

Master in Chemical Engineering

Study and develop solutions for silicone accumulation problem

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Study and develop solutions for silicone accumulation problem



Abstract

With the ever-growing automotive interest, the need for product solutions with maximum durability, aesthetic quality and comfort, grows as well. However, when trying to achieve all these requirements, some difficulties must be overcome. At TMG Automotive, most of the final products have a finishing, to meet some requires characteristics. This is formulated with a range of additives added to a polyurethane resin, that may be water or solvent-base. One of the additives, responsible for increasing abrasion resistance and improve touch is a silicone. The downside of working with silicones is the risk of contamination of a process line, affecting the production. At TMG Automotive, the silicone in the finishing formulation migrates and accumulates at the cylinders of the lacquering line.

This thesis studies the raw material's aspect, composition and behavior. It was concluded that the current raw materials are different from the ones from 2017, before the aggravation of the silicone contamination problem. The simplest technique to assess differences between different batches of raw material, is by the aspect of the lacquers, while SEM images of the lacquers and the rheology of the added silicone were also a relevant source of information.

Further along, some changes of the finishing formulation were engineered. To decrease the contaminations by silicone, the size and number of silicone clusters in raw materials must be decreased. To accomplish that, different solvents and crosslinking agents were used, which allowed to improve homogeneity of the lacquer. It was also assessed the influence of the silicone's concentration to thereof migration, and its mobility within the layers applied. The conclusions withdrawn from the first, were that, increasing the proportion in which the silicone was added, does not affect the silicone agglomerations. The information gathered in the last test, was not enough to withdraw conclusions on silicone's mobility.

Resumo

Com o crescente interesse na área automóvel, cresce também a necessidade de soluções de produtos com máxima durabilidade, qualidade estética e conforto. No entanto, ao tentar alcançar todos esses requisitos, algumas dificuldades devem ser superadas. Na *TMG Automotive*, a maioria dos produtos finais tem um acabamento, para dar resposta às características necessárias. Um acabamento trata-se de uma gama de aditivos adicionados a uma resina de poliuretano, que pode ser de base aquosa ou solvente. Um dos aditivos, responsável por aumentar a resistência à abrasão e melhorar o toque, é um silicone. A desvantagem de trabalhar com silicões é o risco de contaminação que estes representam, afetando a produção. Na *TMG Automotive*, o silicone na formulação de acabamento, migra e acumula-se nos cilindros da linha de lacagem.

Esta tese estuda o aspeto, composição e comportamento da matéria-prima. Concluiu-se que as matérias-primas atuais são diferentes das de 2017; antes do agravamento do problema de contaminação por silicone. A técnica mais simples para avaliar as diferenças entre os diferentes lotes de matéria-prima é pelo aspeto das lacas, enquanto análises de EDS das lacas e a reologia do silicone também eram uma fonte relevante de informação.

Mais adiante, algumas modificações da formulação de acabamento foram projetadas. Para diminuir as contaminações por silicone, o tamanho e o número de clusters de silicone nas matérias-primas devem ser reduzidos. Assim, foram usados diferentes solventes e agentes de reticulação, o que permitiu melhorar a homogeneidade da laca. Também foi avaliada a influência da concentração de silicone em sua migração, e sua mobilidade dentro das camadas aplicadas. As conclusões retiradas da primeira, foram que, aumentando a proporção em que o silicone foi adicionado, não afeta as aglomerações de silicone. As informações coletadas no último teste não foram suficientes para retirar conclusões sobre a mobilidade do silicone.

Declaration

I hereby declare, on my word of honour, that this work is original and that all non-original contributions were properly referenced with source identification.

Porto, February 11, 2019

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Notation and Glossary

T _g	Glass transition temperature	K
v	Velocity	rpm
l	Thickness	μm
	Weeting tension	mN/m
η	Viscosity	Pa·s
γ	Shear rate	1/s
τ	Shear stress	N/m ²

List of Acronyms

AAS	Atomic Absorption Spectroscopy
ARCP	<i>Associação Rede de Competência em Polímeros</i>
EDS	Energy-Dispersive X-ray Spectroscopy
FTIR	Fourier-Transform Infrared Spectroscopy
GC-MS	Gas Chromatography- Mass Spectroscopy
GPC	Gel Permeation Chromatography
IR	Infrared Spectroscopy
MEK	Methyl Ethyl Ketone
NMR	Nuclear Magnetic Resonance Spectroscopy
OEM	Original Equipment Manufacturer
PVC	Polyvinyl Chloride
SEC	Size Exclusion Chromatography
SEM	Scanning Eletron Microscope
SFC	Super Critical Chromatography
TMG	Têxtil Manuel Gonçalves
TOF-SIMS	Time of Flight- Secondary Ion Mass Spectrometry
UPTEC	Science and Technology Park of University of Porto
XPS	X-ray photoelectron Spectroscopy
XRF	X-ray Fluorescence Spectroscopy

1 Introduction

1.1 Framing and presentation of the work

TMG Automotive is a company of the Têxtil Manuel Gonçalves (TMG) group that stands as a major European partner in the supply chain of plastic fabrics and other coatings for car interiors. This company exports 99.4 % of what produces, 8.2 % of which is shipped to China, 3.2 % to the United States of America, 1.1 % to South Africa and the biggest share, approximately 86.9 %, is for Europe where the German market stands as its largest client with brands like BMW and Mercedes.

For winning new contracts, TMG should produce according to the requirements established by the Original Equipment Manufacturers (OEM) and for that reason. This requires often that over the substrates it should be applied a finishing consisting in a selection of lacquers that, depending on their properties, are applied as a basecoat, an intermediate and a topcoat.

In February 22nd, 2018, the lacquering process was stopped at TMG after an alert issued by the laboratory due to the presence of glossy spots in the article surface and during the inspection of the lacquering equipment it was possible to observe an abnormal residue accumulation in the cooling cylinders. A Fourier-transform infrared spectroscopy (FTIR) analyses proved it to be a silicone-based hand modifier, an additive that provides an effective increase of abrasion resistance and slip. In order to eliminate the non-quality of the product, the lacquering process must be stopped various times to proceed to the cleaning of all the equipment. If production lines are held up, some severe financial penalties may be imposed by the OEMs, this means that any production problem must be quickly identified and fixed (Fung and Hardcastle, 2001). So, even though the preventive measure of making scheduled stops for cleaning has proved to be effective in the elimination of the glossy spots in article, it is essential to expand the knowledge about the problem and work on a more permanent and beneficial solution.

The present dissertation is divided in two directions. First the diagnose of the problem and the possible causes behind it, which consisted in a search for differences in the process, the finishing and the final product. Followed by the attempt to decrease the accumulation of silicone in the lacquering process's equipment by making changes in the finishing's formulations.

1.2 Presentation of the company

The *Fábrica da Fiação e Tecidos do Vale de Manuel Gonçalves* was founded in 1937 in São Cosme do Vale (Vila Nova de Famalicão). Three decades later the company had been transformed in

an anonymous society, renamed “Têxtil Manuel Gonçalves, S.A.” and had achieved the position of largest national textile company.

It was initially concentrated in the textile industry but soon initiated a diversification strategy that led to the ownership and significant positions in different activities. Nowadays, TMG is involved with interiors for the automotive industry (TMG Automotive), retail and distribution of sportswear (Lightning Bolt), aerial assets (HeliPortugal), systems and solutions for energy, engineering, environment and transport (Efacec), wine production and distribution (Caves Transmontanas and Casa de Compostela) and participates in the financial area as co-founder of the largest private bank in Portugal (Millennium BCP). In 2009, the two biggest clients of TMG Automotive, based in *Campelos (Guimarães)*, were OPEL (27%) and Toyota (24%) and the factory invoiced around 20 million euros. In 2017 it had five times more sales and the biggest clients were BMW and Daimler with 55%, followed by Volvo Cars and brands like Jaguar, Porsche or Maserati.

In 2017, the existing factory had achieved its maximum capacity which led to an investment of around 50 million euros in a new unit based in *São Cosme do Vale (Vila Nova de Famalicão)* that started the manufacturing process in January 2018.

1.3 Contributions of the Work

The author of this document was responsible for the preparation of all materials used in the several tests performed throughout the duration of the internship at TMG Automotive. It was responsible for engineering every alteration within the lacquer’s formulation or manufacturing process. Except for the Sem-EDS analysis and the use of *Mathis* (lacquering instrument), that had to be operated by someone qualified to handle those equipments.

The work done was of great importance to the company. Its knowledge on the raw materials, the formulation and manufacturing procedure of the finishes, was increased with each test performed.

1.4 Organization of the thesis

This thesis is divided into 6 chapters. In this first chapter (chapter 1) is introduced the situation at TMG Automotive, regarding the silicone accumulation in the lacquering process. Herein is also described the first steps taken by the company towards the identification and comprehension of the problem. In chapter 2 is made the contextualization of the materials, processes and products of TMG automotive, with an explanation of the many aspects that these might have. The third chapter presents a detailed description on the internal materials and analysis methods, and characterization techniques. Chapter 4 contains the results and discussion of the work developed to diagnose the problem, also of the work to try to reduce

the consequences of silicone contamination. Chapter 5 is the most important chapter, herein are the conclusions reached throughout the development of this work. In last place, the chapter 6 gathers a list of accomplishments of this thesis, suggestions for the future and a personal opinion on the work carried out.

2 Context and State of the Art

2.1 Coated textiles for car interiors

Historically, the earliest recorded use of a coated textile is by the natives of Central and South America, who applied latex to a fabric to render it waterproof (Sen, 2001). Since then, advances have been made on polymer and textile technology which led to a massive growth in the variety of characteristics that coated textiles can possess. For that manner, this grants them innumerable applications such as in defense, health care, sports, space, and many other diverse end-use products but the one being under scope in this dissertation is the application of coated textiles in the automotive industry (Sen, 2001).

Coated textiles present certain advantages over unsupported films or sheets such as much higher tensile and tear strengths, better puncture resistance and better handle (Carr, 1995). This type of fabrics was used for the following purposes: to confer liquid- and gas-resistant properties on flexible textiles, mainly water-resistance; to provide a soil-resistant, easy-to-clean surface; and to provide alternatives for the real leather and other animal skins used as fabric, without jeopardizing any physical characteristics or desired aesthetics (Carr, 1995). In *Textile Advances in Automotive Industry* (2008) it can be read that leather to interiors and its substitutes are used in the automotive industry as upholstery material for seats, headrests, covering material for dash boards, back shelves and door linings, gear shifts as well as for center consoles. A selection of compound materials made of a textile and a variable number of polymeric layers are named artificial leather (Shishoo, 2008).

Such end-use products are constructed by application of coating technique through which a coating fluid (PVC, PUR, TPE, TPO, TPU) is applied onto a substrate (usually paper or a textile fabric). The coating technique has different types distinguished by the means of application of the fluid, such as: gravure coating, reverse roll coating, air knife coating, knife-over-roll coating, immersion (dip) coating and extrusion coating.

2.1.1 Polyvinyl Chloride Substrates

Polyvinyl Chloride (PVC) polymers can be found in a wide range of industrial applications. Citing Ashish Kumar Sen (2008), “the popularity of this synthetic polymers is due to its low cost, excellent physical properties, unique ability to be compounded with additives, and usefulness for a wide range of applications and processability by a wide variety of techniques.” The basic unit of PVC is illustrated in *Figure 1*. PVC can be considered an amorphous polymer, with a crystallinity of around 10 %. Even though, this property varies according to the conditions under which polymerization occurs. Chloride concentration in the molecular structure of the PVC

assures its high polarity, which increases its affinity and allows a good mixture with a large range of additives. It was also found that PVC is stable on heating up to 130 °C but decomposes rapidly at higher temperatures (Titow, 1984).

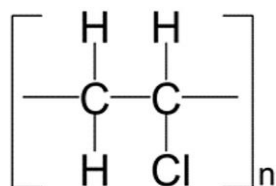


Figure 1 Repeating unit of a polyvinyl chloride structure (Anon., s.d.).

The formulation of PVC paste usually consists not only of a binder but also of functional additives, typically organic molecules that are added to polymers in small amounts in order to improve the properties of the polymeric material. The additives used in PVC (Wiley, 2011 and Titow, 1984) pastes can be categorized as polymer modifiers, used to change the physical and mechanical properties (plasticizers and foaming/blowing agents); performance enhancers such as flame retardants and stabilizers provide functionality not inherent to the polymer itself; and as processing aids, mostly surface-active agents, added to improve throughput and alter the surface properties of the substrate (lubricants). In Figure 2 is described the layout of the different layers of a *pelgon*, a TMG material designed to fit the demands of various parts of a car interior such as seat covers, head rests, arm rest, door panels, gaiters and seat pockets.

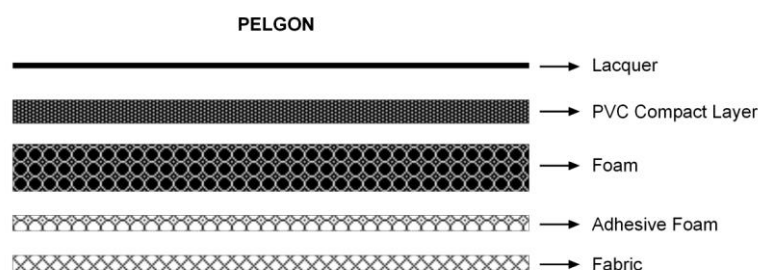


Figure 2 Layout of the assemble of a pelgon.

The differences between the PVC foam and compact layers reside in their formulation. A PVC compact layer is assembled by a plasticizer, the most important group of additives, which in an appreciable proportion, lower the modulus and may reduce the strength and hardness of the material; a stabilizer both for heat and light; PVC and pigments for aesthetics. The foregoing layer, a polyvinyl chloride foam is a paste also composed by a plasticizer, PVC and pigments, but not only by that. To create a foam structure, this last PVC paste adds to its composition a kicker which function is to accelerate what is normally a very long process of decomposition of the blowing agent, by decreasing the decomposition temperature (from 200 °C to 170 °C); flame retardants are used in plastic materials to inhibit ignition and retard the spread of flames; and at last a blowing agent, the responsible for the foamed structure of the layer. The information

gathered from Titow (1984) and Wiley (2011) on the manner of PVC pastes additives, introduces that chlorinated polymers, especially PVC, decompose during processing and release HCl via dehydrochlorination reactions, which is why are applied heat stabilizers that act by trapping the release HCl and by reacting with labile chlorides on the polymer chain formed during polymerization. Concerning to the selection of the proper flame retardant, there are important features that must be taken in account such as efficiency and compatibility with the polymer matrix, since the flame retardant should disperse well and even dissolve in the polymer if possible; the additive should also be stable having minimal effect on processing and on the rheological properties. The blowing agents may be inorganic or organic additives, widely used in PVC polymers but also in polyethylene (PE), polypropylene (PP), and polystyrene (PS) to produce a foamed structure, improve properties and appearance; chemical blowing agents decompose thermally during the coating process which leads to the release of gases, increasing the thickness of the layer and giving its foamed like characteristics. At last, plasticizers are one of the most important additives to the paste, which only affects the finished material properties (flexibility, softness, extensibility and toughness) but also plays an important role in heating-process by reducing melt viscosity and providing internal lubrication. The plasticizers molecules inserted between the polymer chains, increase the distance between the molecules, enabling their movements (rotation) and inhibiting lateral interaction with the neighboring molecules. For such additive, it is important that presents high compatibility with the PVC resin, usually are used phthalates and triaryl phosphates for very soft and flexible applications including paste moldings and coatings.

2.1.2 Air Knife Coating Process

Coating is the process wherein a viscous fluid (or formulated compound) is applied on a textile substrate; while laminating is the process wherein a pre/polymer film is bound together with one or more textiles (Sen, 2008). The assemble of the polyvinyl chloride material previously described is made by knife-coating technique, illustrated in *Figure 3*. This technique based itself in the direct application of the coating fluid onto the surface of a textile fabric wherein the thickness of the coating is controlled by the adjustable gap between the knife and the substrate. The main disadvantage in the use of a knife is that the gap has a pre-established value, for although the coating thickness can be controlled, deformities in a previous layer or a patch passing under the knife are likely to jam causing the substrate breakage (Horrocks and Anand, 2000).

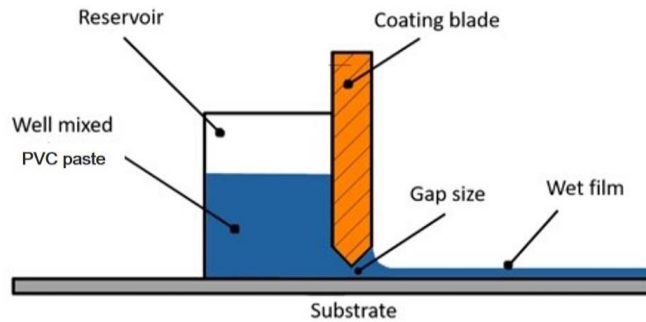


Figure 3 Representation of the air knife coating technique.

The PVC pastes are prepared in tanks and then feed to the reservoir of the coating machine by a system of pumps. In the reservoir is fixed a level value that guaranties that there's no lack of paste throughout the entire width of the article. The first step in the coating process is the introduction of the paper that will work as a base where the actual components of the material will be deposited after a heating treatment to eliminate possible porous on the surface and humidity. After the application of the first layer, inside an oven of 16,5 meters with temperatures reaching to 200-205 °C, the PVC disperse in the plasticizer starts to swell till the point of total fusion between the PVC resin and the plasticizer - gelation process described in Figure 4. The second layer is subjected to a temperature of 135 °C in an oven of 24 meters wherein takes place a pre-expansion of the foam. The third layer is immediately followed by the textile which is the basecoat of the article. The last oven, with a length of 27,5 meters, goes up to 210 °C in order to insure the total gelation of the adhesive foam and finish the expansion of the foamed layer. The last steps of the coating process are unwinding the paper and wind the final coated product with the topcoat facing up.

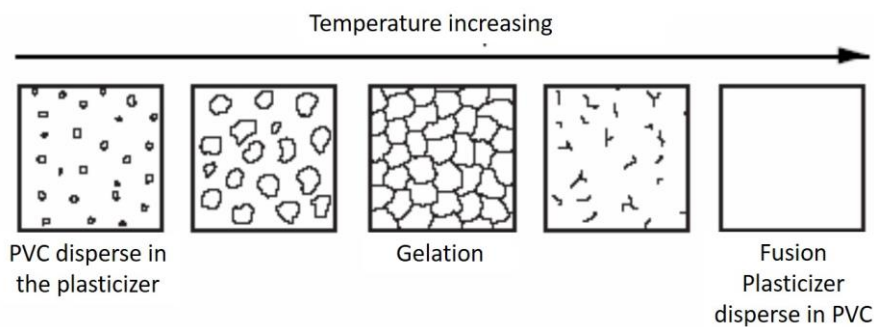


Figure 4 Gelation stages of polyvinyl chloride polymer with plasticizer (Zaioncz, s.d.)

2.2 Finishing for automotive artificial leather interior materials

In order to sign new projects, the products must fulfill the requirements established by the OEMs such as UV, heat and water/moisture resistance, flexural endurance, emboss ability, thermoform ability, OEM's cleaning products resistance, anti-soiling, anti-squeak, and finally

abrasion/scratch resistance. To ensure surface protection, and achieve the aesthetics aspect and touch required, is applied a thin finishing layer (lacquer film) over the materials.

The lacquers are made with polyurethanes that may be water- or solvent-based systems. Water-based systems are more environmentally friendly, with lower volatile organic compounds (VOC) emissions and lower unpleasant odor. According to U.S. Patent No. 4.876.302, the aqueous polyurethane dispersions present high deficiencies when used as a finish agent for PVC materials. In DE 3.134.161 it is reached the conclusion that the subsequent application of this polyurethane dispersions could not meet the demanding criteria for this role. Since then it has been found that water-based systems wherein the percentage of solids content in the dispersion have an extremely high content of urethane groups due to the incorporation of large quantities of low molecular weight polyols. Notwithstanding, PVC finishing based in a polyurethane system dissolved in organic solvents have a better compromise between good adhesion and the high quality level demand in the coating industry; *i.e.* high softening point, good mechanical strength, stability under hydrolysis aging, minimal swelling in plasticizers, blocking action against the migration of the PVC plasticizers, avoidance of coloring at the gelling temperatures of the PVC plastisol and pleasant, dry hand (Noll, et al., 1989)

There are several main features that each layer of the finish must meet and so it is constructed according to *Figure 5 Schematic layout of a typical finishing construction over the substrate.* The basecoat is the layer in contact with the substrate and for that reason, must provide good adhesion to the material used (in the case of materials based in polyolefin it requires a previous surface treatment, for example a corona treatment) and work as a barrier against the migration of substances from the substrate. It's possible to have one or more intermediate layers once the quantity applied can play an important role on several characteristics (wear and chemical resistance), it uses the same binder type of the topcoat, but with lower proportions of crosslinker and hard modifiers. The final layer of the finish is recognized as the topcoat, the layer responsible to present every required property related to slip, anti-squeak performance, surface touch and aesthetics.



Figure 5 Schematic layout of a typical finishing construction over the substrate.

Figure 6 describes the technique of knife-over-roll coating, used for application of the finish layers, and different geometries of the engraved roll that correspond to different quantities of lacquer application. Like what happens in the coating process of the PVC material, also the lacquers are fed to the reservoir by a system of pumps that work depending on the level of

lacquer read inside the reservoir, always ensuring enough quantity to a correct wetting of the article surface throughout thereof entire width. The engraved roll is in contact with the formulation in the reservoir, which accumulates on the surface of the roll. With the aid of a knife (or “doctor blade”) that scratches the surface of the roll, is ensured that the right amount of lacquer is applied onto the surface of the material. The application occurs when the article passes between the engraved roll and a pressure roll made by rubber, in order to allow a little room for the case of zones with different thickness.

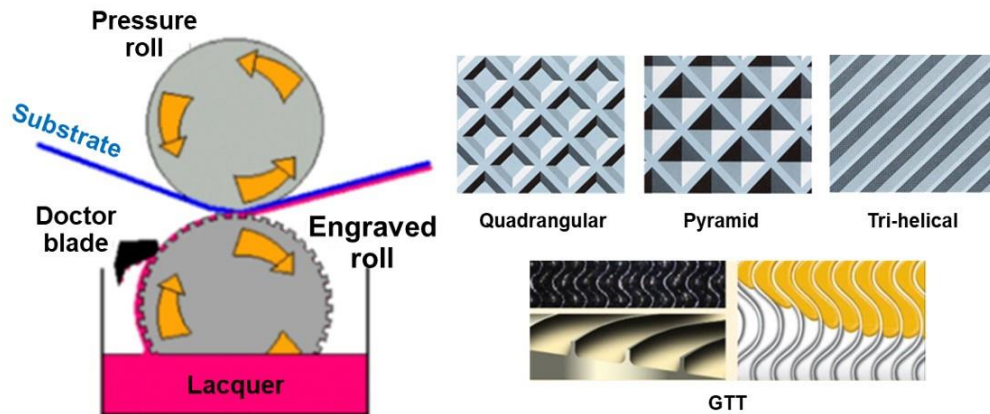


Figure 6 Lacquering technique and different geometries of the engraved roll (Anon., s.d.)

The base raw material of the formulation is responsible for the main properties of the final finish. An acrylic binder presents better resistance to yellowness, better heat resistance and a greater barrier to PVC plasticizer migration, however, it shows poor results of thermoplasticity and flexibility behavior at lower temperatures; all these disadvantages can be minimized using a system of an acrylic and a vinyl binder. The most used binder type are polyurethanes, presenting satisfactory level of flexibility, even at low temperatures, and a wide range of possible variations in chemistry. Some of the disadvantages of this kind of systems reside in the low heat resistance (120 °C) and yellowness.

Similar to what happens with the PVC pastes, also a great deal of characteristics of a lacquer rely on additives such as: defoamers, that like the name indicates, are used to reduce the tendency of foam generation at the different stages of production and lacquering line (mainly used in water-based systems); levelling agents, or surfactants, that improve flowing properties and help on eliminating application defects such as cratering of the lacquer; hand modifiers, responsible for modifying the lacquer formulation in order to improve touch/haptic, slip, anti-squeak or blocking performance; matting agents that may be silicon based, with high effectiveness on the gloss of the surface, but possible decrease in quality of the abrasion properties and anti-squeak performance; UV stabilizers that increase the UV resistance of the lacquers, retarding the yellowness of the material and the loss of mechanical properties; rheology modifiers which maintain under control the lacquer viscosity to a desired level; and

lastly, crosslinkers (polyisocyanate, polycarbodiimid), responsible for increasing material's strength and hardness, abrasion and chemical resistance, water resistance and adhesion to substrates or to another finish layer.

2.2.1 Polyurethane Binders

Polyurethanes (PUR) are polymers that contain the group urethane, result of the reaction between the isocyanate group (-NCO) and the hydroxyl group (-OH). Linear polyurethanes are obtained through the reaction of difunctional monomers (diisocyanates and diols), forming a pre-polymer with low molecular weight and a -NCO terminal group. One of the variables to control, is the ratio between the reactive groups NCO/OH (in figure 7 represented a case where the ratio between this groups is 2).

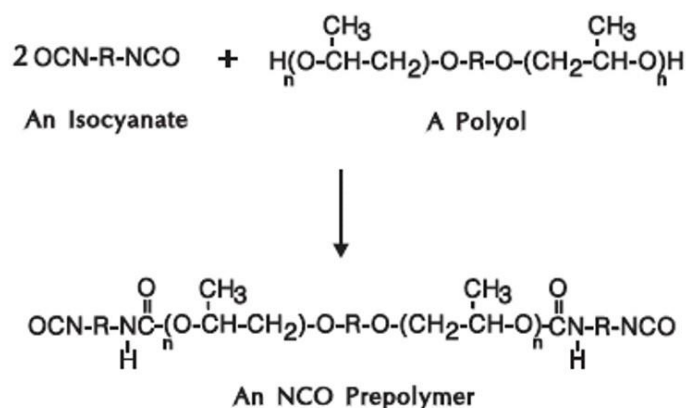


Figure 7 Reaction of the production of the -NCO terminated polyurethane pre-polymer (Anon., s.d.).

In order to obtain a polyurethane with high molecular weight, in solvent-based systems, chain extenders, which react with the terminal isocyanate groups of the pre-polymer, are used. The use of diols or diamines chain extenders with a short chain, allow to obtain predominantly linear polyurethanes. In the case of using a diol (functionality -OH) urethane groups are formed, while using a diamine as a chain extender (functionality -NH₂) urea groups. This translates in the final product as a urea-polyurethane. If some reticulation needed, chain extenders tri- or poly-functional, can be used. The information gather from the supplier of this raw material, as a solvent-based system, makes clear that the pre-polymer is prepared in an inert solvent (such as toluene and xylene); the quantity of solids is approximately 60 - 70 %; and at last, explains that while there's free -NCO terminal groups in the mixture (measured by FTIR), the reaction with the chain extender will continue to happen.

In the course of this dissertation, there were two polyurethanes to which all the attention was directed, *Permuthane LS-13-225* and *Permuthane EVO-LS-6609*. The last one was created to replace the first being Butane, Toluene and Xylene free. However, the total replacement of

one on other is not yet possible due to the poorer performance of the second polyurethane resin, *permuthane EVO-LS-6609*. *Permuthane LS-13-225* is an organic solution of aliphatic PUR, modified by matting agents and touch modifiers, particularly the silicone *permuthane HM-13-595*, the same silicone detected in the contamination residues. Once the polyurethane has in its own formulation the *silicone HM-13-595*, it presents excellent characteristics anti-squeak, resistance to hydrolysis and UV light, excellent resistance to scratch and solvents. It is recommended by the manufacturer and supplier of the lacquer that these characteristics can be further improved by the addition of crosslinkers based in aliphatic isocyanates (*Permuthane XR-40-102* or *Permuthane EVO-XR-96-901*). Some of the counter-indications explain the importance of a meticulous cleaning of every lacquering equipment that at some point may have been in contact with this raw material. The contamination resulted would be caused by the presence of the silicone, incompatible with the solvents in the lacquer formulation.

2.2.2 Silicone as a touch modifier

With repetitive use and friction, seat fabrics become worn out, therefore, a silicone polymer in an organic solution is added to the lacquer. This additive acts as a hand modifier, that can improve touch/haptic, lower the “stick-slip” phenomenon and/or improve the abrasion resistance of the material. Silicones in industry usually are refer to linear polydimethylsiloxanes (PDMS), the most common silicone polymers, which consist in a polymeric backbone of alternating silicon and oxygen atoms with methyl groups attached to silicon as shown in *Figure 8*. The methyl groups along the chain can be substituted by other functional groups to change its compatibility and mobility inside the thermoplastic matrix (Ryan, et al., 1999). In fact, a small fraction of phenyl groups along the main chain, can indicate a crystallization reduction, and maintain the material flexible at very low temperatures. If instead, the methyl groups of the PDMS structure are replaced by trifluoropropyl groups, the solubility of the polymer increases. Silicone materials are available in a wide variety of molecular weights as a result of the different lengths possible of the backbone that translates in the number of repeating units. The presence of the “organic” groups attached to the “inorganic” backbone, turns the polymer attractive in fields as different as aerospace (low and high temperature performance), electronics (electrical insulation), health care (excellent biocompatibility) or in the building industries (resistance to weathering) (Andriot, et al., 2009).

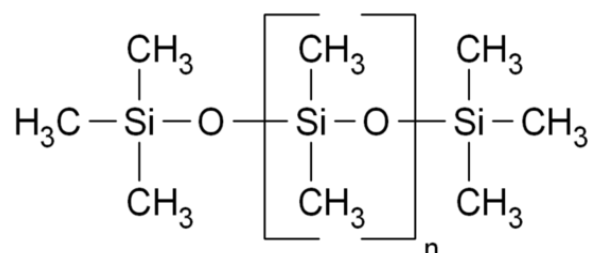


Figure 8 Chain structure of a PDMS (Morent, et al., 2007)

The flexibility and free volume of the silicone chain are essential properties to be possible ultra-high molecular weight (UHMW) silicone polymers as transparent fluids with viscosities increasing as molecular weight increases. On the other hand, lower molecular weight silicone polymers, with viscosities below $1000 \text{ mm}^2 \cdot \text{sec}^{-1}$, are continuously used as an external release agent on the mold surface by the plastics industry. However, it's the silicones with viscosities ranging from $10,000$ to $60,000 \text{ mm}^2 \cdot \text{sec}^{-1}$ that have been used as internal additives in thermoplastic polymers in order to improve the previously listed properties of the surface of the final product (Ryan, et al., 1999). Silicones, with its critical surface wetting tension (24 mN/m), higher than its own surface tension, promote good film formation and good surface covering. The minimal interaction between silicones molecules present consequences such as: very low glass transition temperature (T_g) (e.g., 146 K for a polydimethylsiloxane compared to 200 K for polyisobutylene, the analogue hydrocarbon); the high free volume, when compared to hydrocarbons, explain the high solubility, high permeability to oxygen, nitrogen and water vapor, and high compressibility; the activation energy to the viscous movement is very low, and viscosity is less dependent on temperature compared to hydrocarbon polymers. Besides that, entanglements of the chain contribute to limit the viscosity reduction (Andriot, et al., 2009).

Stahl, the TMG Automotive's supplier of this hand modifier named *Silicone Permethane HM-13-595*, provides some indications and counter-indications for handle and use of this organic solution. This silicone permethane HM-13-595 is an additive to modify solvent-borne lacquers and because of its high concentration of active matter, its recommended that the addition must remain between 1 and 3 %, and for optimum compatibility, is recommended thereof pre-dilution in organic solvents such as di-acetone-alcohol, dimethylformamide, butyldiglycol or N-ethyl-2-pyrrolidone. A counter-indication is that this additive should not be part of the intermediate layers once it harms the adhesion between layers. In the preparation of the lacquer, the introduction of HM-13-595 must be performed in a temperature-controlled room, with temperatures always lower than $35 \text{ }^\circ\text{C}$, and be always added slowly and while stirring. The solvent composition of the silicone lacquer includes 25 - 35 % of 1-methoxy-2-propanol, 7 - 10 % of alcohols, 7 - 10 % of 2,2-oxybisethanol and a small amount, only up to 1 % of, octamethylcyclotetrasiloxane, all substances classified as a physical, environmental and health danger.

For any material that has silicones in its formulation, it is fundamental to know everything about it. The characterization of silicones can be done by most of the analytical methods commonly used for organic materials. Widely available and the easiest technique for detecting the presence of silicones and register information about their structure is infrared spectroscopy and, in particular, Fourier transform infrared spectroscopy (FTIR). It doesn't allow a precise quantification, but gas chromatography coupled with mass spectroscopy detection (GC-MS) it

also used to detect silicones in a material formulation. In addition to GC, gel permeation chromatography (GPC) (also called size exclusion chromatography or SEC) or supercritical fluid chromatography (SFC) can be used to identify and/or quantify even the lowest molecular weight species present in silicones polymers. A nuclear magnetic resonance spectroscopy (NMR) collects information about the type of organic substituents on the silicone backbone such as methyl, vinyl, phenyl or polyester groups, and the degree of substitution. Atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (TOF-SIMS), are all able to provide, some more than other, meticulous information that allows the characterization of the silicones.

The downside of using silicone is that contamination is very common and is known to have a negative impact in manufacturing processes such as soldering, adhesive bonding, wire bonding and coating (Meyer & Smith, s.d.). A manufacturing process may consist of numerous operations such as the ones previously described that are undertaken simultaneously in TMG Automotive, therefore, it can be complicated to control the entire process which can cause unexpected failures due to silicone contamination. In the case of equipment contamination, it's necessary to proceed to the hardware cleaning and silicone removal, costly actions, which presents the need to spot manufacturing activities, thus pushing these activities behind schedule or even over budget.

2.2.3 Rheology modifiers

Surfactants are extremely versatile and therefore can be found in the most diverse range of products such as pharmaceuticals, detergents, the drilling muds used in prospecting for petroleum (Rosen & Kunjappu, 2012) and are even used in the finishing for PVC coated textiles. A surfactant is a substance that has the ability of adsorbing onto the surfaces or interfaces of a system, increasing or decreasing the minimum amount of work required to create the interface; this means that the surfactant changes the interfacial (or surface) tension between two phases of the product. Knowing the surface tension, it's possible to understand a little more about the nature of the two phases meeting as the greater the dissimilarity in their natures, the greater the surface tension between them (Rosen & Kunjappu, 2012).

Also, in *Surfactants and Interfacial Phenomena* (2012), there is a list of circumstances under which the differences that a surfactant introduces into the interaction of two or more components of the product play a significant role in the system. One of these circumstances is when the phase boundary area is so considerably large, relatively to the total volume of the system, that a substantial fraction of the total mass of the system is present at boundaries (e.g., in emulsions, foams, and dispersions of solids). This introduces great concern about the damage that can come from an almost insignificant change, such as the use of a different

surfactant in a silicone or polyurethane dispersion, once its proportion to the rest of the composition is minimal.

2.3 Embossing

The embossing of the article surface is achieved by a technique very similar to the one used in the application of the lacquers in the lacquering line. Although, this process won't apply a coat of anything on the article but mark a design on the surface. In *Figure 9* are illustrated different patterns developed by the design team of TMG Automotive. In this step of the manufacturing process of the complete and final product, the engraved roller has the pattern intended to be passed onto the article surface, and the pressure roll is now made of steel. The foregoing step is the pre-heating of the materials surface in order to facilitate the embossing. According to Titow (1984), depending upon the nature of the material and the emboss design, the engraved and the pressure rollers may be set to a fixed gap, and both be water-cooled. The conditions in which is performed the embossing process must be regulated in order to prevent excessive collapse of the cell structure in the foam layer due to the heat and pressure applied. The operation of roller-embossing may form part of the production line and take place after or before the application of the surface lacquer coats. In some cases, the lacquer coats precede the embossing process.

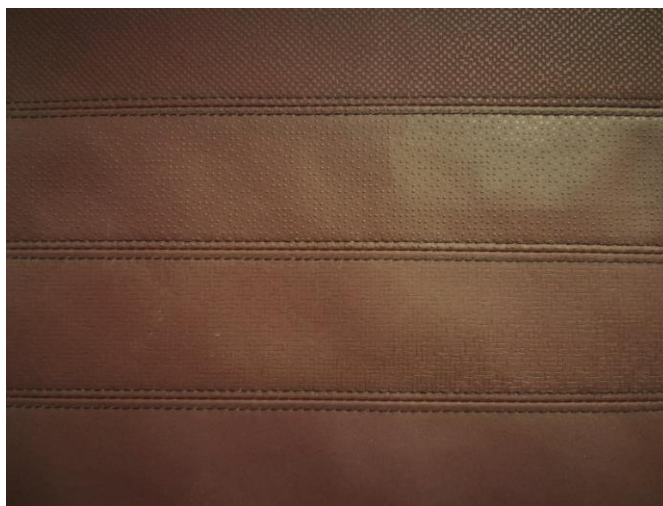


Figure 9 Examples of embossed designs in articles surface (developed by TMG Automotive)

3 Materials and Methods

Throughout the course of this dissertation, the work will focus on *pelgon 54*. This article was chosen because of the many difficulties that presents during manufacturing, widely prone to non-qualities, and above that, because it is one of the process lines with the most critical consequences of silicone contamination. To study the problem, product of current production was used.

3.1 Lacquering Simulation in Laboratory

The application of the finishing process (explained in chapter 2.2.1) was simulated in laboratory. Herein, there were used two techniques for the application of the finishing layers. One of these methods is using the *MATHIS* (see *Figure 10*), a lacquering instrument that functions in the exact same way that the lacquering process in current production (explained with more detail in chapter 2.2).



Figure 10 MATHIS, equipment for lacquering simulation in laboratory.

In the lacquering process, the finishing layers are applied in line, unlike what it is possible to do in a laboratory scale. *MATHIS* requires constant cleaning of the equipment when the engraved roll and the lacquer change between layers. This is a lengthy process, that it is only possible with the help of a technician with the formation to handle the equipment. Because, at this point the most important thing was to apply the same quantities of lacquer as in current production, this process was only used for one of the tests made. Having said that, to circumvent around these difficulties, the mainly used lacquering method was using a selection of spiral-bars, such as the example in *Figure 11*. They come with different geometries that correspond to different quantities of lacquer applied (the same principle of the engraved rolls). Beforehand, the surface of the article must be completely clean and free of particles of

dust, to ensure a correct wetting of the specimen, for which it may be used compressed air to assist thereof cleaning.

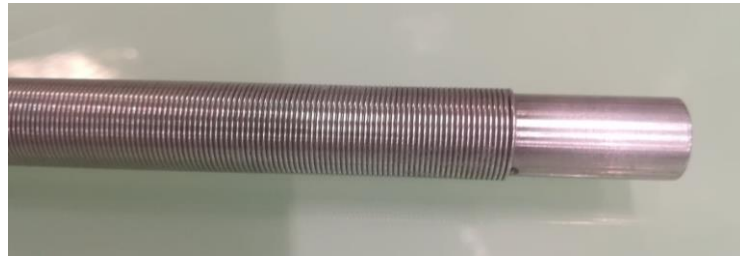


Figure 11 Example of a spiral-bar structure.

This method is very simple, as the main steps represented in *Figure 12* shows. Once the article is secure by a weight placed at its top margin, the spiral-bar is placed centrally with the article. The lacquer should be poured in front of it, and then with both hands grabbing the spiral-bar's ends, makes it slide over the surface till the end of the sample. One should be careful not to pour lacquer on the points of the spiral-bar, but instead deposit most of it in the center. If lacquer is applied by the tip of the spiral-bar, that isn't engraved, it jeopardizes the quality of the finishing. Also, it should not be applied to much pressure down on the article, otherwise the layers below may be scrapped off and the quantity of lacquer be different from the one intended. Once the lacquer wet film is applied, the article goes in an oven at 140 °C for 15 seconds, except the last layer that must be heated for 40 seconds.

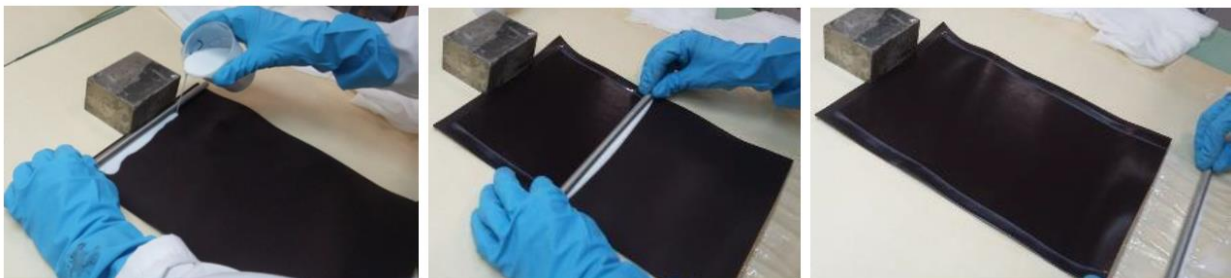


Figure 12 Steps of the lacquering process by using spiral-bars (adapted from Diz J., 2018)

3.1.1 Lacquer Film

One of the methods for determination of the polyurethane and formulated lacquer's quality is their visual aspect; in *Figure 13* can be seen an example of a lacquer film considered (a) *NOK* (quality non-OK) and one considered (b) *OK*. After completing the formulation, stirring and filter, it was applied a lacquer film with 90 μm of thickness, onto the surface of a clear polyester sheet. In *Figure 14* is the film applicator, model *BAKER 286*, with a capacity to apply 30, 60, 90 and 120 μm , used. The procedure to apply the wet film was the same of the lacquering simulation with spiral-bars described above. Afterwards, the polyester sheet is placed in a heating plate for a pre-heating phase at 50 °C for four minutes and then, one more minute in an oven at 140 °C. For a better evaluation of the lacquer's aspect, the clear polyester

sheet was analyzed using the light of a lamp in the background. However, for a more detailed analysis, all lacquer films done throughout the course of this dissertation were observed in an optical microscope.

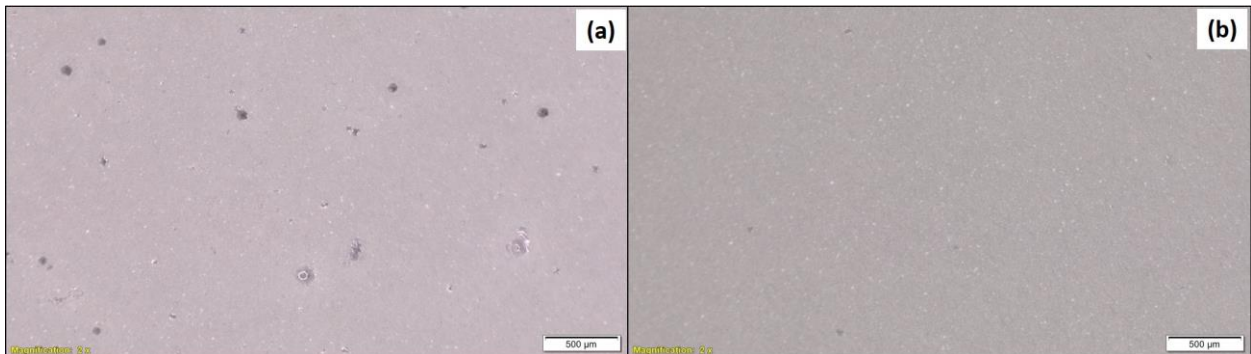


Figure 13 Example of two lacquer films with a visual aspect considered as (a) NOK and one (b) OK.



Figure 14 Film applicator BAKER 286 by ERICHSEN.

3.2 Techniques of Characterization of Coatings

3.2.1 Scanning Electron Microscope

The principle behind the operation of a SEM is based on the incidence of an electron beam in a defined map zone of the specimen surface and the subsequent collection of the electronic signals issued from the target-material (Faix, 1992 and Smith B.C., 2011). The samples are traversed sequentially by a beam of electrons accelerated by a tension that varies between 0 and 40 kV, focused by a system of electromagnetic lenses. The interaction of the electron beam with the specimen's surface results in an emission of electrons and x-rays with unique energy that can be captured by an EDS detector that allows the determination of the material's composition. In Figure 15 are represented the principle of SEM analysis and all different types of electrons that leave the sample's surface after excitation. The simultaneous analysis of the different electrons recovered by their detectors allows the characterization of every point of the surface in terms of topography, by the secondary (SE) and backscattered electron (BSE)

electrons; atomic number (BSE); crystalline properties (BSE); elemental chemical composition (BSE); magnetic fields (BSE); and local crystalline orientation of the sample.

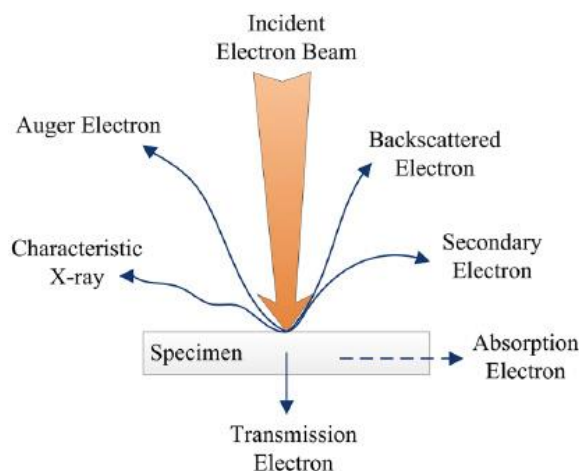


Figure 15 Electron behavior after excitation of the specimen's surface (Zhu, et al., 2014)

For the preparation for the samples for SEM analysis, is important to make sure that the specimen presents good electrical conductivity in its surface. Samples of *pelgon 54* meet these conditions, but the lacquer films applied over clear polyester sheets does not, so it was necessary to apply a thin film of gold (Au). Through the combination of SEM-EDS analysis it's possible to obtain tridimensional images of the specimen alongside composition maps of the elements found in thereof surface. SEM-EDS analysis were performed at UPTEC, in ARCP's equipment.

3.2.2 Rheological Measurements

The surfactant in the *silicone permuthane HM-13-595*, used in finishing formulations, changes the interfacial tension between two phases (Smith, W.C., 2001). The change of surfactant would affect the mixture properties of the raw materials affected. Rheology tests are a global measure of the mixture's quality. If changes in the flow behavior of the samples are recorded, then, the formulation of the samples are different.

In the duration of this work, it was used a *DV-III Ultra Rheometer* by AMETEK Brookfield, property of the *Associação Rede de Competência em Polímeros (ARCP)* at UPTEC laboratory; instrument illustrated in *Figure 16*. Some of its main features are the multiple parameters that can be read directly in the equipment monitor or saved in a computerized system, such as viscosity (Pa·s); velocity (rpm); shear rate (1/sec); shear stress (N/m²); torque (%) and temperature (°C or °F). Moreover, this *Brookfield* can read in a viscosity range that goes from 1.5×10^{-2} up to 6 000 Pa·s, with a velocity from 0,01 up to 250 rpm. Measurements of the fluid's viscosity are often the quickest, most accurate and most reliable source of information on the most important factors affecting the performance of the raw material and the final product. This is the measure of the internal friction of a fluid, which becomes apparent when a layer of

this fluid is forced to move in relation to another layer; the greater the friction, the greater the amount of force per unit area required to cause this movement (*i.e.* shear stress).



Figure 16 DV-III Ultra Rheometer (Brookfield, s.d.)

The selection of the spindle is made accordingly to the viscosity of the sample. Relating the viscosity (Pa·s) of the fluid with the ratio between the spindle coefficient and the velocity (rpm) stipulated by the operator, it is possible to estimate the maximum value of viscosity that the spindle can obtain. Even so, that are some conclusions that can be made with only by the visual analysis of the fluid, like to differ low viscosities (spindle LV) from high viscosities (spindle HV). If there is not any other information available about the viscosity of the fluid, it's necessary to test different spindles (see Figure 17), and in order to be the right choice, the spindle must work within 10 to 100 % of torque. In one hand, when at maximum velocity it's obtained a very low torque, around 10 %, it must be selected a spindle with a higher coefficient, on the other, when at the same velocity it's obtained a very high value of torque, it must be chosen a different spindle, with a lower coefficient. For *permuthane LS-13-225*, with a viscosity range of 150-400 mPa·s (at 20 °C), and the *silicone permuthane HM-13-595*, with a viscosity range of 300-550 mPa·s (at 20 °C), was used the spindle LV-2.

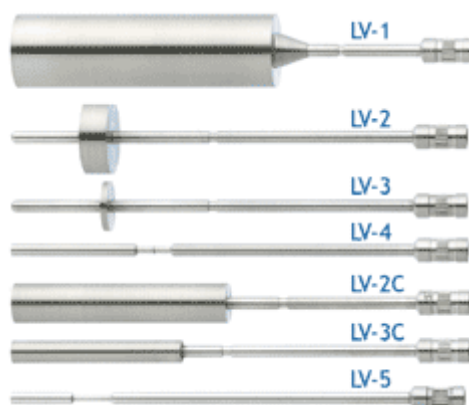


Figure 17 Set of spindles for different levels of low viscosities (LV) (Brookfield, s.d.)

Before any measure in the rheometer, all the samples must be well stirred in order to guarantee its full homogeneity and kept in a container with a diameter of at least 8 centimeters so that the resistance offered by the walls of the container can be eliminated. The depth at which the spindle must be placed depends on the characteristics of the spindle, each marked with the height that the fluid must meet in order to a proper reading.

3.2.3 Abrasion Resistance

After the conclusion of the manufacturing process, the final products must pass in some mechanical, chemical and physical tests that evaluates thereof properties, such as soiling with a variety of cleaning products of the own OEMs, coffee, ketchup, etc; aging; UV, water and abrasion resistance, amongst others.

For abrasion tests there are multiple methods and equipments that may be used. In the study explained in chapter 4.3.4, the equipment used for the abrasion tests was the *Gakushin* of *SDL ATLAS*. This is an instrument unit with six arms, each with a different geometry of the test media (see *Figure 18*). The functioning of this instrument is based on a back-and-forward movement of a platen wherein the material sample is fixed by clamps. For *pelgon 54* it was used a total load mass of 1 400 g, a triangular head, and sandpaper and as the friction media. The number of cycles, combination of the back and forward movement (one cycle equals two strokes), is adjustable, and because this report was a new experience and it must be retrieved the most information possible, it was selected a set of 500 cycles, and in the end of which the sandpaper was substituted for a new one. At every 500 cycles, before continuing the test, the surface of the sample was observed with the aid of a magnifying glass for state control of the finishing's surface at the point. The abrasion resistance is determined by the total number of cycles that took place before the appearance of lacquer failures in the surface of the sample.



Figure 18 On the left, the arrangement for abrasion tests in *Gakushin*; on the right, the triangular test media used.

4 Results and Discussion

As said, this thesis addresses the need to start to understand the causes behind the excessive accumulation of the *permuthane silicone HM-13-595* found in some formulations of lacquers that compose the finishing of the materials. To do that is to study everything involved in the manufacturing process, since the components in the raw materials to the final product itself, which is why some focus has to be given to the study of the starting materials that are used and their respective properties since this information leads to an understanding on how the materials will behave during production and product use. However, as important as it is to find the cause of the problem, it is equally important, or even more important for the time being, to find a way of retarding the accumulation of the silicone in the lacquering equipment and at the same time predict when this phenomenon will be more accentuated.

Accordingly to that line of thought, in this chapter are initially presented and discussed the results obtained from studying the raw materials in order to know if there were changes that may have led to the problem in the lacquering process, followed by a series of different versions of the recipe and manufacturing process of the finishing in order to test solutions for decreasing silicone's agglomeration, predict when this problem will be more or less accentuated, allowing to a correction of the times at which the lacquering line is stopped for cleaning, and/or create new finishing solutions.

4.1 Study of the raw material's properties and behavior

Polyurethanes are the main provider of the articles and finishing properties. Since the worst-case scenarios always involved solvent systems that combined the *silicone permuthane HM-15-595* and the *permuthane LS-13-225*, these were the raw materials in which these studies focused on. Because the accumulation of the *silicone permuthane HM-15-595* worsened drastically during the first trimester of 2018, it was studied batches from before that time and more recent ones. Batches are numbered sequentially, so BC 72262 from September 2017 and BC 75664 from Mars 2018, are representative of the composition, behavior and aspect of a "good" raw material and a "bad" one, respectively. This "good" and "bad" terminology refers to a raw material that shouldn't create any problems in the lacquering equipment on current production, and one that is likely to do so.

4.1.1 Visual aspect of the lacquer

The quickest and easiest way of detecting differences between the "good" and "bad" raw materials is by observation of thereof aspect. The first effort in this direction was the preparation of a lacquer film, with 90 μm worth of thickness, in a clear polyester sheet. Before

the film application of any raw material, it must be well stirred for 5 minutes, at a velocity rate non-greater than 500 rpm, filtered, and only then can be spread on the polyester sheet. The images captured in an optical microscope from both batches, are side to side in Figure 19, and as can be seen, older polyurethanes, from 2017, have a very homogeneous and “clean” aspect, unlike the polyurethane lacquer from the batch 75664, which is full of irregular, clear forms, silicone clusters. This is the first evidence of differences within the formulation of the raw materials under scope in the present chapter, so it can be confirmed that the problem didn’t originated from inconsistencies or changes in the coating, lacquering and/or embossing processes.

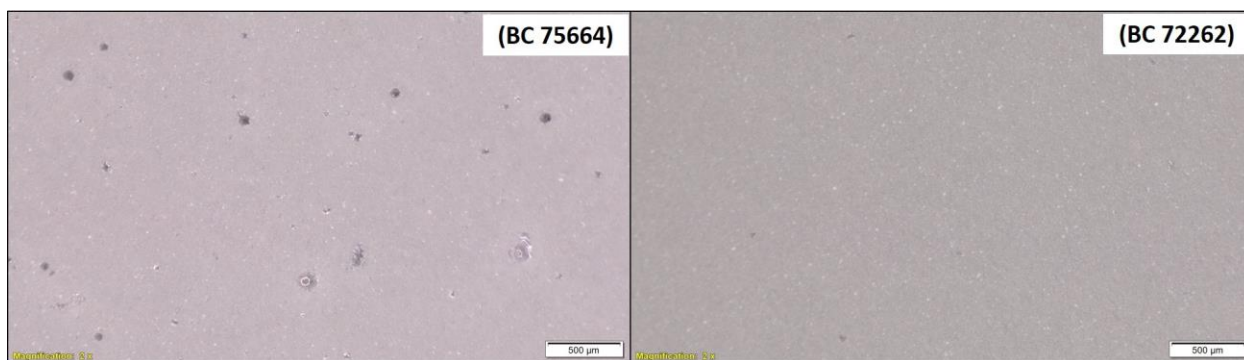


Figure 19 Images of films of Permutthane LS-13-225, BC 72262 on the left and BC 75664 on the right.

The incredibly detailed images of the films of polyurethane, obtained by SEM, in Figure 20, show a much rougher surface on the batch 75664. The silicone clusters mentioned above, are also perceptible in the SEM image of the BC 75664, zones with a more matte and smooth aspect. The first impression would be that those clusters are the reason, or a symptom of the reason why there was a drastic increase of silicone’s contamination so early in the process line.

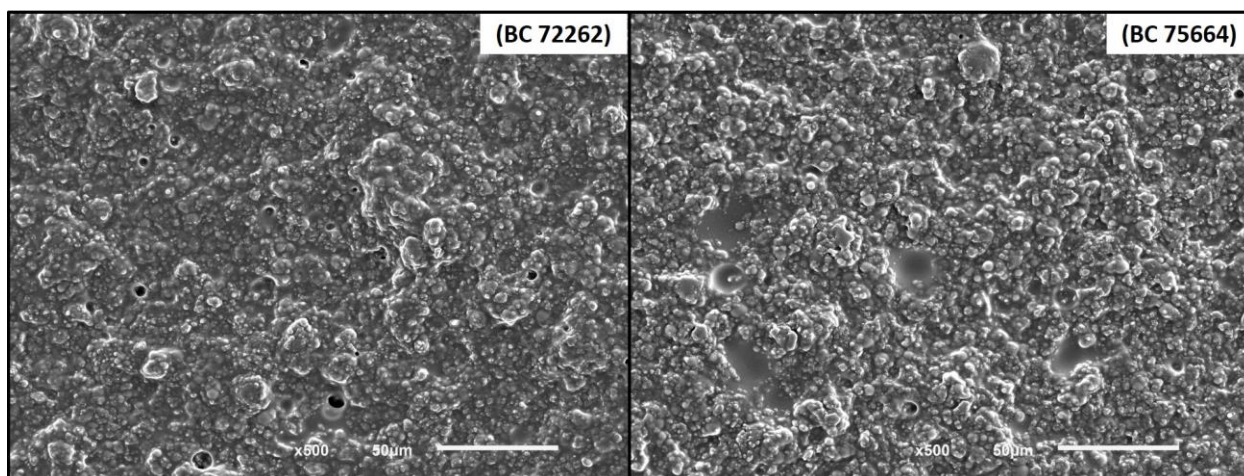


Figure 20 SEM images of permuthane LS-13-225 from the batch (1) BC 72262 and (2) BC 75664.

4.1.2 Chemical composition

By EDS it was obtained the atomic composition of both samples. Prior to the problems, *permuthane LS-13-225* presented an atomic concentration of silicon over 11.6 % smaller than the one on the BC 75664, received 5 months later (see Figure 21). A higher concentration of silicon atoms does not necessarily mean that the polyurethane lacquer had a higher concentration of silicone added to its formulation. More silicon atoms may suggest a longer backbone structure of the *silicone permuthane HM-13-595*, which mean a higher number of repeating units of PDMS. However, more repeating units of silicone should also translate in an increase of the atomic concentration of carbon because of the additional methyl groups. This analysis alone, is not enough to take further conclusions about possible changes in the polyurethane base.

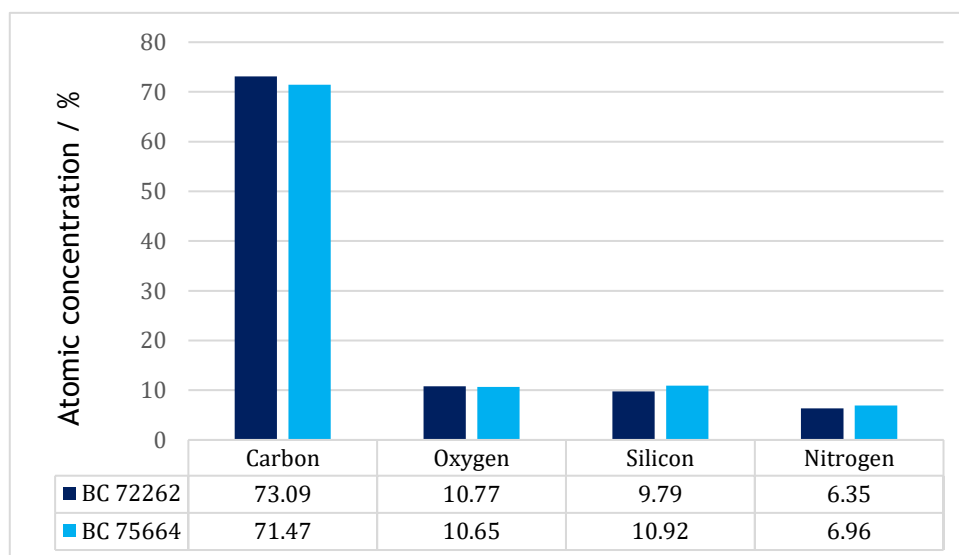


Figure 21 Atomic composition of batches of polyurethane LS-13-225 before (BC 72262) after the problem appeared (BC 75664).

The *permuthane EVO LS-6609* was created with the purpose to substitute the *permuthane LS-13-225*. Although, further studies, especially abrasive, proved that this new polyurethane didn't lived up to the level of performance of the one foregoing. In Figure 22 are, once again, the atomic concentrations of the batch 75664, but this time sided with the results of a recent batch of *permuthane EVO LS-6609*. The main feature that differentiates *EVO LS-6609* from *LS-13-225* is that the first doesn't have silicone *HM-13-595* in its formulation, where the other has 2.5 parts. The concentration of silicon atoms is 3.5 times higher in the *permuthane LS-13-225* formulation.

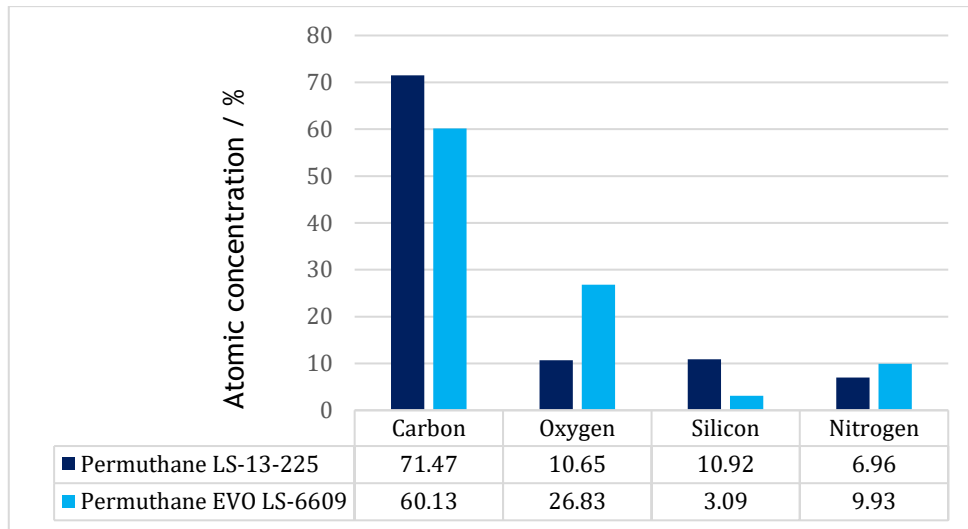


Figure 22 Chemical composition of permuthane LS-13-225 (BC 75664) and permuthane EVO LS-6609.

4.1.3 Rheological behavior

Because of the low concentration of surfactant in silicone’s composition, it is difficult to identify the surfactant properties. Therefore, it is necessary to study the change in form and in the flow of the raw materials. In the chapter 3.2.2, were explained all the functioning principles surrounding *Brookfield’s* utilization. For this study were used two samples of *permuthane LS-13-225*, one of a batch from before and another from after the aggravation of the silicone contamination. The viscosity behavior of both samples is presented in Figure 23.

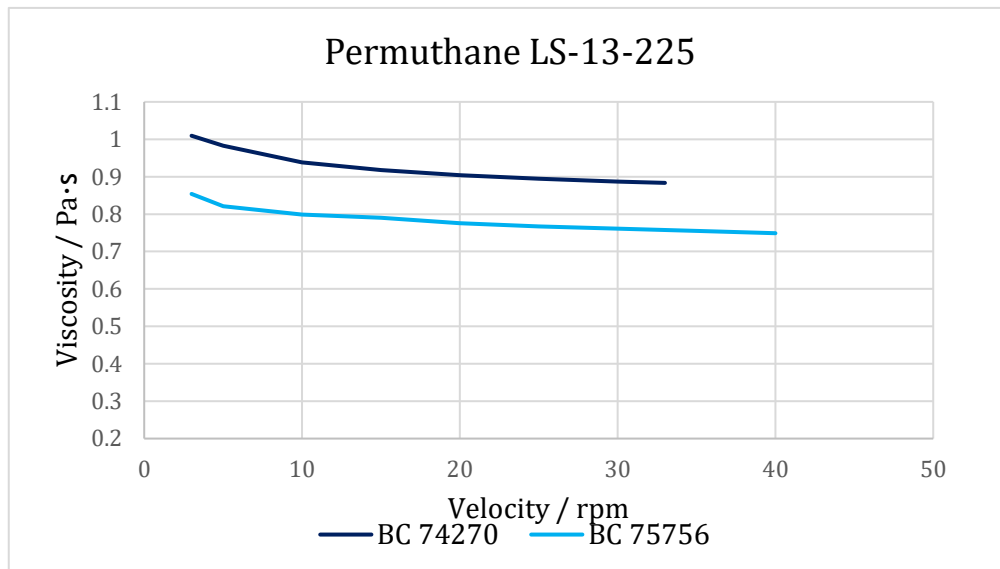


Figure 23 Mixture behavior of Permethane LS-13-225.

The viscosity values were recorded to a velocity rate of 3 rpm, 5 and then increased in passes of 5 rpm. The sample from BC 75756 reached 100 % torque at 40 rpm, while for BC 74270, at 35 rpm it had already exceeded torque’s limit. With the increase of velocity, the viscosity

values decreased in a very similar profile on both samples. In BC 74270, at 33 rpm, the viscosity had decrease in over 0.1 Pa·s (100 cP). The BC 75756 also recorded a decrease in viscosity around 0.1 Pa·s (100 cP). Additionally, the rheological measurements shown that the older batch had a viscosity 0.15 Pa·s (150 cP) higher than the most recent one. This is explained by the evaporation of the solvents over time, despite being conditioned in closed containers.

The same study was conducted on different batches of *silicone permuthane HM-13-595*. The results from the rheometer were very instable in both samples, reading a large range of viscosities at the same stress rate. The most probable reason is that the spindle used wasn't the ideal for this mixture. This happened because there were spindles missing and it had to be used one with the most similar reading range, instead. However, for the time being, the important thing was to determine if the lacquer's behavior was different. For this reason, medium values were used in order to compare the behavior of the different batches - Figure 24. The results showed a very heterogeneous behavior of the mixture for recent batches. This means that the formulation of the lacquer was different, and so should be its interaction with other components.

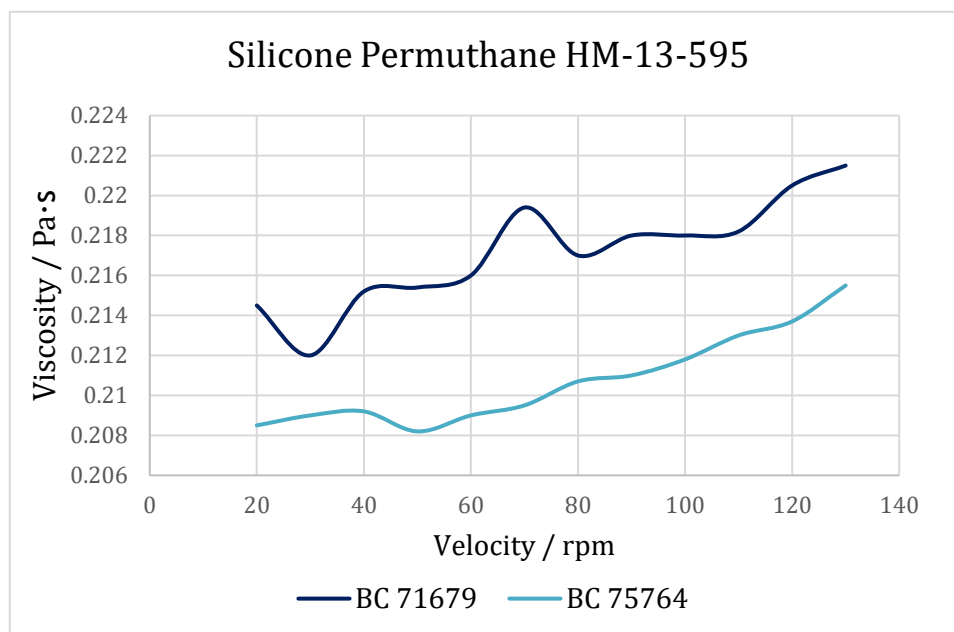


Figure 24 Mixture behavior of silicone permuthane HM-13-595.

4.2 Influence of the substrate

The finishing of an PUR based material, or PVC, or TPO, is designed for each substrate, whether based in a PUR, a PVC or a TPO polymer, a finishing that would better benefit the material's requirements.

As said before, the plasticizer is the additive responsible for the main characteristics of the polymer, which is why, it's the factor that better differentiates two PVC materials. Once the

pelgon 54 has 46 % of plasticizer in its composition, it was chosen the *pelgon 27* for further comparisons of the substrate's influence on the behavior of the finishing; *pelgon 27* has 39 % of plasticizer in its composition. Two finishes, with the same preparation procedure but different polyurethanes base, were engineered. One uses the *permuthane EVO LS-6609* (version A) and the other, the *permuthane LS-13-225* (version B). This way makes it possible not only to study the influence of the substrate but to also continue to gather information on the PURs. Naturally, any other variations in the finishing formulation and/or manufacturing must be discouraged to an optimal reading of the results. For this reason, was made sure that the silicone was added at the same proportion in both finishes (remember that *permuthane LS-13-225* has 2,5 parts of silicone *permuthane HM-13-595*).

An SEM analysis provided detailed images of the finishes, applied in both *pelgon*, that may be seen in Figure 25. Both samples treated with finishing B, present a very heterogeneous surface. In addition to a more porous surface, this images also reveal circular forms of a more matt tone of grey, with bright frontiers. Silica is known for having this almost white appearance, which suggests that these spots are in fact, clusters of silicone. Once these agglomerations are not so clear, or at all present, in the version A of the finishing, the problem must be in the PUR base. The surface 1-A has the best distribution of the finishing's components and so, the most homogeneous surface of all four. The version A of *pelgon 27* also has a considerable amount of porous in its surface, which are believed to be the result of a bad wettability of the surface. This suggests that the level of plasticization of the PVC materials, influences its wettability and adhesion of the lacquers to the surface of the article.

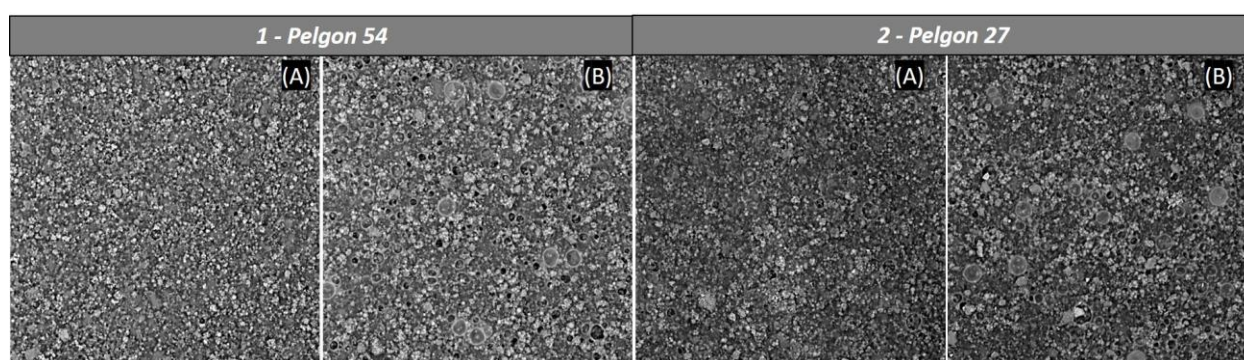


Figure 25 SEM analysis of *pelgon 54* and *pelgon 27* treated with version A and B of the finishing.

An EDS analysis came to confirm that the visible spots in images 1-B and 2-B (from Figure 26) are indeed silicone clusters. In these, it's clear that the distribution of the silicones throughout the entire field of view is poorer in systems with polyurethane *LS-13-225*. The surface in image 2-A in addition to a bad distribution of silicon, also reveals a much lower concentration thereof (see Figure 27). In the samples of *pelgon 27*, carbon atoms seem to cover almost completely the field of view, in comparison with *pelgon 54*. Since the atomic concentration of carbon is

very similar to the materials 1-A and 2-B, it means that upon application, the other components adhered better to the substrate.

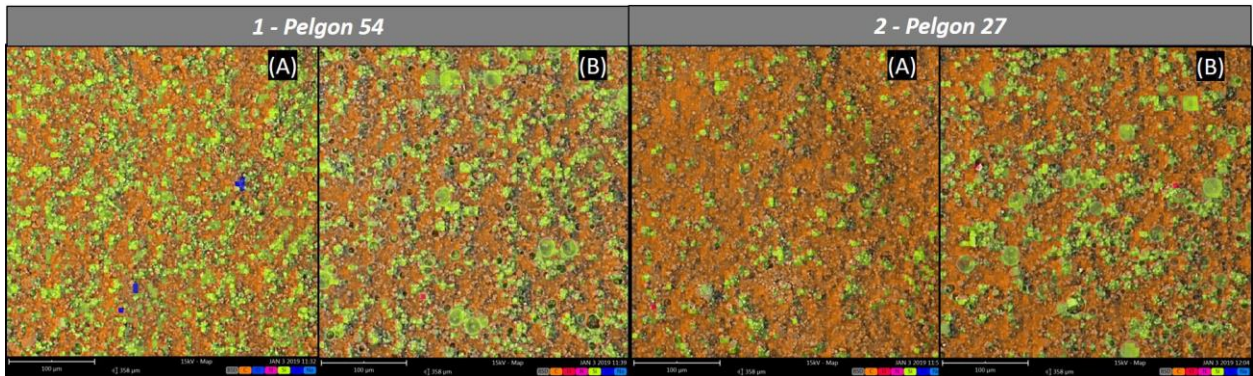


Figure 26 Chemical distribution maps of pelgon 54 and pelgon 27 treated with versions A and B of the finishing.

The data gathered in Figure 27 shows that, the atomic concentration of silicon in *pelgon 54 - A* is alarmingly higher than on the others. On the other side, this concentration reaches its lowest value in *pelgon 27 - A*. Samples of *pelgon 54* present an atomic concentration of silicon higher than in both *pelgon 27*. Once the adhesion is more efficient in this last, the concentration of silicon atoms at the material's surface is lower.

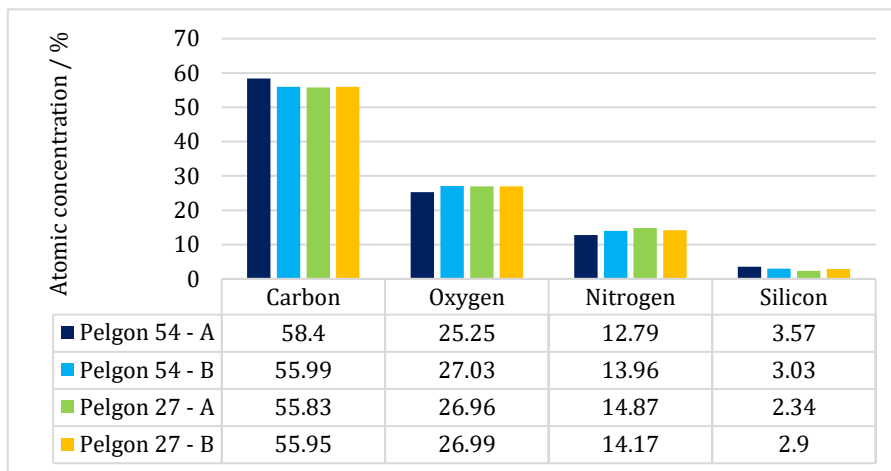


Figure 27 Atomic concentration of the elements in the chemical composition of pelgon 54 e 27 with finishes A and B.

4.3 Study of the formulation and manufacture of lacquers

4.3.1 Pre-dilution of *Silicone Permuthane HM-13-595* and *Permuthane LS-13-225*

In TMG Automotive's database of raw materials, is listed a group of counter-indications, cares that one must have when handling with the polyurethane *LS-13-225*. All the equipment of the lacquering line that had been in contact with it, must be extremelly well cleaned with THF, otherwise, it may cause the contamination of the next article passing through it. This

contamination is fruit of the insoluble character of the silicone. For this reason, the formulations of the lacquers developed, were adjusted to bare the same proportion of silicone. In this chapter, it is introduced a study where the PUR and the silicone were diluted with different solvents. Since polyurethane *LS-13-225* displayed the largest silicone clusters - Figure 28, the solvents chosen were methoxypropyl and methyl ethyl ketone (MEK). This were the solvents advised for the dilution of the polyurethane, and possible combinations of them are also encourage.

In Table 1 Formulation of the samples L1, L2, L3 and L4 Table 1 are de formulations of the 4 versions of dilution of the polyurethane and silicone created. The proportions of the raw materials were, once again, inspired by the original formulation of the lacquer 7631 (Table 3), which takes 5 parts of solvent. But then, this quantity may be of great interference in the silicone's physical state. So, more than study other solvents behavior, was also studie the behavior that results from an addional 5 parts of solvent to the original 5.

Table 1 Formulation of the samples L1, L2, L3 and L4

Component	L1	L2	L3	L4
<i>Permuthane LS-13-225</i>	50	50	50	50
Methoxypropyl	5	2,5	--	1,25
Methyl Ethyl Ketone (MEK)	--	2,5	5	1,25
<i>Silicone Permuthane HM-13-595</i>	1,25	1,25	1,25	1,25

After the lacquer preparation, they were mixed at a rate of 550 rpm for 5 minutes, filter and then applied in clear polyester sheets. The images of the lacquer films (Figure 28), revealed the presence of silicone clusters in all of them. Which doesn't come as a surprise, once all batches of *LS-13-225* had this aspect since the switch of surfactant. In terms of quantity, the films L2 and L4 presented less agglomerates of silicone. This could suggest that a combination of methoxypropyl and MEK forms a better solvent system. Even though, the bigger clusters in the films have similar sizes in all versions, the formulation of L2 and L4 seem to have dissolved the smallest agglomerates. Between these versions, in L2 the clusters are smaller and fewer

that in L4, once the proportion of solvent was doubled in its formulation. The use of either the solvents alone, L1 and L3, don't present any significant differences.

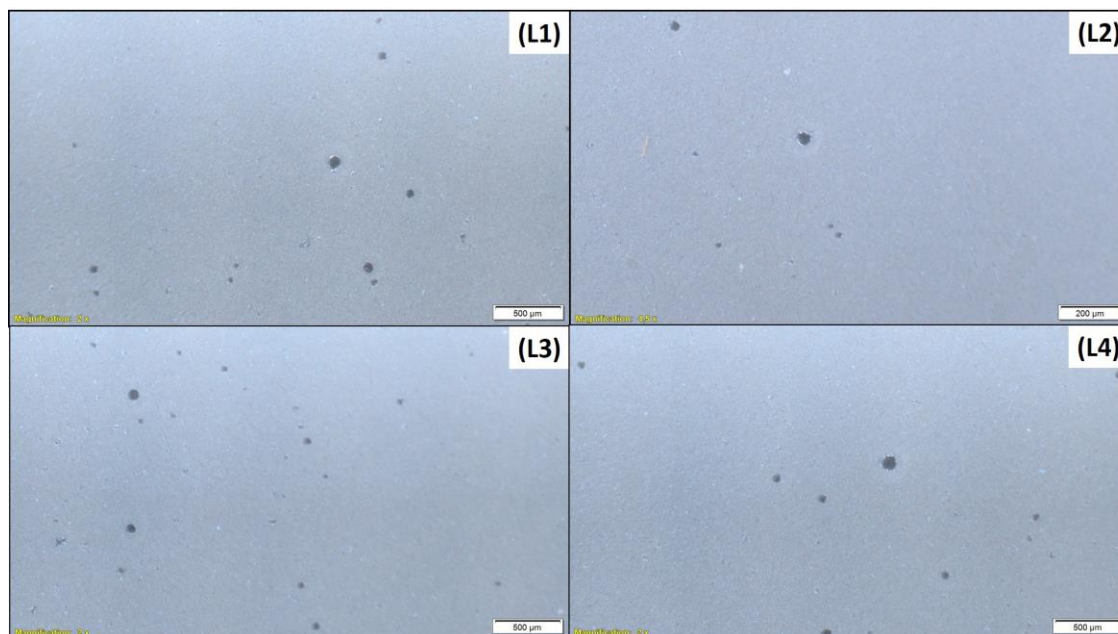


Figure 28 Comparison of quantity and size of silicone clusters in lacquers L1, L2, L3 and L4.

After these results, was decided to test the influence of the stirring velocity of the lacquers. The same formulations were mixed at a rate of 1050 rpm for 5 more minutes. The Figure 29 shows that was an overall decrease on the agglomerate's size excepted in the version L3. The use of MEK alone doesn't decreases the size of the clusters, even with a higher velocity of mixture.

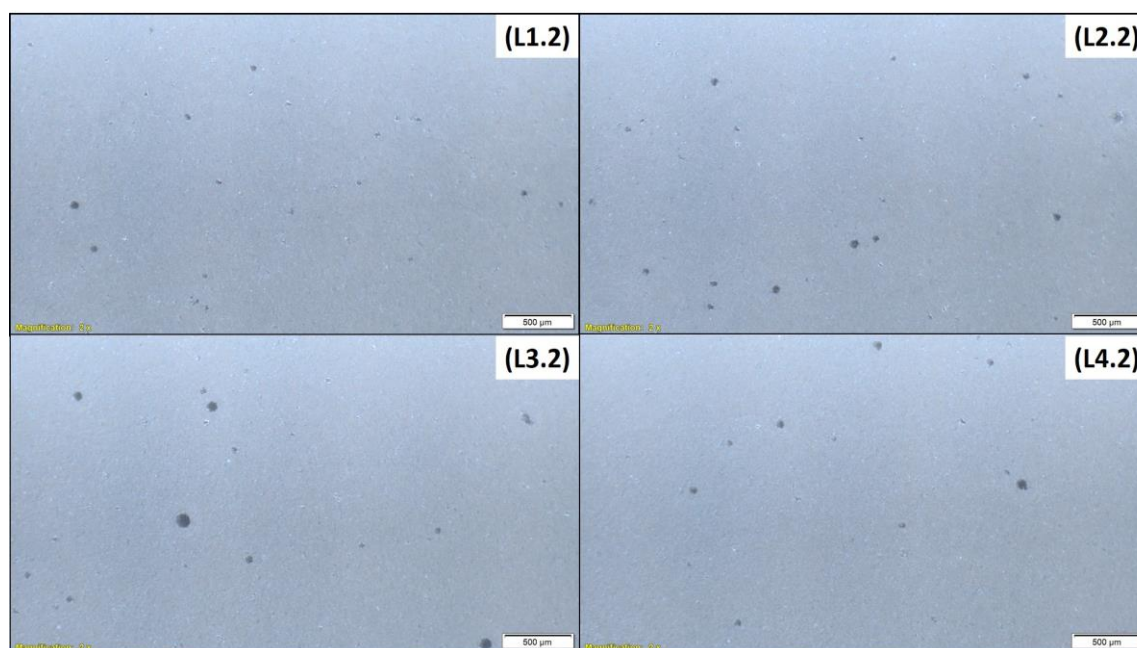


Figure 29 Comparison of quantity and size of silicone clusters in lacquers L1, L2, L3 and L4.

4.3.2 Substitution of the crosslinker

Polymeric materials for car interiors require durability of its properties. For this reason, aliphatic isocyanates are often used to act as crosslinkers. When added in excess, the isocyanate ensures that there is no hydroxy functionality remaining. This allows the reduction of molecular mobility as the finishing reaches an advanced stage of cure (Lukey, 2001).

Permethane XR-40102, a 1,6-hexamethylene diisocyanate (HDI), was used in the lacquer's formulation of the *pelgon 54*, and later substituted for the *permuthane EVO XR-96-901*. The elimination of a solvent system extremely toxic (containing xylene and toluene) was the motivation behind this substitution. When applied a temperature of 150-160 °C for 2 minutes, the *permuthane XR-40102* immediately reacts. In TMG's lacquering process, the temperature of the oven is set to 140 °C. At this temperature not all the isocyanate had reacted, however, after 48 to 72 hours at room temperature, all properties would be established.

In this section, the influence of the crosslinker in the lacquer formulation was considered. The same lacquer was produced with the same quantity of each crosslinker; the formulation may be seen in Table 2. After all components are mixed together, and the lacquer filter, were made films in clear polyester sheets for microscopic observation.

Table 2 Formulation of the lacquer L1 and L2.

Component	L1	L2
<i>Permethane LS-13-225</i>	100	100
<i>Silicone Permethane HM 13-595</i>	5	5
Stabilizer	0.5	0.5
Methoxypropyl	5	5
<i>Permethane EVO XR-96-901</i>	10	--
<i>Permethane XR-40102</i>	--	10

In Figure 30 Aspect of the lacquer films with different crosslinker; (1) *Permethane EVO XR-96-901* and (2) *Permethane XR-40102* Figure 30, are shown the aspect results of for this study. Image (1) shows the aspect of lacquer L1, with *permuthane EVO XR-96-901*, and image (2), the aspect that the lacquers with *permuthane XR-40102*. The other components in both formulations remained the same, this means that the differences observed, came from the way that the crosslinkers interact with the matrix of the finishing. Image (2) shows that the old crosslinker, *permuthane XR-40102* was more prone to interact with the silicone clusters of the PUR base and therefore, increase the quality of the mixture. Herein, the homogeneity of the

lacquer was better than in image (1), wherein the agglomerations of silicone were much more evident.

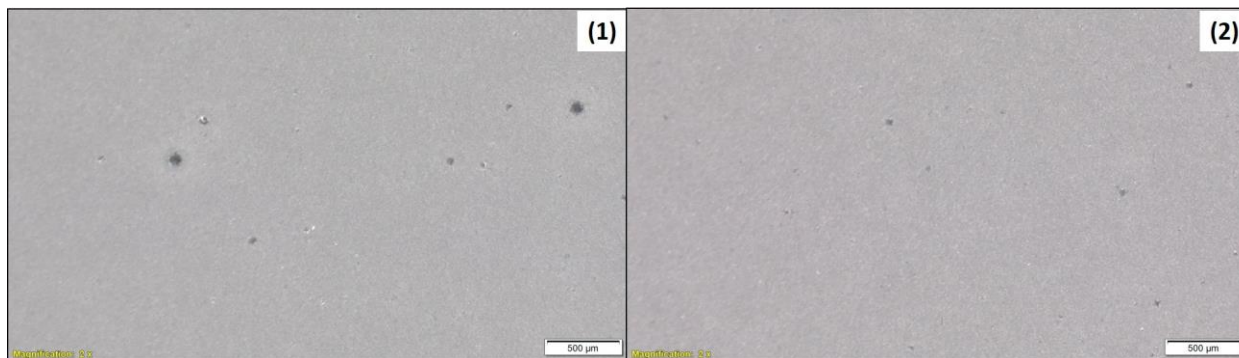


Figure 30 Aspect of the lacquer films with different crosslinker; (1) Permuthane EVO XR-96-901 and (2) Permuthane XR-40102

The solvents in *permuthane XR-40102* are extremely toxic and it is important to eliminate these compounds of the lacquer's formulation. Unfortunately, this results in a crosslinker with worse capacity to abolish the silicone aggregations.

4.3.3 Concentration/proportion of Silicone Permuthane HM-13-595

It is not certain that the silicone clusters observed, were the reason for the increased contamination of the lacquering machine. Although, since these were the biggest difference recorded by the lacquer aspect, the objective was to eliminate them or reduce their size. After being able to do so, the method should be tested in the current production to see if the problem derived from these agglomerations.

In this section, the influence of the silicone concentration in the formation of such clusters, was studied. To accomplish that, samples of polyurethane *permuthane LS-13-225* were prepared with different concentrations of *silicone permuthane HM-13-595* (6, 8, 10 and 12 parts). The formulation with 6 parts of silicone correspond to the reference. The aspect of the formulation-reference on image (6p), in Figure 31, shows a homogeneous, silicone cluster free, lacquer. With the increase of the silicone proportion in the formulation, there are no significant changes, aspect wise. These results show that the silicone added to the lacquer formulation is not responsible for the creation of thereof aggregations. Instead, the number and size of silicone clusters may be from the silicone incorporated on the PUR base.



Figure 31 Films of a lacquer with 6, 8, 10 and 12 parts of silicone permuthane HM-13-595.

4.3.4 Pre-mixture of the *Silicone Permuthane HM-13-595* and crosslinker

In this section, the manufacturing procedure of the lacquers started with the mixture of the *silicone permuthane HM-13-595* with the crosslinker *permuthane XR-96-901*. The purpose of this was to study the possibility to promote an interlocking behavior between the hand modifier and the crosslinker.

For the lacquer's preparation were used the proportions registered in Table 3. The difference between the usual manufacture procedure of a solvent-based lacquer and this one is in the first step thereof production. In this study, were manufactured 4 versions of the original finishing used in *pelgon 54*, with the crosslinker *permuthane EVO XR-96-901* being added to the *silicone permuthane HM-13-595* at different times before the end of the lacquer's preparation. These pre-mixtures were stored in isolated containers, inside a closed cabinet, protecting them from being exposed to the light and humidity of the room. Because the crosslinker has a highly reactive activity, the viscosity of the mixture starts to increase significantly, and so, to prevent the formation of agglomerates and afterwards, a poor homogeneity of the lacquer, one must stir the couple every hour. For every sample, were made the four lacquers of the finishing. The reference (REF), is an exact replica of the *pelgon 54* in terms of formulation and manufacturing. The preparation of the other versions was determined by the duration wherein the silicone and the crosslinker were conditioned together, the first version (P1) began with the mixture and slight stir of these two components that was immediately followed by the addition of the

remaining components. The second (P2) and third (P3) versions were complete within 3 and 24 hours after.

Table 3 Formulation of the finishing.

Component	7769	7630	7631	7632
<i>Permuthane EVO LS-6609</i>	100	100	100	100
<i>Silicone Permuthane HM-13-595</i>	--	2,5	5	6
<i>Silicone Permuthane EX-HM-43-070</i>	--	--	--	3
<i>ESTAB TINUVIM 770 DF</i>	0,5	0,5	0,5	0,5
<i>Methoxypropyl</i>	18	5	5	18
<i>Permuthane EVO XR-96-901</i>	10	8	10	10

After all lacquers had been prepared, stirred and filter, was made a film of each in clear polyester sheets to confirm the lacquer's quality. Finally, the lacquers were applied in the *MATHIS*, with the same cylinder geometries used in current production, except for the second layer that was applied with a *Mesh 40* model (applies 12 g/cm²) instead of a *GTT XXL* (applies 10 g/cm²), because it was unavailable, and the *Mesh 40* is the most similar in terms of the amount of wet lacquer applied.

From the films made, they were selected those of each version of the 7631-lacquer formulation (L7631_REF, L7631_P1, L7631_P2 and L7631_P3), because it only has the *silicone permuthane HM-13-595* and its proportion is higher than in the 7630-lacquer formulation. The distribution maps of elements on the surface of the film, can be seen in Figure 32, where silicon was represented in green. In terms of atomic concentration, the fraction of silicon is very similar in the four samples, which was expected since there were no variations in the proportion of the silicone between them. These results allowed the analysis of the distribution of silicon, which gives an idea of the distribution of the silicone. Both REF and P1 versions, show a complete coverage of the surface of the sample by silicon, although in the P1 image it seems that the silicon is distributed in smaller spots. The aspect of the versions P2 and P3 were very different. In those, it was very clear the formation of large agglomerates of silicon, that were likely to be agglomerates of silicone formed during the conditioning time. From these results, the conditioning of the silicone and the crosslinker, for more than 3 hours, would have to be

disregarded, once the presence of such agglomerates suggests and even worse scenario of silicone contamination in the lacquering line.

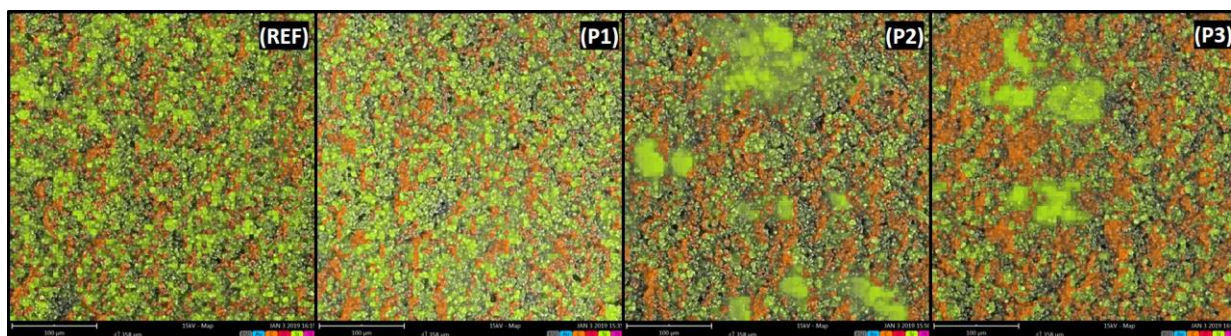


Figure 32 Element's distribution on the four versions of lacquer 7631.

The finished article was then submitted to an abrasion test in the *Gakushin*. The number of cycles registered in Table 4 correspond to the number of cycles passed when were first noticeable small holes in the finishing (see Figure 33). All the versions wherein the silicone was mixed with the crosslinker, showed better results than the original article, which finishing worn out after 5 500 cycles. The best performance was from the version P1, that had also shown good results in terms of homogeneity, lasting for 10 500 cycles. Even though the versions P2 and P3 had shown an increased abrasion resistance by more than 3 500 cycles compared to the reference, those were worse than P1's. This suggests that the mixture of silicone and crosslinker can improve the abrasion resistance of the finishing, but the longer the crosslinker was exposed to the silicone and the environment inside the container, the worst was the performance.

The great motivation to continue using the *silicone permuthane HM-15-595*, was that it presents the best resistance to abrasion results. If this property can be enhanced by this new lacquer's manufacturing process, the total substitution of this silicone may be possible, and so the present situation would be solved.

Table 4 Evaluation of the lacquer's visual aspect.

	REF	P1	P2	P3
Number of cycles	5 500	10 500	9 500	9 000

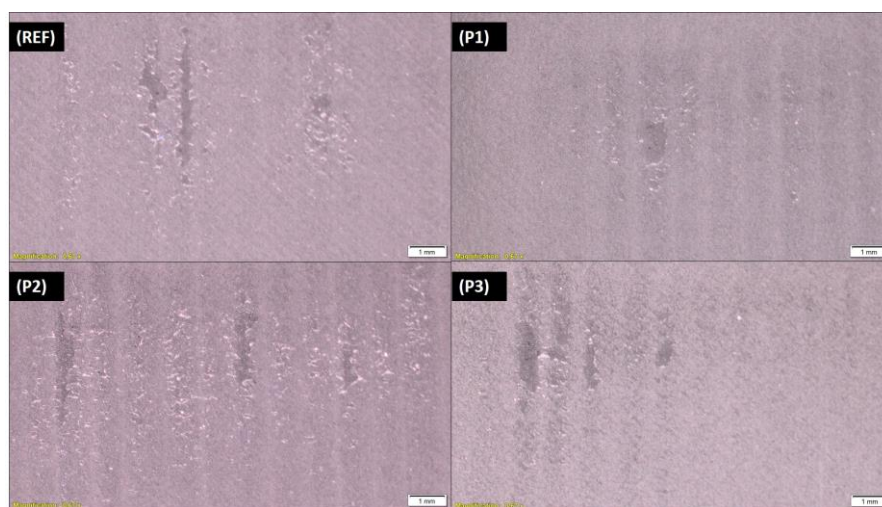


Figure 33 Versions REF, P1, P2 and P3 of the finishing worn out.

4.4 Silicone's mobility within the finishing layers

In this section, the movement of the silicone inside the finishing, was analyzed. In Figure 36, the atomic concentration of silicon in a *permuthane EVO-LS-6609* is about 3.09 %. So, this work was based on the creation of a polyurethane barrier between the layers of the finishing that have silicones and the 2 μm at the surface of the article that EDS analyses. This, to determine if silicon of the layers below travel within the finishing matrix, *i.e.* if silicone moves towards the surface after application.

Firstly, it was necessary to study what it is the relation between the mass per area that is applied in each layer and the resulting thickness of the layer when dry. Through a SEM images study, was possible to associate the application of 10 $\text{g}\cdot\text{cm}^2$ to a dry thickness of 2.5 μm . The version PUR has only *permuthane EVO LS-6609* in its formulation, which was used to determine exactly the atomic concentration, in percentage, of silicon in the raw material. In Version 1, the first three layers correspond to the original formulation of the lacquers and only in the fourth lacquer were eliminated the silicones, and the same thing was made in version 2. However, this last version was conditioned for 27 days in order to study the evolution of the finishing's composition with time. At last, the version 3 is an extension of the study wherein the silicone and the crosslinker were mixed together in the beginning of the lacquer production. In this version, the silicones were again eliminated from the 7632-lacquer formulation. The difference between version 1 and 1.2, version 3 and 3.2 is that, V1.2 and V3.2 had a fifth layer of polyurethane applied on top of the lacquer 7632. Once the thickness of the fourth layer (lacquer 7632) is approximately 2.5 μm , the margin for error in the application of the finishing throughout the entire sample is critically low, so in order to eliminate possible readings of the composition below what was intended, the application of a fifth layer of polyurethane was the

solution to decrease errors in the results. See in Figure 34 and Figure 35, that the level of heterogeneity is very similar in all samples. However, in the sample with a finishing of polyurethane (PUR), the pink tone (silicon) is more “fogged” that in the other images. This suggested that its atomic concentration is more distributed within the 2 μm of thickness analyzed, that in the remaining samples. Herein, the pink tone (blue in the version 2) is brighter, indicating a bigger presence of silicon at the surface.

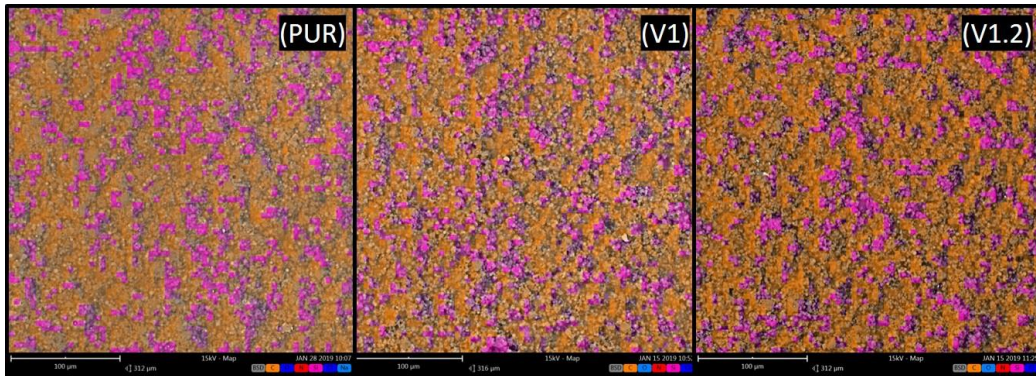


Figure 34 Chemical composition distribution in the surface of the finishing PUR, V1 and V1.2.

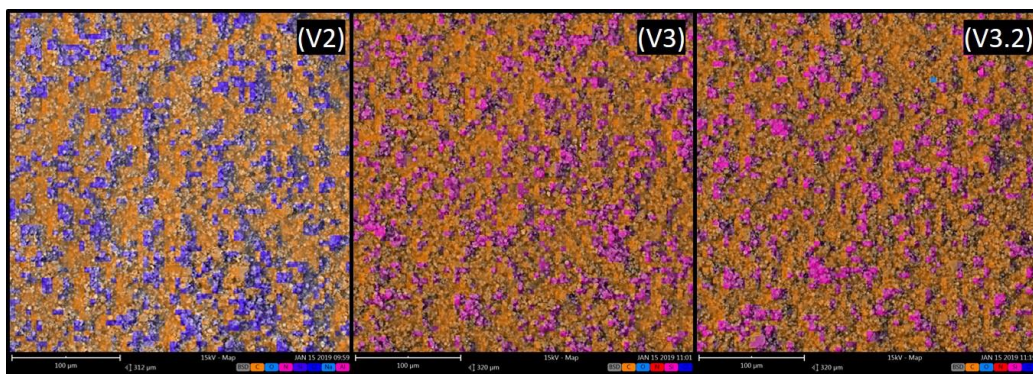


Figure 35 Chemical composition distribution in the surface of the finishing V2, V3 and V3.2.

In the Figure 36 are presented the atomic concentrations of the elements at the surface of the samples, and as previously said, the atomic concentration of silicon in a *permuthane EVO-LS-6609* lacquer is 3.09 % of the composition. The values of atomic concentration of silicon in the versions 1 and 1.2, 3 and 3.2 differ from each other, which means that without the application of a fifth layer on top of the usual finishing, the EDS was detecting silicon from the *silicone permuthane HM-13-595*, present in the lacquer 7631 formulation. There are many ways of contamination of the field of analysis, such as the incorrect application of the lacquers and poor cleaning of the spiral-bars, used for lacquering the samples. Disregarding these contaminations, the difference between version 1 and version 2 is in the age of the finishing. The results from versions V1.2 and V3.2, do not allow further conclusions. If the silicone were to move within the matrix of the finishing, this would be the way to see an increase of the atomic concentration of silicon. Instead, thereof concentration decreased 0.01 % over time. No further conclusion may be withdrawn from this procedure.

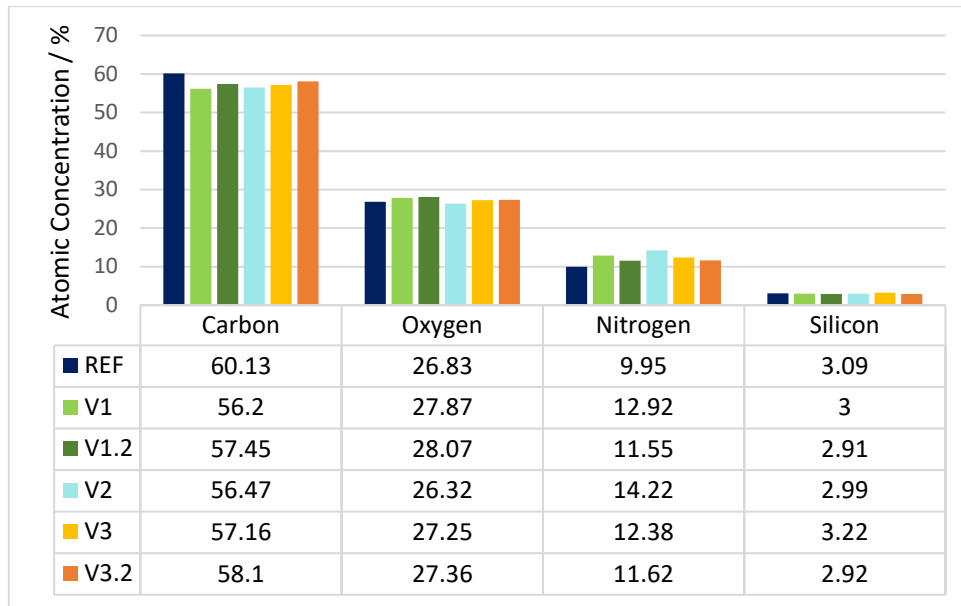


Figure 36 Chemical composition by EDS of PG54 with different versions of the finishing (PUR, V1, V1.2, V2, V3 and V3.2).

5 Conclusions

In this thesis, while diagnosing the migration of silicone onto the surface of the lacquering cylinders, differences in the raw material were discovered. Microscopic images of lacquer films in clear polyester sheets revealed a different matrix between an old and a new sample, using respectively the old and new silicone formulation. Batches of *polyurethane LS-13-225*, since January 2018, show the presence of unidentified agglomerations. More detailed images of the lacquer film, obtained by SEM analysis, confirmed the agglomeration of some components present in the lacquer formulation. This led to analyze the composition of the raw materials. To understand the cause of the problem, it was necessary to understand the changes on behavior of the polyurethane. Based on EDS analyse of the *permuthane LS-13-225*, it was discovered that the silicon atomic concentration is 12 % higher, since the moment wherein accumulation of silicone in the lacquering equipment became unbearable. The substitute for this polyurethane (*permuthane EVO LS-6609*) was also analyzed, only to discover that its silicon concentration is 3.5 times lower. The results obtained from the rheology study of the polyurethanes, showed a similar decrease of viscosity for different shear rates, approximately 0.1 Pa·s. However, the older batch of polyurethane has a viscosity 0.15 Pa·s higher than a sample of a more recent batch. This may be related to the changes in the mixture recorded by the rheological behavior, or it may be just a solvent migration effect.

When analyzed the visual aspect of a finishing surface, some features observed seemed to be caused by thereof characteristics. A *pelgon 27* (39 % of plasticization) with the same finishing that *pelgon 54* (46 % of plasticization), revealed a more porous surface and a worse distribution of the lacquer's components. The results of EDS for the finishing based on polyurethane *LS-13-225*, confirmed the agglomerations previously seen were indeed silicone.

To decrease the size and quantity of the silicone clusters and improve its mixture properties, the silicone *HM-13-595* and the polyurethane *LS-13-225* were diluted with different solvent systems. The films wherein were used a combination of MEK and methoxypropyl showed better homogeneity, with less agglomerates of silicone. Doubling the proportion of solvents, resulted in the dilution of some smaller clusters. A test to determine the influence of the mixture velocity during the phase of preparation of the lacquers was also performed. This showed that at a higher rate, the silicone cluster's size decreased significantly, except in the lacquer dissolved in just MEK.

Mixing the silicone and the crosslinking agent beforehand, proved to be an effective procedure for improving abrasion resistance of the material. Every version on this study, P1, P2 and P3, performed better than the reference, which means, it lasted more cycles before worn out. The longer the exposure of the mixture to the environment inside and out the container in which they are conditioned before the termination of the lacquer, worse their performance. Ideally,

after mixing the silicone and the crosslinker, the lacquer formulation should be immediately terminated. This means that throughout this experience, the crosslinker interlocked the silicone in its matrix and by doing so, retarded thereof wear.

The final test arranged involved the elimination of silicone in the superior layers of the finishing. This would allow the observation of an increase on silicon concentration at the surface of the article. Although, the results recorded did not allow to withdraw conclusions on the behavior of the silicone within the finishing layer.

6 Assessment of the Work Done

6.1 Objectives Achieved

The first objective of this thesis was the study of the raw materials most responsible for problem of silicone accumulation. Through a rheological study, the properties of the mixture of the raw materials were compared between old and recent batches. It was possible to determine that recent batches of PUR *permuthane LS-13-225* and the *silicone permuthane HM-13-595*, have different formulations from older batches. Also, when observing the new *permuthane LS-13-225* lacquer's aspect, were identified silicone clusters.

The second objective was to engineer a new formulation or manufacturing process of lacquers, to decrease the migration of silicone. This work brought advances in techniques that can be used to decrease silicone cluster's size. The use of a solvent system containing equal parts of MEK and methoxypropyl, and a higher stir velocity, improve the homogeneity of the lacquers. A new process for lacquer preparation was also developed. The pre-mixture of the *silicone permuthane HM-13-595* and the *permuthane XR-96-901* (crosslinker) increased significantly the abrasion resistance of the material.

6.2 Limitations and Future Work

The internship that made this project possible was two weeks shorter, due to a delay with the insurance papers.

TMG Automotive already started with the next step on the study of the pre-mixture of the *silicone permuthane HM-13-595* and the *permuthane XR-96-901*. In the future, tests with other silicones should be developed, to validate this procedure as a method of improving abrasion resistance. This would weaken the need to continue using the problematic raw materials.

In terms of knowledge on the raw materials composition and behavior, size exclusion chromatography and x-ray photoelectron spectroscopy should be considered.

6.3 Final Assessment

My time in TMG Automotive, provided the opportunity to increase my knowledge in polymeric materials, coating processes, and even more, about the automotive industry. This was a great first experience in an industrial environment. The chance to develop my dissertation in a family company that occupies high ranks of the automotive industry, proved to be very fulfilling.

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