fully replaces phosphatization and dispenses with the use of two further steps (activation and passivation), as shown in Figure 03:

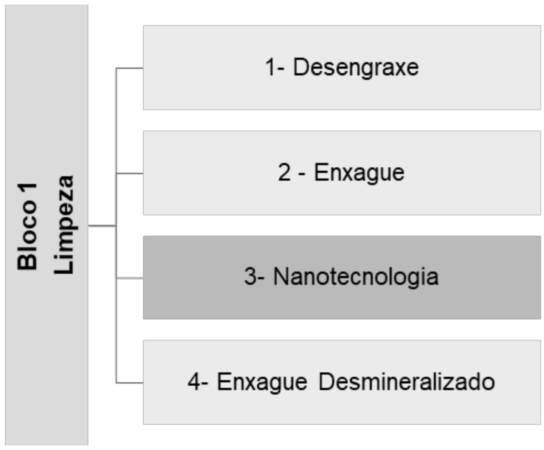

Figure 3 - Representative diagram of steps in a nanotechnology-based painting process
Source: Jacinto, K; Costa, L. 2021.

Another characteristic is that its process does not require such high temperatures, being able to work at ambient rates, dispensing with the use of heating in the treatment.

The nano "layer", also known as the conversion layer, also allows for an increase in production cadence, since the conversion of the treated surface takes place in less time, with little influence from temperature (which makes the process even more independent and with less risk). The reduction in production time happens not only because of the shorter process times, but also because of the reduction of its production steps.

However, the maintenance costs also decrease as a result of the type of treatment. In phosphatization the maintenance needs to be constant, since the equipment is directly linked to the waste generated by the process. In the nano process, in addition to the absence of heavy metals and the absence of waste, there is a low viscosity, which allows a bolder maintenance plan spaced out due to the reduced need.

Regarding The Environmental Issue

TTS, as stated throughout this study, is green. This means that the involvement of chemicals in its process is limited, with lower risk classifications, free of hazardous substances over a long period of time, especially phosphate and nickel, which are highly carcinogenic substances.

Its impact also extends to water and electricity consumption, because, its working temperature is ambient and there is no production of sludge (process waste), which has high rates of heavy metals.

In water consumption the reduction is considerable, mainly by subtracting the processes. The bath also has greater durability and conservation, which makes it even more attractive and advantageous to environmental issues.

Regarding Economic Issues

The nano surface treatment is of medium viscosity and with low concentrations of use, as already mentioned, it has a longer useful life, does not cause damage to the equipment by the chemical components, and reduces the investment in maintenance. In addition, it reduces process steps, reduces equipment in use, spending on electricity for process control and maintenance, investment in industrial water and demineralized water. One cannot forget the cost reduction with the treatment of rejects and sludge, effluent treatment, environmental risk reduction, and chemical cleaning.

The use of nanotechnology in surface treatment also reduces material costs, process time (gain in increased capacity and reduced added value and labor per vehicle), and temperature reduction of the entire process. Its applicability is compatible with the existing process, which reduces the investment value.

Regarding The Quality Of The Bath

It causes the suppression of two stages of the conventional process, dispensing with the use of activation and passivation that are vital in the bath with the presence of phosphate, but maintaining the quality. In addition, it is multi-metal, which makes it suitable for use in exterior parts, structural parts, reinforcements, among others, increasing the adhesion of subsequent processes and greater resistance to corrosion.

Paint Layer

The paint layer or film is the junction of all the processes performed and is one of the main factors in the final quality of the product and its characteristics. Figure 04 demonstrates the thickness of the phosphate-based painting process and Figure 05 the thickness of the nanotechnology one and its comparison.

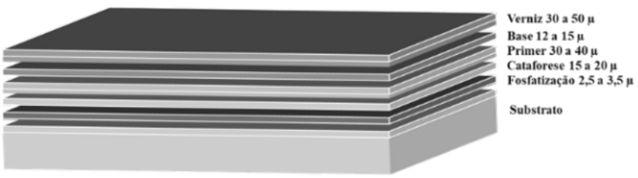

Figure 4 - Diagram of the Phosphate-based TTS painting process
Source: Jacinto, K; Costa, L. 2021.

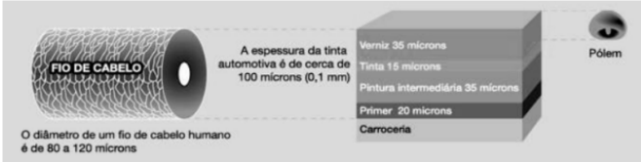

Figure 5 - Thickness of a nanotechnological painting process
Source: Jacinto, K; Costa, L. 2021.

The nanometer "layer" as noted in the image above is so thin that it is not considered a layer. Calculations state that its thickness is 50 times less than the phosphatized one and can only be measured by microscopes. The application of this material also makes it possible to reduce the thickness of other layers in the process, since it increases the protection against corrosion and adhesion of the following steps. An example of this is the cataphoretic layer that today, in some industries, is already below 15µ. Its application has proven to be even more advantageous in the new upgrades that have been occurring with the suppression of the primer layer.

ADVANTAGES

Nanotechnological Surface Treatment has several extended advantages in the environmental, energy, production, legislative, operational, competitive and economic spheres.

-It is simpler and allows the use of the structure already existing in the plant;

-It is a more robust process;

-High technological quality;

-It is a conversion layer;

-Suppresses 2 steps of the conventional process;

-Eliminates the use of heavy metals;

-It produces little waste and does not harm the environment;

-Reduces the need for chemical cleaning;

-Reduces the need for effluent treatment;

-Reduces water and electricity consumption;

-It's safer;

-Economical, because the deposited layer is much smaller,

-It increases the adherence of the later stages;

-Allows application by sprinkling/immersion;

-Reduces the working temperature of the process;

-It extends the useful life of the equipment;

-Reduces maintenance costs

-Reduction of greenhouses in the process

DISADVANTAGES

-Due to the technology of the bath, it requires a better quality body, because, unlike phosphatization, which suppresses some defects by deposition of a high layer, it tends to reveal the irregularities of the surface on which it is applied;

-Few suppliers have these technologies (currently 3 suppliers in the national territory);

-Common layer measurements are not applicable, since the deposition is nano. For this case an x-ray gun and accompanying radio protection are required;

ANALYSIS AND RESULTS

All information that could make the company's data known has been modified in order to ensure company secrecy.

In order to understand the complexity of the theme presented as well as its results, two objectives were defined: the understanding of the forms of surface treatment (phosphate and green) and their impacts supported by two methodologies, exploratory research and case study, which made it possible to obtain the results shown.

The substitution of phosphatization in the Surface Treatment of the corporation in question made it a pioneer in the use of the new technology. Its implementation is responsible, today, for savings of more than half a million reais per year, considering only direct costs, extending its effects throughout the entire production chain.

On the environmental side, the impacts were even more significant. With regard to the use of industrial water, its reduction represented a drop of approximately 82% in the year, leading to an increase in the rate in the following years. The use of demineralized water, vital to the process, fell by a little more than 14%, as well as the reduction of waste, which was previously in larger quantities and with heavy metals, and post green TTS with a reduction of 56.94% and free of heavy metals. With regard to chemical cleaning, the reduction is even more alarming totaling a 100% drop.

As for the energy aspect, the same can be observed regarding the reduction. The decrease in the use of energy was responsible for savings of more than R$ 630 thousand reais in the year, since there was a reduction not only in the amount of equipment, but also in the lower needs of the new process.

Nevertheless, the advantages also extend to general cleaning, which equaled a reduction of more than R$216,000 in the year.

When making the simple calculation over all the values shown, it will be noted that the financial reductions generated to the organization, besides the technological gains and the reduction of the process complexity, are based on more than R$700,000 per year.

FINAL CONSIDERATIONS

The study conducted throughout this paper allowed us to know, more intrinsically, the impact of the use of nanotechnology in Surface Treatment (SPT) in detriment to the use of phosphate in a company in the automotive sector and allowed its defense after the knowledge of the data and its expressiveness in the organization.

Its applicability in painting, more specifically in the first block of the process, has proven to be highly recommended and based on the sequence, considered positive, of effects with the new process and the financial results already harvested within the first months.

With the use of green TTS the first impact was the reduction of process steps, followed by the reduction of some equipment no longer needed and reduction of industrial and demineralized water supply. In the following month the results were consolidated by the reduction of electricity costs and materials supply.

When considering the entire process, the impacts do not stop. There was also a reduction in chemical cleaning, elimination of process waste, adjustment of maintenance in its variability, due to lower process requirements.

In view of this, the data presented above corroborate the use of nano in surface treatment, not only in its direct financial reductions, but also in its process characteristics. Direct reductions now represent a considerable percentage of the organization.

The advantages of its use have become more than proven, as well as the benefits to the product, process, environment, legislation, operation, energy, and industrial competitiveness, even more so considering that the global trend is for environmental rules to become even stricter for the sector, which is worrisome when dealing with a process that produces residues with heavy metals.

Therefore, given the excellent results demonstrated and proven, it is suggested to extend the study to the suppression of the primer step, suppression that has proven to be highly profitable and would result even more in the reduction of the layer applied and costs involved in the process, without demerits to the final quality of the product.

REFERENTIALS

[1] MATHEW.J; JOY.J; GEORGE.S.C. Potential applications of nanotechnology in transportation: A review. **Journal of King Saud University – Science**. Índia, March, 2018.

[2] Instituto Inovação. Nanotecnologia. Disponível em: <http://www.institutoinovacao.com.br/downloads/inovacao_set05.pdf>. Acessado em: Set, 2005.

[3] TAUCITA, Fabrício de Mello; SANTOS, Pâmela Marcélia de Siqueira; ALMEIDA, Valquíria de**. Presença de Robôs de Pintura na Indústria Automotiva**. 2013.

[4] VERGÉS, Gisele Ribeiro. **Estudo do desempenho de sistemas de pintura para materiais das redes de distribuição de energia elétrica situadas em regiões litorâneas**. Dissertação para o Curso de Pós-Graduação em Engenharia, Área de Concentração em Engenharia e Ciências dos Materiais, da Universidade Federal do Paraná. CURITIBA 2005.

[5] DALMOLIN; GONÇALVES; PACHEKOSK. Avaliação da remoção da camada primer num processo de pintura automotiva, efeitos econômicos e impactos ambientais. Revista do Centro do Ciências Naturais e Exatas - UFSM, Santa Maria**. Revista Eletronica em Gestão, Educação e Tecnologia Ambiental –** REGETeISSN 2236 1170 - v. 15 n. 15 Out. 2013, p. 3045-3054.

[6]. PIJPERS, A. P.; MEIER, R. J. Adhesion behaviour of polypropylenes after flame treatment determined by XPS (ESCA) spectral analysis. **Journal of Electron Spectroscopy and Related Phenomena**. Holanda. v.121. p. 299-313. 2001.

[7] FAZANO, C. A T. V. Tintas: Método de controle de pinturas e superfícies. **Editora Hemus**. 6ª edição. Curitiba-PR. 2002.

[8] FAZENDA, J. M. R. TINTAS & VERNIZES – Ciência e Tecnologia. 3ª Edição. **Editora Edgard Blucher**. 2005.

[9] KOTTWITZ, Leandro. **Controle de qualidade da repintura automotiva em oficinas de pequeno porte**. Rio Grande do Sul – UNIJUÍ. Panambi. 2019

[10] TEIXEIRA, Renata Cristina. **Pintura por Eletrodeposição: Proteção Anticorrosiva de Materiais**. Projeto de Graduação, Universidade Federal de Uberlândia. Uberlândia – MG, 2009.

[11] PIEROZAN, L. **Estabilização de processos: Um estudo de caso no setor de pintura automotiva**. Dissertação do curso de Mestrado Profissionalizante em Engenharia. Porto Alegre. 2001.

[12] SANCHEZ, S. M.; SANCHEZ, P. J.; RAMBERG, J. S.; MOEENI, F. **Effective Engineering Design through Simulation**. Int. Trans. Opl. Res. v. 3. n□2. p. 169-185. University of Missouri. USA.1996.

[13] CAMILO, Deise Mariana. **Avaliação dos Parâmetros de Processo de Fosfatização Tricatiônica**. 2011. Monografia para Graduação em engenharia Química. Escola de engenharia de Lorena, Lorena, 2011

[14] COSTA, S. L. F. A.; RUBIM, J. C; AGOSTINHO, S. M. L.Spectroelectrochemical study of the corrosion of a copper electrode in deaerated 1.0 M HCI solutions containing Fe(lll)-Effect of the corrosion inhibitor benzotriazole **Journal Electroanalycal Chemistry**, v. 220, p.259-268, 1987.

[15] BANCZEK, E.; OLIVEIRA, MARILEI; CUNHA, MAICO; RODRIGUES, PAULO. Study of the Electrochemical Behaviour of Tolitritriazole in Phosphating Bathings of Carbon Steel 1008.**Portugaliae Electrochimica Acta** 23; 379 – 391, 2005.

[16] ABTS. **REVISTA TRATAMENTO DE SUPERFÍCIE**, Edição n°150 – Julho/ Agosto-2008

[17] AMORIM, Amanda Miller; BATISTA, Mariana Gomes; COELHO, Thaiza Regina Ferreira. **Estudo do Processo de Pré-tratamento e Antioxidação da Carroceria Automotiva e Ferramentas de Qualidade Usadas para Controle**. Monografia (Graduação em Engenharia de Produção) – Centro Universitário de Barra Mansa, Barra Mansa, RJ, 2016.

[18] GALVANO, **Catálogo de Produtos**. 2011

[19] BEM, Patrícia. **Minimização do Efluente Gerado em Pré-Tratamento de Pintura Automotiva: Um caso Industrial.** Dissertação de Mestrado. Departamento de Pós Graduação em Engenharia Mecânica. Universidade Federal do Paraná. Curitiba, 2008.

[20] DONOFRIO, J. Zinc phosphating. In: **Metal Finish**,2003

[21] BOSSARDI, K. **Nanotecnologia aplicada a tratamentos superficiais para o aço carbono 1020 como alternativa ao fosfato de zinco**. Porto Alegre, 2007. Dissertação para obtenção do título de Mestre em Engenharia. Universidade Federal do Rio Grande do Sul

[22] Carné, Josep Vives PhD. (2008). **Manual de fosfatación y nuevas tecnologias alternativas**. PROQUIMIA S.A.

[23] MIGUEL, A; SOUSA, H. **Tratamento de superfícies metálicas por nanotecnologia.** Lisboa, 2013. Trabalho Final de Mestrado para obtenção do grau de Mestre em Engenharia Química e Biológica. INSTITUTO SUPERIOR DE ENGENHARIA DE LISBOA

[24] Basf. Chemetall Expect more. Disponível em: <https://www.chemetall.com/oxsilan>. Acessado em 30 out. 2021.

[25] JACINTO, K; CARNEIRO, L. **O IMPACTO DO USO DA NANOTECNOLOGIA NO TRATAMENTO DE SUPERFÍCIE EM INDÚSTRIA AUTOMOTIVA.** Resende, 2021. Trabalho de Monografia. Associação Educacional Dom Bosco. Faculdade de Engenharia de Resende.