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# Treball Final de Grau

**Optimizing a glossy black Topcoat of direct adhesion on plastic substrates.**
**Optimització d'un Topcoat negre brillant d'adherència directa sobre substrats plàstics.**

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*Si una persona és perseverant, encara que sigui dura d'enteniment, es farà intel·ligent; i encara que sigui dèbil es transformarà en forta.*

Leonardo da Vinci

# REPORT

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# 1. SUMMARY

All the objects are vulnerable in their surface, since this is the one which is in permanent contact with the air and with all the factors that can make them some damage. To prevent or to reduce the lesions that can cause this damage, layers or coatings are applied to protect the paint surfaces. Apart from that, the paint also serve to add colour and lustre, to smooth and make disappear the caused irregularities in the fabrication process.

In this project, a specific type of paint is used, a topcoat or a single layer paint. This paints must comply with a several properties and requirements to ensure a good quality of the coating.

From the components that the paint incorporates, the resins are noted, since they are the component which forms the film that identifies the paint and the pigments, which are the particles that determinates the colour of it. In automotive coatings, the paints are applied to a certain conditions of temperature and viscosity. These are applied on a specific substrate, with automotive coatings, it is usually used a certain plastic named PC-ABS (a mix of polycarbonate and acrylonitrile butadiene styrene) or on PP (polypropylene). In this project, the application is carrying out using the conventional aerographic method, with paint applicators or suction guns. It is important that after applying the paint, the solvents are evaporated and a dry film is formed.

For the acceptance of a paint in the automotive industry, a several exigencies has been to accomplish which are imposed by the OEMs (Original Equipment Manufacturer). These specify a several tests to accomplish the chemical and mechanical resistances that has to present the paint to be accepted by the customer.

In this project, it is wanted to achieve a topcoat that has good adherence, good appearance, a good abrasion scratch resistance and good chemicals resistance. To this end, some different tests are performed that will show if the studied topcoat has the wished mechanicals properties.

**Keywords**: Topcoat, hardener, adherence, resistance to scoring by abrasion, chemicals resistance, OEM (Original equipament manufacture), brightness.

# 2. RESUM

Tots els objectes són vulnerables en la seva superfície, ja que aquesta és la que es troba en contacte permanent amb l'aire i amb tots els factors que poden fer-los malbé. Per prevenir o reduir els danys que poden ocasionar aquest desgast, s'apliquen capes o revestiments per protegir les superfícies, les pintures.

En aquest projecte es treballa un tipus de pintura en concret, el topcoat o pintura d'una sola capa. Aquestes pintures han de complir amb una sèrie de propietats i exigències per garantir una bona qualitat del recobriment.

Dels components que incorporen les pintures es destaquen les resines, ja que són el component que formen la pel·lícula que identifica la pintura i els pigments, que són les partícules que determinen el color d'aquesta. En automoció, les pintures són aplicades a unes condicions de temperatura i viscositat adequades. Aquestes, s'apliquen sobre el substrat indicat, en automoció sol ser sobre PC-ABS (mescla de policarbonat i acrilonitril butadiè estirè) o sobre polipropilè. En aquest projecte, l'aplicació es realitza utilitzant el mètode aerogràfic convencional, amb aplicadors de pintura o pistoles de succió. És important que després d'aplicar la pintura s'evaporin els dissolvents i es formi el que anomenem pel·lícula seca.

Per l'acceptació d'una pintura en la industria d'automoció s'han de complir una sèrie d'exigències que imposen les OEMs (Original Equipament Manufacturer). Aquestes, especifiquen una sèrie d'assajos a realitzar per complir les resistències químiques i mecàniques que ha de presentar la pintura per a que aquesta sigui acceptada pel client.

En aquest projecte es vol aconseguir un topcoat que presenti una bona adherència, un bon aspecte, que tingui una bona resistència al ratllat per abrasió i bona resistència als químics. Per aquest fi, es realitzen diferents assajos que marcaran si el topcoat estudiat presenta les propietats mecàniques desitjades.

**Paraules clau**: Topcoat, enduridor, adherencia, resistència al ratllat per abrasió, resistències químiques, OEM (Original equipament manufacture), brillantor.

# 3. INTRODUCTION

All objects are vulnerable on the surface. The surface is in constant contact with the air, which contains moisture that can oxidize and corrode the surface. The surfaces of objects left outdoors can suffer attacks from the sun, air, rain, fog, dew, ice and snow. Furthermore, the objects undergo wear due to everyday use, producing scratches, dents and abrasions upon their surfaces. Layers or coating are applied to protect surfaces to prevent or reduce injuries that can occur. These layers also are used to decorate objects or items, to add colour and lustre, to smooth and remove wrinkles or irregularities caused in the manufacturing process. Therefore, the function of any layer is double: to protect and decorate.

There are many layers and coatings that fulfil these functions: wallpaper, sheets of plastic, silver, chrome, etc. But the most versatile coating material is paint; as it can be applied in any surface, whatever shape or size have the object. [1]

## 3.1. INTRODUCTION TO THE TECHNOLOGY OF PAINT

Paint is essentially a pigment suspended in a suitable liquid, called vehicle. The vehicle can be a drying oil or dissolution or suspension of natural or synthetic resins in an aqueous or organic solvent.

### 3.1.1. Components painting

Paints for automotive plastic are mainly composed by resins (binder), pigments, solvents and additives.

*3.1.1.1. Resins*

The resin is the film-forming component that identifies the paint. A variety of resins and polymers (materials that will undergo reaction to form a resin) are used in paints.

The formulation of a paint material and the particular chemicals used are influenced by the particular resin or resin combination used. [2]. It is commonly used combinations of resins, with the aim of achieving the best performance in terms of grip, durability and final appearance. There are many types of resins, such as polyesters, acrylic or epoxy resins.

#### *3.1.1.2. Pigments*

Pigments are particulate solids that are dispersed in paints to provide certain characteristics to them, including colour, opacity, durability, mechanical strength, and corrosion protection for metallic substrates. In order to achieve the desired results, pigments have to possess certain properties. Pigments may be inorganic and organic materials. Organic pigments are used primarily for decorative purposes, while inorganic materials have traditionally been added for protective properties. Extenders are used in conjunction with pigments to modify the properties of the paint. [2].

#### *3.1.1.3. Solvents*

A solvent is mixing of liquids that is used to make the paint flowable prior to its application. [2]. In general, combinations of solvents are used, according to their chemical characteristics, evaporation rate and to dilution.

Solvents are chosen based on the resins that compose the paint, the process of application and drying, the support on which is painted and legal recommendations like toxicity. It's important to choose the correct solvent, for example sometimes a good solvent paint for the paint can also be a solvent that dissolves the plastic on which is painted.

#### *3.1.1.4. Additives*

Additives are chemicals that are added, usually in small quantities, to achieve special improvements and specific properties (appearance, gloss, adhesion, leveling, opacity, corrosion resistance, stability over time, easy to apply, etc.). [2]

### 3.1.2. Type of paint according to its function

There are four kinds of paints according to their function:

#### *3.1.2.1. Primers*

A primer is the first coat applied to surface. Its usual job is to fight against corrosion, guarantee a smooth surface where basecoat will be paint, without imperfections and enhance the adhesion of subsequent coatings applied over the primed surface. [2].

#### *3.1.2.2. Basecoat*

The basecoat is applied after the primer, giving the wanted colour. It has a poor brightness and a bad chemical resistance, so it is needed another layer to protect it.

#### *3.1.2.3. Clearcoat*

The clearcoat is the last layer applied. It provides weather resistance, chemical resistance and a nice appearance.

#### *3.1.2.4. Topcoat*

A topcoat has a composition similar than a clearcoat but pigmented. It is used to protect and provide the desire colour and appearance. It has good chemical and weather resistances. Usually, the corrosion resistance of the topcoat is minimal.

These four types have different properties, that is why in the automotive industry it is applied layer for maximum protection and provide the desired colour. On the surface of a plastic it is normal applied three layers: the primer, then the basecoat and finally the clearcoat. In the case of using a topcoat, the last two layers are replaced by it, it is applied the primer and then the topcoat.

## 3.2. PAINT SYSTEMS FOR PLASTICS SUBSTRATES.

There are two types of paint according to their mechanism to form the dry film, the systems that are commercialized in one container (1-K Technology) and systems that are commercialized in more than one container (2-K Technology).

### 3.2.1. One component system (1-K Technology)

These systems consist on a single component. All the paint is sold in a single package and is stable up to its application. The curing of the paint can be done in different ways:

- Reaction between paint components with high temperature.
- Wet way (contribution of water vapour from the air) that generates films with satisfactory resistance to water, solvents and weathering but not chemical agents; they have good resistance to impact and abrasion. Oxygen and water vapour react with binding agents (resins) and other unsaturated compounds to produce free radicals that produce the polymerization chain.
- By evaporation of solvents. The binder’s molecules are big enough to achieve good characteristics after the film creation. The drying is just physical.

### 3.2.2. Systems of two components (2-K Technology)

These are the systems that are commercialized in more than one container, because they have components that react at low temperature. The most commons types 2-K systems are:

- Acrylic-polyurethane. They follow the reaction of the polyurethane (reaction between the isocyanate and a polyalcohol)
  R1-N=C=O + R2-OH → R1-NH-CO-O-R2
  They exhibit excellent resistance to weathering, chemicals agents, alkaline hydrolysis and discoloration.
- Epoxy reactions. The cured of the film is done with polyamines or polyamides at ambient temperature.

In this project the Topcoat used is an acrylic polyurethane 2-K system that dries by evaporating their solvents.

## 3.3. AUTOMOTIVE TOPCOATS

In this project we will focus on the study and modification of the properties of an automotive Topcoat. As it has been explained previously, a Topcoat is a heterogeneous mixture consisting of pigments, resins, solvents and additives used to protect automotive plastic parts.

### 3.3.1. Properties Automotive Topcoat

The basecoats, clearcoats and topcoats must pass the requirements imposed by the original equipment manufacturer (OEM). OEM is the owner of a brand that manufactures cars, for example Ford, Renault, Volkswagen, etc. The properties are required:

#### *3.3.1.1. Gloss*

The gloss is a visual perception which occurs when surfaces are observed. The perception of gloss is higher as higher the light is reflected. Automotive coatings should reflect the most light possible, so that allows a specular effect. A well-levelled surface favours a specular effect, where the angle of reflection is equal to the angle of incidence. However, rough surfaces spread the incident light in all directions, reflecting a blurred image and low gloss. Also, the coating influences the gloss (the metallic colours reflect more).The gloss can be manipulated by addition of ingredients that provide hazing to reduce reflection or smoothness to increase reflection. [2].

*3.3.1.2. Hiding power*

The ability of a paint to cover a surface and mas kit from view is referred to as hiding power. Since most paint binders are transparent, the job of hiding the surface falls primarily to the pigment. Pigments contribute to hiding power in three ways. They may reflect, refract, or absorb the light that enters the paint film.

With reflection and refraction, the light is turned back out of the film before it reaches the painted surface. [2]

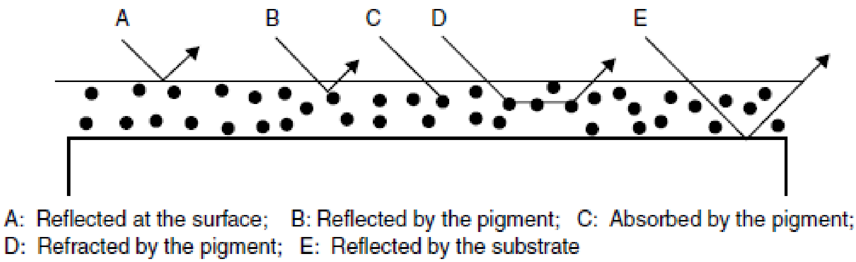


Figure 3.1. Light behaviour on a painted surface. *(Image from Paint technology handbook, reference 2)*

*3.3.1.3. Colour*

The colour of a paint material is primarily due to the pigment interaction with light. Ordinarily, while light is composed of all the colours visible to the human eye. Pigments have the ability to absorb some of these colours and reflect or transmit others. The paint film will be the colour of the reflected or transmitted light. Therefore, the pigment in a red paint absorbs all colours except red. [2]

*3.3.1.4. Hardness*

Hardness is the resistance to penetration or scratch (the paint must endure the scratch of different effects, such as the impact with gravel, hail, scratch in a car wash, etc.). There are scratch hardness tests (maximum hardness supported the film without scratches).

*3.3.1.5. Chemical resistance*

The paint must withstand the effects of humidity, salinity in the air, acid agents, UV radiation, etc. Without modifying the properties of the dry film, so that it is sufficiently robust to different atmospheric conditions.

*3.3.1.6. Adherence*

The adherence is the subjection (bond strength) of the paint on previous primer layers or to the substrate. There are several tests to determine the adhesion of the dry film on the substrate.

*3.3.1.7. Thickness*

The thickness is the amount of paint layer that has been deposited on the substrate. The amount of paint applied should be sufficient to ensure good coverage of the substrate and thereby prevent defects stretching or shine.

*3.3.1.8. Leveling*

The leveling is the stretching the paint on the piece. If there is a bad levelling waves are perceive. This is known as orange peel. The orange peel can be seen in high-gloss surfaces as a wavy pattern of light and dark areas.

*3.3.1.9. Viscosity*

The painting must have a viscosity that allows a good spray application smoothly. The paint manufacturer recommends the customer a specific application viscosity, so the paint is diluted before being applied. Also some specific conditions of temperature and humidity and recommended to guarantee a correct application.

*3.3.1.10. Stability*

The paint should be stable, that is, its properties can't vary over time due to changes in temperature, avoiding worsening the appearance of the liquid paint, increasing viscosity, phase separation or precipitation of solids.

*3.3.1.11. Fineness*

When the solids contained in a paint are not enough dispersed, the dried film is not going to be sufficiently smooth and homogeneous, and it forms small particles that effect the gloss of the finish. Fineness is defined as the maximum diameter of the solid particles present (in microns), and that provide an idea of the degree of dispersion paint.

Each OEM imposes the minimum value of these properties that painting should have. With the aim of evaluating the properties required of the Topcoat studied, the techniques and equipment used are explained in the section Materials and Methods.

### 3.3.2. Defects that may present a Topcoat

The topcoats, and other types of paint can cause defects in the painted surface. It is important to study these defects to reduce them and fix them to get a quality paint. The most common defects are defined below.

#### *3.3.2.1. Sagging*

It is the presence of threads in the paint layer. It appears especially on the edges and corners of the piece (this is the area where more paint is acumulated). This is due to the drying speed is too low, the viscosity of the paint is too low or the paint flow is very high. It can also come due to a poor choice of hardeners and solvents.

Figure 3.2. Paint defects. Sagging. (*Image from Paints defects, reference 4)*

#### *3.3.2.2. Clouding*

They are spots and stripes, and can be light or dark. These can occur because of a bad application method, or the use of unsuitable thinners.

Figure 3.3.Paint defect. Clouding. (*Image from Paints defects, reference 4)*

*3.3.2.2. Solvent popping*

These are holes that appear on the surface of the film. They may appear because the film of paint has dried too fast, that is, evaporation of solvents is complicated and cause holes. It may also be due to an incorrect choice of the hardeners and thinners or because it is used an incorrect spraying technique (method of application).

Figure 3.4. Paint defect. Solvent popping. (*Image from Paints defects, reference 4)*

*3.3.2.3. Orange peel*

Orange peel appears to lack of levelling paint because this looks wavy. This defect is caused by an extension of the painting because of the lack of fixation of the film. May be due to an incorrect application viscosity or a combination of solvents inadequate. It can also occur due to excessive temperature.

Figure 3.5. Paint defect. Orange peel. (*Image from Paints defects, reference 4)*

*3.3.2.4. Inclusions*

They appear when dirt or dust remained below the layer of paint. To avoid this defect, the Topcoat should be filtered before the application, and the substrate pieces must be cleaned and degreased.

Figure 3.6. Paint defect. Inclusions. (*Image from Paints defects, reference 4)*

# 4. OBJECTIVES

The main objective of this project is to optimize the formula of a paint of a single layer (Topcoat) glossy black of direct adhesion on plastic substrates for automotive. To make this possible, it will carry out the following sub-objectives:

1. It will use a formula already marketed by AkzoNobel and optimize it in terms of the type and amount of additives to achieve the required mechanical and chemical properties.
2. It will define a new base formulation and it will analyse the mechanical and chemical properties.
3. It will use a new base formulation, optimize it in terms of the type and amount of additives and compare mechanical properties with the initial formula.

The properties that are required in the project are these: have a good adhesion, a good appearance, a good chemical properties, and improve scratch. All these properties must meet the quality standards of the OEM's (Original Equipment Manufacturer).

# 5. MATERIALS AND METHODS

For the realization of this project, it studies a paint of a single layer (Topcoat) of acrylic base produced it and marketed it by AkzoNobel Car Refinish. This paint is composed of an acrylic resin, a black pigment, a mixture of solvents and additives.

This is a 2-K Topcoat, that is, it is sold in two containers. On the one hand it contains the mix of acrylic resin, pigment, the mixture of solvents and other additives and catalyst containing isocyanates. These isocyanates react with hydroxide which presents Topcoat and gives a polyurethane.

In this project it performs studies of a Topcoat using two different catalysts. The two catalysts are aliphatics polyisocyanates but one consists of a mixture of isphorone diisocyanate (IPDI homopolymer) and diisocyanate hexamethylene (HDI) while the other catalyst is comprised only for isophorone diisocyanate. The catalyst is added just before applying the paint and form a hardened film that depending on the components may take more or less time to harden the coating. The catalyst provides durability to the paint and improves the mechanical and chemical properties. In this project, the catalyst composed of two different diisocyanates provides better resistance to chemicals than other catalyst.

In the realization of this project it has followed a specific procedure. First of all, preparing the paint on the lab, then applies the plastic determined by the appropriate application method. Finally it performs mechanical tests and chemical resistance tests and analyze their results. Next, it describes all processes used in this project.

## 5.1. PREPARING THE PAINT ON THE LAB

For the realization of this project it has been used three topcoats, one of which has been made to an external company to AkzoNobel, because the pigment that incorporates is a pigment powder and the pigment particles need to disperse it or to separate each other, to be distributed evenly throughout the paint. To make this process, it requires a ball grinder, and to make the necessary amount is not available a grinder with appropriate dimensions.

### 5.1.1. Grinding

The ball grinder is a cylinder that rotates about a horizontal axis, which is partially filled with porcelain balls, steel or glass. The speed of rotation is such that the balls rise to the movement and then cascading down, crushing and breaking the pigment. Depending on the method of charging, the ball grinder gets the grinding or the reducing the size of the particle for impacts. The grinding time is long, so only used in cases in which the dispersion of pigments is difficult.

### 5.1.2. Determination of fineness

After grinding, a fineness test is performed to verify that it has reached the desired particle size. This test is performed using a grindometer. The meter consists of a steel plate on that have been made two slots in the form of inclined wedge. These slots pass uniformly from the maximum depth at one end of grindometer to the point zero at the other end of the block of steel. The depth of the wedge can be read on the scale engraved on one side. To perform the test, the block is cleaned and degreased, on the deepest end is placed a small amount of sample (must be an amount that when it is extended it gets wet the entire width of the block), and the sample is dragged to the other end (the zero depth) with the help of a scraper. Before the sample began to dry, it is placed immediately the block to the height of the eyes and the scattered painting is seen against light, and it looks the measuring point where coarse particles are observed. That is, the boundary between the area where the paint is completely smooth (deepest zone) and the area where it begins to have granulation (area more superficial). The depth of this limit, read the graduated scale, represents the maximum diameter of solid particles present in the paint.

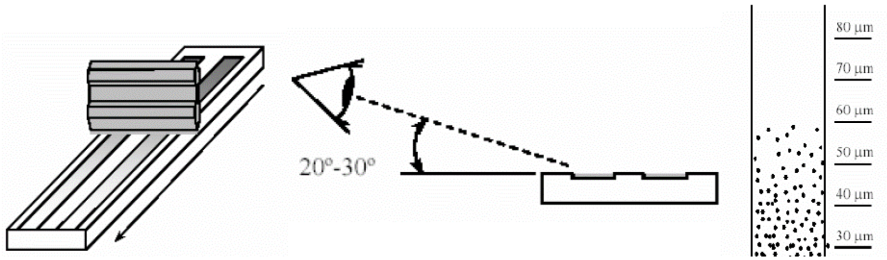


Figure 5.1.Diagram of fineness determination

### 5.1.3. Agitation

For the realization of this project, it has analysed the different topcoats with a number of additives. These additives have incorporated in the paint on a small scale and to homogenize the mixture of paint and additive, it has used a Vollrath agitator, shown in the following figure 5.2.

Figure 5.2.Vollrath agitator type

### 5.1.4. Viscosity adjust

After preparing the paint, the viscosity is adjusted to the adequate supply viscosity, according to the specific technical sheet, that is, the amount of solvent required is added to achieve the proper viscosity. The viscometer cups are used to adjust the viscosity, with which it is not necessary to know the absolute viscosity of the substance, but the time it takes to drain the cup. The time it takes to empty the cups, can be associated to a tabulated value of absolute viscosity. In this case, the viscosity of topcoats has been adjusted with a DIN 4 cup at 23ºC.

To apply the Topcoat is necessary adjust it to an application viscosity with the solvent indicated, as specified at the technique blade and add the percentage of hardener (catalyst) required, as is a K-2 system. To adjust the viscosity is also used the specific viscometer cup. In this case, the different topcoats were adjusted in a Ford cup 4 to 23ºC.

Figure 5.3. Viscometer cup Din 4 and Ford 4

## 5.2. PAINT APPLICATION

Relying on the tests performed, paints are applied in one or another substrate. In this project, the topcoats have to apply on panels PC-ABS, which is a blend of polycarbonate and acrylonitrile butadiene styrene.

Before painting the substrates, it should rub them with isopropanol to remove dirt that may exist. The panels application is performed in a painting booth (Figure 5.4). These painting booths remain at 24ºC and 65% of relative humidity.

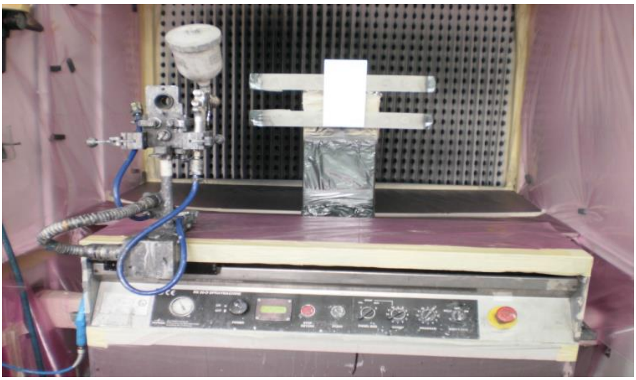

Figure 5.4. Painting booth

Before applying, the panels are blown with compressed air to remove any particles of dust or dirt that may have remained on the panel.

The application method used is the conventional airbrush method. It is based on creating a spray cloud that is projected onto the surface of a support by compressed air. That is why it is used guns suction that mix an air flow at a pressure between 3 and 6 bars with diluted paint, projecting it through a mouthpiece with small diameter.

Figure 5.5. Conventional Airbrush.

The paint applicators or suction guns are mounted on robots RX-20, shown in Figure 5.4. The panels are painted according to several automatic application programs that are already recorded on the device. This project has used a standard application program.

Once the parts are painted, they are left for 10 minutes at room temperature and are cured at 80°C for 30 minutes to evaporate the solvent and it is formed the dry film. To perform the tests of mechanical and chemical properties, the panels were left to cure 7 days at room temperature.

### 5.2.1. Colour adjustment

Before applying definitely the panels, should consider whether it need a colour adjustment. To make it, it paints a panel applying the necessary conditions and the colour is analysed.

#### *5.2.1.1. The colour study parameters*

The colour is measured in the space *CIEL*a*b*.* It is a space of uniform colour and it allows to specify colour stimuli in three-dimensional space. Here you can find all the colours visible to the human eye. The three axes L*a*b* of the space represent: brightness of colour L (L=0 black and L=100 white), its position between red and green (a* the positive values indicate red hue and the negative, green hue) and its position between yellow and (b* the negative values indicate blue and the positive, yellow).

This colour space is based on the theory of opposite colours. This theory says that yellow in front of blue and red in front of green are opposing signals. The ordering of colours is based on that all the chromaticities may contain a component of red or green, but never both sensations simultaneously.

With the theory of opposite colours, the colour sensation is organized along two axes. The first axis (a) encodes the composition red-green of a colour, while the second axis (b) encode the sensation blue-yellow of a light stimulus. The intersection of these axes encodes the light intensity on a third axis perpendicular to both axes.

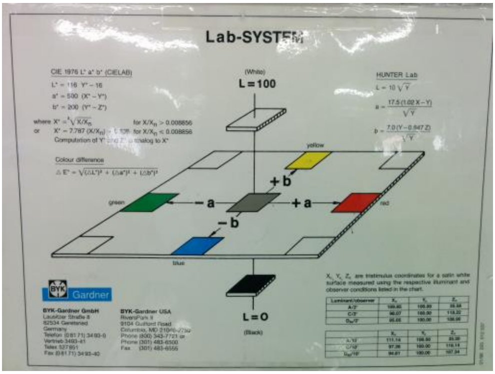


Figure 5.6. Diagram CIE L*a*b*.

In the industrial world of paint, the colour is measured and expressed as differences there are between two colourful samples. In this case, a pattern that provides the customer and the developed colour by AkzoNobel.

### *5.2.1.2. Colour parameters measurement*

Colour parameters measurement is performed with a reflectance spectrophotometer. To perform it, the spectrophotometer detector is placed exerting a moderate pressure on the panels and this transfer the data into a computer where it is connected.

Figure 5.7.Reflectance Spectrophotometer

Completed the measurement of the colour parameters, it has to make the necessary adjustment of colour for the paint has the same colour than the pattern given by the customer. That is, the missing colour base is added and it is proceeded to a new application and checking of the colour.

## 5.3. EVALUATION OF MECHANICAL AND CHEMICAL PROPERTIES

For the acceptance of a paint, in the automotive industry, a series of requirements imposed by OEMs must be met. That is why, the OEMs specify a series of tests to perform to meet the chemical and mechanical resistance. On this project, some of the methods used by OEMs are used to corroborate the adherence of the topcoat to the plastic and the chemical resistance that simulate everyday situations like a scratch on the car, to wash the car with pressurized water or the marks caused by different products that may end with the car surface.

Next are detailed how the different tests for prototypes studied are developed.

### 5.3.1. Adherence

6 parallel cuts and 6 perpendicular cuts are made, separated for 1mm and that reach the substrate forming a grid as shown below. An adhesive tape is glued on the grid and it is ripped off quickly.

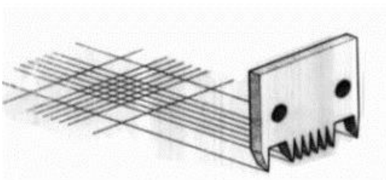

Figure 5.7. Grid for adherence test.

### 5.3.2. Pressurized water test

With pressurized water tests were been performed referring to two different OEMs, each with its specifications.

The first test is performed according the standard PV1503 of the specification TL 211 from Volkswagen and the second test is performed according the standard D25 5376 of the specification B15 5050 from PSA Peugeot-Citroën. Two cross-shaped cuts are made, how specifies each standard and this area is subjected to pressurized water. Then, it is observed whether there has been loosening of the paint on this area.

Figure 5.8. Testing machine with pressurized water

The differences between the two tests are that it is used a different nozzle and that the conditions of pressure, temperature and flow are modified.

### 5.3.3. Resistance to scoring by abrasion

Abrasion tests were performed referring to two different OEMs, each with its specifications.

The first test is carried out according to the standard D42 1775 of the specification 47-03-003J from Renault. To perform this test it is used a specific machine, which is represented on the next figure.

Figure 5.9. Crockmeter used for Renault abrasion test.

The test involves passing the specific abrasion paper previously wet with deionized water, pushing with the weight of the machine, over the panel to test. It is passed twice (going and return). Then, the damages caused by abrasion are analysed. The initial brightness of the panel and the brightness of the panel after performing the test are measured. The brightness is measured using the micro-gloss BYK-Gardner at 20º. It is desirable that the brightness loss as low as possible. This brightness loss is calculated according to the following formula:

$$\%Gloss\ retention = \frac{Gloss\ abraded}{Original\ gloss} \cdot 100$$

Equation 5.1. Determination of gloss retention

The second abrasion test is performed according the standard FLTM BI 161-01 of the specification WSS-M16J9-B2/B3 from Ford. To perform this test it is used the represented machine to the following figure:

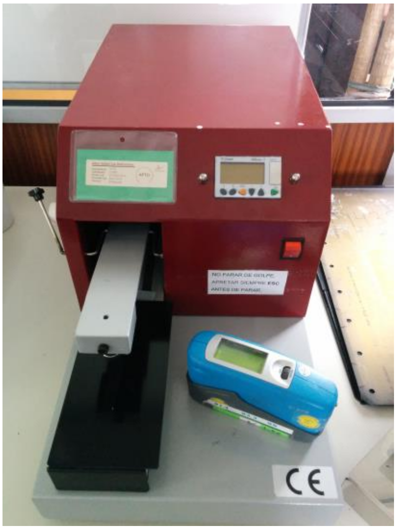

Figure 5.10. Crockmeter used by the abrasion test Ford and micro-gloss BYK Gardner

The machine performs 10 rubs to the piece with a specific abrasion paper for this test. And it compares the initial brightness from the piece with the brightness measured after performing the test. The brightness measurement is performed with the micro-gloss from BYK-Gardener at 20º, as in the previous case. The brightness loss is calculated according to the formula shown above.

### 5.3.4. Chemical resistance

The mark left by the pancreatin, tree resin, diesel, biodiesel, brake fluid, coolant, fuel test FAM, 95 petrol and engine oil is evaluated according the specification TL 211 de Volkswagen. A criteria with three degrees of marks has been chosen: Unbranded, marked and strongly marked.

For the analysis of the marks of diesel, biodiesel, brake fluid, coolant, FAM fuel testing and petrol 95, it is used a piece of hydrated cotton with the substance and it is let stand on the panel during the time stated in the standard in each case. However, for the substances: pancreatin, tree resin and engine oil, a few drops of the substance are deposited on the panel during the time and the temperature that marks the standard in each case.

# 6. RESULTS AND CONCLUSIONS

Below are presented and discussed the experimentally obtained results in the conducting of this work. These are presented in three sections. On one hand, the optimization of the initial glossy black topcoat; moreover, the new formulation is analysed; and finally, the optimization of a third base formulation and its comparison with the initial formula.

## 6.1. OPTIMIZATION OF A GLOSSY BLACK TOPCOAT OF DIRECT ADHESION

In this section it is analysed an already marketed topcoat by AkzoNobel. To analyse this topcoat, five prototypes are tested, each one with a different combination of additives:

- A prototype is the glossy black topcoat without additives.
- B prototype includes the glossy black topcoat and a mixture of additives in surface. The first additive is a dispersion surface-treated silica nanoparticles to improve the scratch resistance of solvent-borne coatings. The other is a silicone additive composed by a solution of a polyether-modified polydimethylsiloxane, it is used for humidify the substrate, avoiding the craters and improving the sliding on the surface.
- C prototype includes the glossy black topcoat and a mixture of additives in surface. The first additive is a dispersion of surface-treated aluminium oxide nanoparticles that it is used to improve the scratch resistance to solvent-based coatings. The other one, is a silicone additive composed by polyether-modified polydimethylsiloxane that it is used to improve the sliding on the surface.
- D prototype includes the glossy black topcoat, the mixture of additives used on B prototype and includes a resin composed by a slightly branched polyester polyol that improves the flexibility and the durability of the coatings.
- E prototype includes the glossy black topcoat, the mixture of additives used on C prototype and includes the resin used on prototype D.

All prototypes also include an application additive included in the application solvent. This additive is a special phosphoric acid ester that it is used to improve the adherence of the paint.

As it is mentioned in the section of *Materials and methods*, it has applied each prototype with two different hardeners (catalysts), one of which is composed by a mixture of isphorone diisocyanate (IPDI homopolymer) and hexamethylene diisocyanate (HDI) (hardener 1), while the other catalyst is just composed by isophorone diisocyanate (hardener 2).

Below are presented and discuss the experimentally results to assess the mechanicals and chemicals resistance of this prototypes applying what is explained on *Materials and methods*.

### 6.1.1. Adherence

To realise the adherence, has proven that using the relevant technique, the topcoat has good adherence with the substrate.

In all cases it has been observed that the Topcoat presents good adhesion with the substrate because in all cases there is not detachment of the paint. Below there are shown on the next figures some examples from the adherence test using both hardeners.

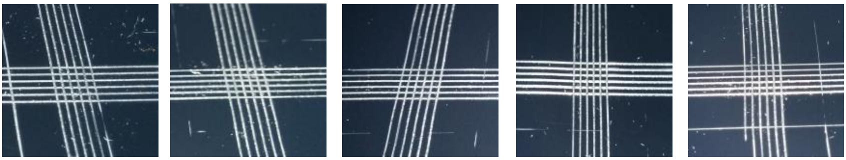

Figure 6.1. Adherence of prototypes A (left), B, C, D and E (right) applied with the hardener 1

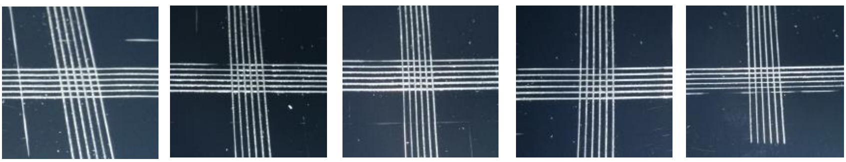

Figure 6.2. Adherence of prototypes A (left), B, C, D and E (right) applied with the hardener 2

### 6.1.2. Pressurized water test

As is mentioned on *Materials and methods*, the test has been performed using two different standards. The obtained results in each case are shown below.

### *6.1.2.1. According to the standard PV1503 of the specification TL211 from Volkswagen*

On the performing of this test, the panels applied with the topcoat are submit to the conditions of this standard and it is checked if there is some detachment of the paint.

Figure 6.3. Pressurized water test according the standard of Volkswagen with prototypes A (left), B, C, D and E (right) applied with hardener 1

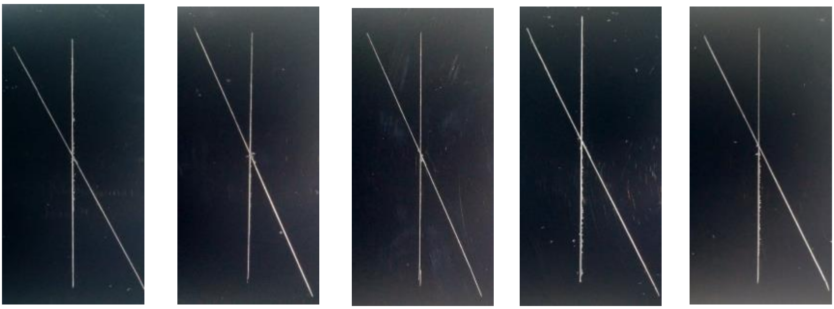

Figure 6.4. Pressurized water test according the standard of Volkswagen with prototypes A (left), B, C, D and E (right) applied with hardener 2

This standard does not admit any detachment of paint, thereby it has been made a measure of the detachments that were obtained in each case using a Vernier. The results are shown in the *Table 1* of *appendix 1*.

### *6.1.2.1. According the standard D25 5376 of the specification B15 5050 from PSA Peugeot-Citroën*

On the performing of this test, the panels applied with the topcoat are submit to the conditions of this standard and it is checked if there is some detachment of the paint.

Figure 6.5. Pressurized water test according the standard of PSA with prototypes A (left), B, C, D and E (right) applied with hardener 1

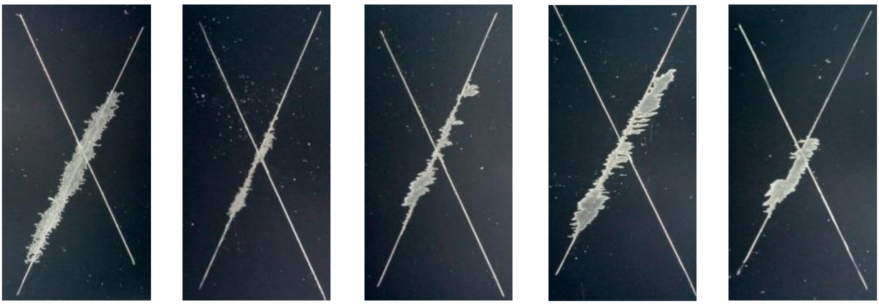

Figure 6.6. Pressurized water test according the standard of PSA with prototypes A (left), B, C, D and E (right) applied with hardener 2

This standard admits a maximum of 1 $cm^2$ of paint detachment, therefore, has been made a detachment measure that were obtained in each case. The results are shown in the *Table 2* of *appendix 1*.

Taking into account the two adhesions with pressurized water, prototypes are compared to each other.

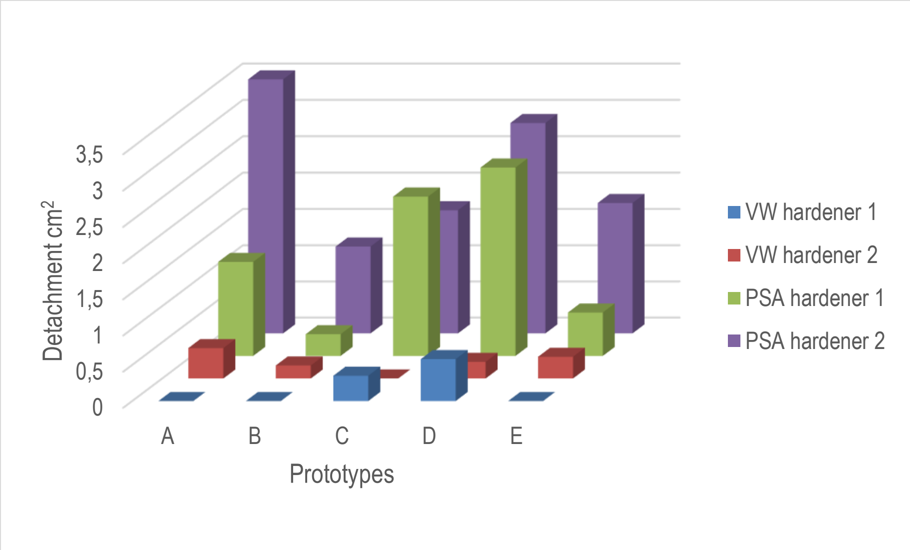


Figure 6.7.Comparative between the tests with pressurized water of prototypes A, B, C, D and E.

As it is observed in the figure 6.7. for the standard of Volkswagen, in all the cases it can be considered that there has not been detachment, since in the cases of the paint detachment it has been imperceptible to the human eye.

As can be seen in figure 6.7. for the standard of PSA, only are two prototypes in which it detaches less than 1cm$^2$, these are prototypes B and E using the hardener 1. So, the best hardener for the adhesion is hardener 1, since the two prototypes that have passed the standard, are using the hardener 1.

Therefore, as shown in figure 6.7., the best prototypes with better adherence are the B and E prototypes, since they present a better pressurized water resistance with both standards and both hardeners.

### 6.1.3. Resistance to scoring by abrasion

As is mentioned on *Materials and methods*, the test has been performed using two different standards. The obtained results in each case are shown below.

*6.1.3.1. According the standard D42 1775 of the specification 47-03-003J from Renault*

In conducting of this test, the topcoat applied panels are subjected to the abrasion following the specifications of the standard. As it has been explained previously, scratch resistance abrasion is evaluated with the loss of brightness in the surface. If it has a greater loss of gloss, the topcoat will have worse abrasion resistance. An example of how the panel is left after the performance of this standard is shown in the following figure.

Figure 6.8. Example of Renault scratch. Prototype C using hardener 1

Below there is a table with the results. The gloss retention was calculated using the *Equation 5.1.*, defined on *Materials and methods* section.

| Prototype | Initial gloss | Final gloss | % gloss retention |
|---|---|---|---|
| **A** | 79,7 | 26,7 | 33,5% |
| **B** | 77,3 | 39,7 | 51,4% |
| **C** | 79,2 | 10,0 | 12,6% |
| **D** | 79,9 | 31,0 | 38,8% |
| **E** | 80,0 | 37,9 | 47,3% |

Table 6.1. Initial and final gloss obtained in carrying out the abrasion scratch resistance test of Renault using hardener 1

| Prototype | Initial gloss | Final gloss | % gloss retention |
|---|---|---|---|
| **A** | 80,0 | 55,9 | 69,9% |
| **B** | 77,6 | 41,0 | 52,8% |
| **C** | 79.8 | 45,7 | 57,3% |
| **D** | 78,3 | 17,0 | 21,7% |
| **E** | 80,1 | 40,6 | 50,6% |

Table 6.2. Initial and final gloss obtained in carrying out the abrasion scratch resistance test of Renault using hardener 2

It is observed that all prototypes present similar initial gloss. After the conducting of the abrasion test it is observed that all prototypes present a high loss of gloss, and also it is observed that there are big differences between some of them. As what needs improvement is the scratch resistance, in this case, it gives an idea of which of the prototypes is better in this angle. Also shows which additive combination is the most suitable in this case. It can be seen that the best option would be to use the hardener 2, because the obtained retentions with hardener 1 are too low, and with the hardener 2, the best prototypes are A and C. In addition, we can conclude that the used additives do not improve the scratch abrasion resistance that has the prototype A (the initial one).

*6.1.3.2. According the standard FLTM BI 161-01 of the specification WSS-M16J9-B2/B3 from Ford*

As it is explained previously in *Materials and methods* section, the abrasion scratch resistance to different prototypes is studied using another standard. As previous case, the surface loss gloss is evaluated after the abrasion. If the loss gloss is higher, the abrasion resistance that presents the topcoat is worst.

An example of how the panel is left after the performance of this standard is shown in the following figure.

Figure 6.9.Example of Ford scratch. Prototype A using hardener 1.

In the next table are shown the obtained results using each hardener and using the specifications indicated in this standard. In this case, it is also analysed the brightness retention after 24 hours, to see if with the help of the hardener, the topcoat recovers brightness. The gloss retention was calculated using the *Equation 5.1.* defined on *Materials and methods* section.

| Prototype | Initial gloss | Final gloss | % gloss retention | Final gloss 24 hours | % gloss retention 24 hours | Recovery difference |
|---|---|---|---|---|---|---|
| **A** | 78,9 | 46,0 | 58,3% | 46,3 | 58,7% | 0,4 |
| **B** | 75,5 | 46,1 | 61,1% | 47,4 | 62,8% | 1,7 |
| **C** | 78,7 | 44,8 | 56,9% | 46,4 | 58,9% | 2,0 |
| **D** | 79,1 | 40,9 | 51,7% | 41,4 | 52,3% | 0,6 |
| **E** | 79,4 | 37,7 | 47,5% | 37,9 | 47,7% | 0,2 |

Table 6.3. Initial and final gloss obtained in carrying out the scratch abrasion resistance test of Ford using hardener 1

| Prototype | Initial gloss | Final gloss | % gloss retention | Final gloss 24 hours | % gloss retention 24 hours | Recovery difference |
|---|---|---|---|---|---|---|
| **A** | 80,1 | 48,9 | 61,1% | 49,8 | 62,2% | 1,1 |
| **B** | 77,7 | 49,7 | 64,0% | 49,8 | 64,1% | 0,1 |
| **C** | 71,7 | 62,2 | 86,7% | 63,3 | 88,3% | 1,6 |
| **D** | 77,3 | 52,2 | 67,5% | 52,3 | 67,7% | 0,2 |
| **E** | 80,1 | 38,3 | 47,8% | 39,3 | 49,1% | 1,3 |

Table 6.4. Initial and final gloss obtained in carrying out the scratch abrasion resistance test of Ford using hardener 2

This standard admits a brightness retention upper than 70%. Therefore, only happens with prototype C using hardener 2, all the other ones can be discarded. Also it can be observed that after 24 hours, the higher brightness recovery is presented by prototype C using both hardeners.

Observing all the results obtained until this point, it is can be deduced that the better combinations of additives for this topcoat it has been the prototype C and the best hardener in this case is hardener 2. Since the main objective of this project is to determinate a topcoat that improves the abrasion scratch resistance without losing adherence and having an acceptable chemical resistance.

### 6.1.4. Chemicals resistance

For the evaluation of chemical resistance, it is used a gradation according the attack that causes the chemical agent to the topcoat. This attack is evidenced with a mark caused to the topcoat. Below are shown the evaluated results at 24 hours after performing the test, because if the topcoat is marked, this mark can recovery. The obtained results on chemical resistance of initial prototype A and prototype C with hardener 2 are compared, since is the best prototype obtained until now. An example of a fuel Brand of the test FAM on the topcoat, is shown in the next figure; particularly is the prototype A with hardener 2.

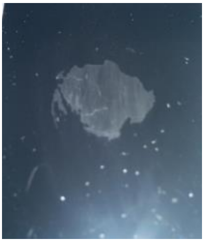

*Figure 6.10. Chemical resistance mark.*

| Prototype / Solution | A | C |
|---|---|---|
| **Pancreatin** | Unbranded | Unbranded |
| **Tree resin** | Marked | Strongly marked |
| **Diesel fuel** | Unbranded | Unbranded |
| **Biodiesel** | Unbranded | Unbranded |
| **Brake fluid** | Marked | Marked |
| **Coolant** | Unbranded | Unbranded |
| **FAM test fuel** | Strongly marked | Marked |
| **Super unleaded fuel** | Marked | Marked |
| **Engine oil** | Unbranded | Marked |

Figure 6.5. Comparison of chemicals resistance with prototypes A and C with hardener 2

Comparing the two prototypes, one can observe that the prototype C is slightly worse by tree resin and engine oil that the prototype A but to FAM test fuel is slightly better. Therefore, we can conclude that in chemical resistance the prototype C does not worsen the chemical resistance of the initial prototype.

The results of the other prototypes with the two hardeners are on *Table 1 and 2 to appendix 1.*

## 6.2. EVALUATION OF THE NEW FORMULATION BASE

In this section has been created a new formulation base of a black topcoat, but in this case has not been achieved to be glossy, but it is a matt black topcoat. It has made a determinate quantity of this topcoat, it have painted panels of PC/ABS using 2 hardeners and subsequently have been performed the same tests that in the previous section, in order to check its mechanical and chemical properties.

In an attempt to improve the appearance, it was an improvement of the formula, to make it pulled a considerable amount of solvent off the formula, so that the paint film stay more stretched and decrease the defects of the layer of paint that presented previously.

The prototype F is the new formulation base, while the prototype G will be the new improved formula. Here are the results of these tests, in both cases.

These prototypes also include the special phosphoric acid ester additive, that it is used to improve the adherence of the paint.

### 6.2.1. Adherence

As it is explained before in *materials and methods* section, to realise the adherence it is checked that using the correct technic, the topcoat has a great adherence with the substrate.

In both cases it has been observed, that the topcoat presents a good adherence with the substrate. On the following figures are shown the examples of the adherence test using both hardeners.

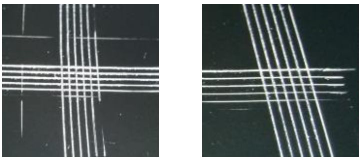

Figure 6.11. Adherences of prototypes F (left) and G (right) with hardener 1

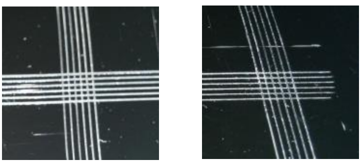

Figure 6.12. Adherences of prototypes F (left) and G (right) with hardener 2

### 6.2.2. Pressurized water test

As it is mentioned before in 6.1.2 section, it has been performed the test according two different standards. Below are shown the obtained results on each case.

*6.2.2.1. According the standard PV1503 of the specificationnTL211 from Volkswagen*

On the performing of this tests, the applied panels with the topcoat are submitted to the conditions of this standard and after the tests it is checked if some paint has detached.

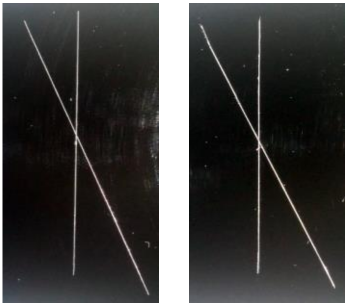

Figure 6.12. Pressurized water test according the standard of Volkswagen with prototypes F (left) and G (right) applied with hardener 1

Figure 6.13. Pressurized water test according the standard of Volkswagen with prototypes F (left) and G (right) applied with hardener 2

This standard does not admit any paint detachment, that is why it has been measured the detachments obtained in each case. The results are collected in the following table.

| Topcoat | Detachment of the paint with hardener 1 | Detachment of the paint with hardener 2 |
|---|---|---|
| **F** | 0 $cm^2$ | 0,05 $cm^2$ |
| **G** | 0 $cm^2$ | 0 $cm^2$ |

Table 6.6. Pressurized water test results according the standard of Volkswagen with prototypes F and G

As it has happened before, it can be considered that there are not any detachment.

*6.2.2.1. According the standard D25 5376 of the specification B15 5050 from PSA Peugeot-Citroën*

On the performing of this tests, the applied panels with the topcoat are submitted to the conditions of this standard and after the tests it is checked if some paint has detached.

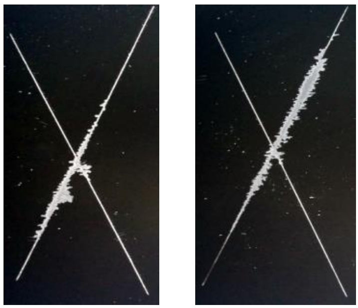

Figure 6.14. Pressurized water test according the standard of PSA with prototypes F (left) and G (right) applied with hardener 1

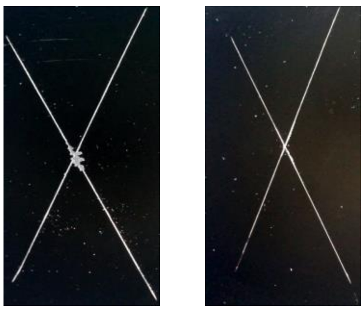

Figure 6.15. Pressurized water test according the standard of PSA with prototypes F (left) and G (right) applied with hardener 2

As is mentioned before in the 6.1.2.1 section, this standard admits a maximum of 1 $cm^2$ of paint detachment, therefore, has been made a detachment measure that were obtained in each case. The results are shown in the next table.

| Topcoat | Detachment of the paint with hardener 1 | Detachment of the paint with hardener 2 |
|---|---|---|
| **F** | 0,9 $cm^2$ | 1,7 $cm^2$ |
| **G** | 0,22 $cm^2$ | 0,09 $cm^2$ |

Table 6.7. Pressurized water test results according to the standard of PSA with prototypes F and G

As it can be observed, this formula is great on adherence, since in all cases, with the exception of prototype F with hardener 2, it has been obtained less than 1 $cm^2$ of the paint detachment.

### 6.2.3. Resistance to scoring by abrasion

As it is mentioned before in the *materials and methods* section, it has been performed the test according two different standards. Below are shown the obtained results on each case.

*6.2.3.1. According the standard D42 1775 of the specification 47-03-003J from Renault*

In the performing of this test, it has been followed the same procedure performed in section *6.1.3.1* obtaining the following results. The gloss retention was calculated using the *Equation 5.1* defined on *Materials and methods* section.

| Prototype | Initial gloss | Final gloss | % gloss retention |
|---|---|---|---|
| **F** | 52,6 | 39,5 | 91,9% |
| **G** | 34,3 | 13,7 | 40,7% |

Table 6.8. Initial and final gloss obtained in carrying out the scratch abrasion resistance test of Renault using hardener 1

| Prototype | Initial gloss | Final gloss | % gloss retention |
|---|---|---|---|
| **F** | 36,3 | 23,1 | 65,7% |
| **G** | 26,6 | 7,0 | 44,6% |

Table 6.9. Initial and final gloss obtained in carrying out the scratch abrasion resistance test of Renault using hardener 2

As it can be observed, although the appearance is better on prototype G, the abrasion resistance is better on prototype F with both hardeners. That is, removing some solvent from formula base makes the abrasion resistance worst.

*6.2.3.2. According the standard FLTM BI 161-01 of the specification WSS-M16J9-B2/B3 from Ford*

In the performing of this test, it has been followed the same procedure performed in section *6.1.3.2* obtaining the following results. The gloss retention was calculated using the *Equation 5.1* defined on *Materials and methods* section.

| Prototype | Initial gloss | Final gloss | % gloss retention | Final gloss 24 hours | % gloss retention 24 hours | Recovery difference |
|---|---|---|---|---|---|---|
| **F** | 48,5 | 37,2 | 76,7% | 37,2 | 76,7% | 0 |
| **G** | 30,2 | 29,1 | 96,4% | 29,9 | 99,0% | 2,6 |

Table 6.10. Initial and final gloss obtained in carrying out the abrasion scratch resistance test of Ford using hardener 1

| Prototype | Initial gloss | Final gloss | % gloss retention | Final gloss 24 hours | % gloss retention 24 hours | Recovery difference |
|---|---|---|---|---|---|---|
| **F** | 32,4 | 23,9 | 73,8% | 24,0 | 74,1% | 0,3 |
| **G** | 34,1 | 28,7 | 84,2% | 29,6 | 86,8% | 2,6 |

Table 6.11. Initial and final gloss obtained in carrying out the abrasion scratch resistance test of Ford using hardener 2

As is mentioned previously in 6.1.1.2 section, this standard admits a gloss retention upper than 70%. That is, it can be observed that all the prototypes are valid for the standard. Further, it can be said that with this standard, the prototype G presents a better abrasion scratch resistance. Also, the gloss recovery from prototype G after 24 hours is a lot better than the others.

In short, although the appearance and the abrasion test according the Ford standard are worst the ones from prototype F; it can be affirm that prototype F is better than G, because it has passed all the mechanicals tests with hardener 1. Meanwhile, the prototype G has not passed the abrasion scratch resistance test from Renault.

### 6.2.4. Chemicals resistance

For the evaluation of chemical resistance, it is used a gradation according the attack that causes the chemical agent to the topcoat. This attack is evidenced with a mark caused to the topcoat. Below are shown the evaluated results at 24 hours after performing the test, because if the topcoat is marked, this mark can recovery.

| Prototype / Solution | F | G |
|---|---|---|
| **Pancreatin** | Unbranded | Unbranded |
| **Tree resin** | Strongly marked | Strongly marked |
| **Diesel fuel** | Unbranded | Unbranded |
| **Biodiesel** | Unbranded | Unbranded |
| **Brake fluid** | Marked | Strongly marked |
| **Coolant** | Unbranded | Unbranded |
| **FAM test fuel** | Strongly marked | Strongly marked |
| **Super unleaded fuel** | Marked | Marked |
| **Engine oil** | Unbranded | Unbranded |

Table 6.12. Results of the obtained chemicals resistance using hardener 1.

| Prototype / Solution | F | G |
|---|---|---|
| **Pancreatin** | Unbranded | Unbranded |
| **Tree resin** | Unbranded | Unbranded |
| **Diesel fuel** | Unbranded | Unbranded |
| **Biodiesel** | Unbranded | Unbranded |
| **Brake fluid** | Marked | Strongly marked |
| **Coolant** | Unbranded | Unbranded |
| **FAM test fuel** | Strongly marked | Strongly marked |
| **Super unleaded fuel** | Marked | Marked |
| **Engine oil** | Unbranded | Unbranded |

Table 6.13. Results of the obtained chemicals resistance using hardener 2

Comparing the two prototypes it is observed that changing the quantity of solvent does not modify the chemicals resistance, since only changes lightly the brake fluid.

It can be said that the chemicals resistance do not affect when it has to choose the best prototype. So, in the comparative between the prototypes F and G it can be confirmed that the best choice is prototype F with hardener 1.

## 6.3. EVALUATION OF A NEW GLOSSY FORMULATION BASE AND ADDITIVE OPTIMIZATION

In this section it has been used a new formulation base of a glossy black topcoat and it has been optimized regarding the quantity and types of additives.

First of all, it has applied the topcoat without any additive using two hardeners and it has checked which one passes the IPA test. This test consists on passing a wet cotton with isopropanol and checking if the cotton has dragged the paint. In this case, with hardener two has no spotted; however, using hardener 1 it has checked that the cotton has dragged some of the paint, for this reason to perform the tests it has opted by using hardener 2.

To improve the formula it were performed four prototypes:

- H prototype is the new formulation base of the glossy black topcoat without any additive.
- I prototype includes the new formulation base of the glossy black topcoat and an additive that is a carefully calculated blend of alkyl-alkyl modified silicones designed to improve mar resistance without the standard recoat problems of common silicones
- J prototype includes the new formulation base of the glossy black topcoat and a silicone additive made by polidimetilsiloxane modified with polyester that is used to improve the sliding surface. This additive is one that has the C prototype in section 6.1.
- K prototype includes the new formulation base of the glossy black topcoat and a silicone additive made by a solution of a polyether-modified polydimethylsiloxane, used to wet the substrate, avoiding the craters and improving the sliding surface. This additive is one that has the prototype B in section 6.1.

These prototypes also include the special phosphoric acid ester additive, that it is used to improve the adherence of the paint.

To compare the obtained results here with the obtained with the initial formula (the one for the first section), it has been performed the same tests to determinate the mechanical properties. Below are these results.

### 6.3.1. Adherence

As it is explained before in 6.1.1 section, to realise the adherence it is checked that using the correct technic, the topcoat has a great adherence with the substrate.

In all cases it has been observed, that the topcoat presents a good adherence with the substrate. On the following figures are shown the examples of the adherence test using hardener 2.

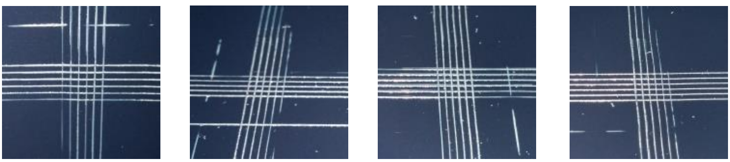

Figure 6.16. Adherence of prototypes H (left), I, J and K (right) applied with hardener 2

### 6.3.2. Pressurized water test

As it is mentioned before in *Materials and methods section*, it has been performed the test according two different standards. Below are shown the obtained results on each case.

*6.3.2.1. According the standard PV1503 of the specification TL211 from Volkswagen*

On the performing of this tests, the applied panels with the topcoat are submitted to the conditions of this standard and after the tests it is checked if some paint has detached.

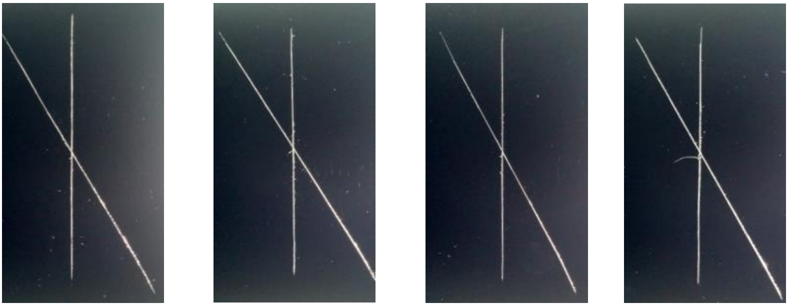

Figure 6.17. Pressurized water test according the standard of Volkswagen with prototypes H (left), I, J and K (right) applied with hardener 2

This standard does not admit any paint detachment, that is why it has been measured the detachments obtained in each case. The results are collected in the following table.

| Topcoat | Detachment of the paint with hardener 2 |
|---|---|
| **H** | 0 $cm^2$ |
| **I** | 0 $cm^2$ |
| **J** | 0 $cm^2$ |
| **K** | 0 $cm^2$ |

Table 6.14. Pressurized water test results according the standard of Volkswagen with prototypes H, I, J and K

As it can be observed, all this prototypes has a great adherence, because they have not present any paint detachment after passing the pressurized water test.

*6.3.2.1. According the standard D25 5376 of the specification B15 5050 from PSA Peugeot-Citroën*

On the performing of this tests, the applied panels with the topcoat are submitted to the conditions of this standard and after the tests it is checked if some paint has detached.

Figure 6.18. Pressurized water test according the standard of PSA with prototypes H (left), I, J and K (right) applied with hardener 2

As is mentioned before in 6.1.2.1 section, this standard admits a maximum of 1 $cm^2$ of paint detachment, therefore, has been made a detachment measure that were obtained in each case. The results are shown in the next table.

| Topcoat | Detachment of the paint with hardener 2 |
|---|---|
| **H** | 4,18 $cm^2$ |
| **I** | 0,25 $cm^2$ |
| **J** | 0,13 $cm^2$ |
| **K** | 0,21 $cm^2$ |

Table 6.15. Pressurized water test results according to the standard of PSA with prototypes H, I, J and K

As it van be observed, if they are compared with the initial prototype, this additives has a better adherence.

### 6.3.3. Resistance to scoring by abrasion

As it is mentioned before in *Materials and methods* section, it has been performed the test according two different standards. Below are shown the obtained results on each case.

*6.3.3.1. According the standard D42 1775 of the specification 47-03-003J from Renault*

In the performing of this test, it has been followed the same procedure performed in section *6.1.3.1* obtaining the following results.

| Prototype | Initial gloss | Final gloss | % gloss retention |
|---|---|---|---|
| H | 74,7 | 12,8 | 17,13% |
| I | 74,8 | 19,8 | 26,5% |
| J | 74,8 | 16,8 | 22,4% |
| K | 74,2 | 16,7 | 22,5% |

Table 6.16. Initial and final gloss obtained in carrying out the scratch abrasion resistance test of Renault using hardener 2

As it can be observed, all the prototypes present a similar gloss after the abrasion, and very low. So, it can conclude that the additives considerably improve the abrasion resistance according the Renault standard.

*6.3.3.2. According the standard FLTM BI 161-01 of the specification WSS-M16J9-B2/B3 from Ford*

In the performing of this test, it has been followed the same procedure performed in section *6.1.3.2* obtaining the following results.

| Prototype | Initial gloss | Final gloss | % gloss retention | Final gloss 24 hours | % gloss retention 24 hours |
|---|---|---|---|---|---|
| H | 75,3 | 47,1 | 62,5% | 49,7 | 66,0% |
| I | 75,3 | 47,7 | 63,3% | 53,5 | 71,0% |
| J | 75,4 | 58,9 | 78,1% | 61,2 | 81,1% |
| K | 75,2 | 53,9 | 71,7% | 59,3 | 78,8% |

Table 6.17. Initial and final gloss obtained in carrying out the abrasion scratch resistance test of Ford using hardener 2

As is mentioned previously in 6.1.3.2 section, this standard admits a gloss retention upper than 70%. So, it can be observed that only prototypes J and K pass the test. Also it can be observed that after 24 hours there are a notable recovery on the gloss, and prototype I would pass the test. Even so, the best prototypes are J and K.

Furthermore, it can go deeper more in the study of this new glossy formula. In fact, some samples of the liquid topcoat are sent to two different companies of additives with the objective of discovering other additives to improve the resistance to scratch by abrasion.

## 6.4. COMPARISON WITH THE NEW GLOSSY FORMULA BASE AND THE INITIAL GLOSSY FORMULA.

### 6.4.1. Pressurized water test

It has been selected the best prototypes, and it has collected their additive information:

- A prototype is the initial glossy black topcoat without additives.
- C prototype includes the initial glossy black topcoat and a mixture of additives in surface (the first is a dispersion of surface-treated aluminium oxide nanoparticles and the other one, is a silicone additive composed by polyether-modified polydimethylsiloxane).
- J prototype is the glossy black topcoat used in section 6.3 that incorporates the same surface additive composed by polidimetilsiloxane modified with polyester used on C prototype.
- K prototype is the glossy black topcoat used in section 6.3 that incorporates the same surface silicone additive composed by a solution of polidimetilsiloxane modified with polyester used on B prototype.

Considering the combinations of the additives, it can be deduced that the surface additive combination composed by polidimetilsiloxane used on prototypes C and J has great results in both tests, in the adherence tests and in the abrasion scratch resistance test.

Below are compared the best obtained results of the glossy topcoats (sections 6.1 and 6.3). The corresponding table with the following figure is attached on *Table 1* to *appendix* 2.

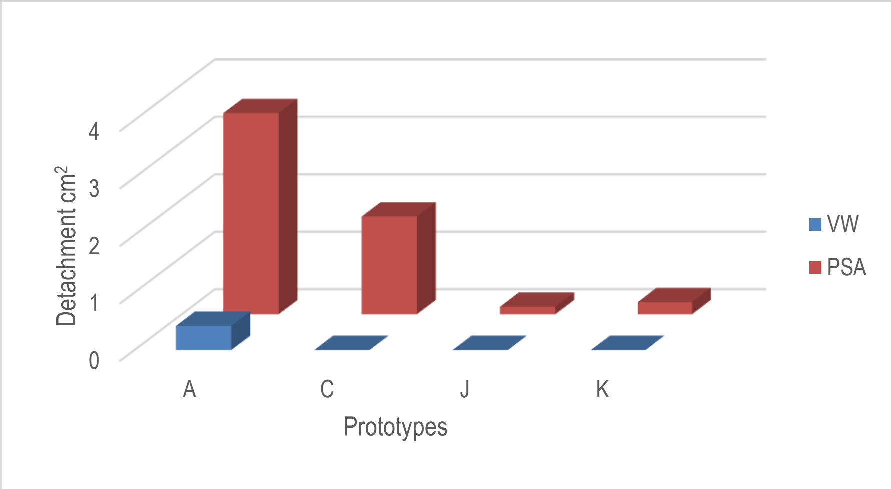


Figure 6.19. Comparison of prototypes A, C, J and K with the adhesion test for pressurized water using hardener 2

Comparing the prototypes, it can confirm that the prototypes with the best adherence are J and K, because both pass the PSA pressurized water test, while A and C do not. Considering the prototypes formulation, it can be said that the influence of the surface additive used on C prototype does lose adherence. However with the other topcoat, only using one of the additives composed by polidimetilsiloxane modified with polyester (used in prototypes J and K) significantly improve the adherence results. From all this, it can be concluded that the new glossy additivated formula base is better than the initial additivated formula.

### 6.4.3. Resistance to scoring by abrasion

Below are compared the obtained results of the best prototypes in each one of the glossy black topcoat formulas (sections 6.1 and 6.3). The corresponding table of the next figure is attached on *Table 2* to *appendix 2*.

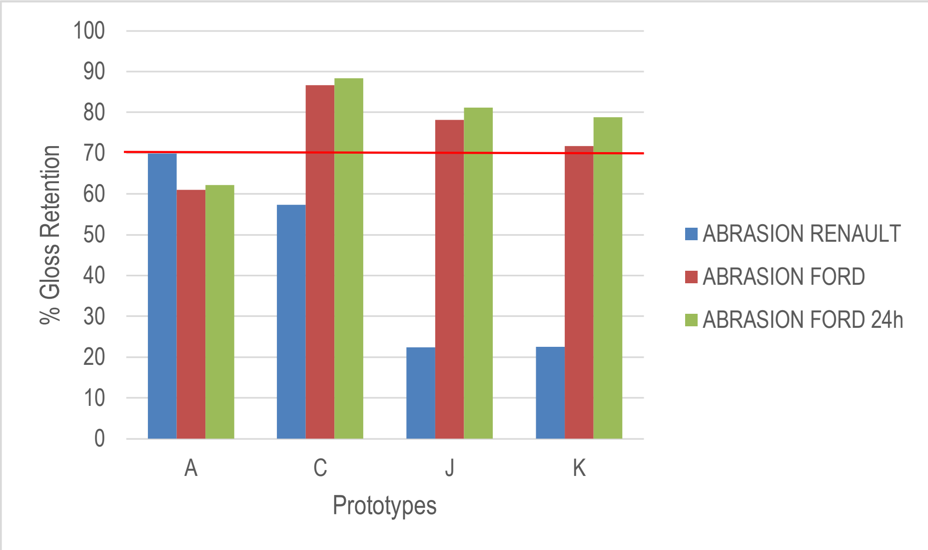


Figure 6.20. Comparison of the prototypes A, C, J and K for the abrasion scratch resistance test using hardener 2

As it can be observed, the initial formula presents a better abrasion scratch resistance according the Renault standard (prototypes A and C) than the new glossy formula (prototypes J and K). While both formulas present a good abrasion scratch resistance according the Ford standard, especially C prototype. Considering the prototypes formulation it can be observed that the additive based on aluminium nanoparticles used in prototype C with combination with the additive composed by polidimetilsiloxne modified with polyester does that the abrasion scratch resistance is better than only using the used additives in J and K prototypes, especially in the abrasion case for Renault standard.

So, the best prototype which presents a better scratch resistance is the C prototype, concluding that it is also the better choice to obtain a glossy black topcoat with an improved scratch resistance.

In short, if what it is wanted is to obtain a glossy black topcoat with a great abrasion scratch resistance, even the adherence could be better, the best choice is prototype C. However, if what is wanted is to obtain a glossy black topcoat with a great adherence and an acceptable abrasion scratch resistance, the best choice would be one of the prototypes J and K.

Given that the combination of additives used in the prototype C is the best combination to improve abrasion scratch resistance, a way to continue researching the new formulation of the glossy topcoat of prototypes J and K, it would incorporate this additives combination and check if this could improve the scratch resistance.

# 10. CONCLUSIONS

Here are shown the conclusions that have been obtained during the development of this project and that can be deduced of the three objectives set before.

The main objective of this project has been to optimize the formula of a glossy black topcoat of direct adherence on automotive plastic substrates, which is improving the mechanicals and chemicals properties of the topcoat. The conclusions that have deduced in this study according to the results are:

- The best additives combination is the one used in C prototype applied with the hardener 2, because is the one which provides a better abrasion scratch resistance, although the adherence does not improve.
- The creation of a new matt formula gives a lot of good results in mechanical and chemical properties. Although with the combination of hardener 1 gives better results than using hardener 2.
- In the new matt formulation, remove some solvent of the formula makes the adherence and the abrasion scratch resistance from Renault standard worst; however, improve the abrasion resistance from Ford standard.
- The new glossy formula gives a lot of great adherence results. It also gives great abrasion scratch resistance results, using the additives from prototypes J and K.
- Comparing the two glossy formulas, depending on customer needs, if they are interested with a great adhesion, the best choice would be J or K prototypes. However, if they are interested with a scratch resistance, the best choice would be prototype C. One way to improve the scratch resistance of the prototypes J and K, it would be to incorporate the prototype C additives combination at the new glossy formula.
- From two hardeners, it is recommended that to obtain better results on mechanical properties it is used hardener 2 in case of using glossy topcoats. However, it has

been checked that if it is used the matt topcoat, the prototype with hardener 1 responses better than hardener 2.

- It can say that the best topcoat is the prototype F, ergo the new formula of matt black topcoat using hardener 1.

# 11. REFERENCES AND NOTES

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# APPENDICES

# APPENDIX 1: OBTAINED RESULTS TABLES

| Topcoat | Detachment of the paint with hardener 1 | Detachment of the paint with hardener 2 |
|---|---|---|
| **A** | 0 $cm^2$ | 0,42 $cm^2$ |
| **B** | 0 $cm^2$ | 0,18 $cm^2$ |
| **C** | 0,35 $cm^2$ | 0 $cm^2$ |
| **D** | 0,58 $cm^2$ | 0,23 $cm^2$ |
| **E** | 0 $cm^2$ | 0,30 $cm^2$ |

Table 1. Pressurized water results test according the Volkswagen standard of the prototypes A, B, C, D and E

| Topcoat | Detachment of the paint with hardener 1 | Detachment of the paint with hardener 2 |
|---|---|---|
| **A** | 1,3 $cm^2$ | 3,5 $cm^2$ |
| **B** | 0,3 $cm^2$ | 1,2 $cm^2$ |
| **C** | 2,2 $cm^2$ | 1,7 $cm^2$ |
| **D** | 2,6 $cm^2$ | 2,9 $cm^2$ |
| **E** | 0,6 $cm^2$ | 1,8 $cm^2$ |

Table 2. Pressurized water results test according the PSA standard of the prototypes A, B, C, D and E

| Prototype / Solution | A | B | C | D | E |
|---|---|---|---|---|---|
| **Pancreatin** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Tree resin** | Strongly marked | Strongly marked | Strongly marked | Strongly marked | Strongly marked |
| **Diesel fuel** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Biodiesel** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Brake fluid** | Marked | Marked | Marked | Marked | Strongly marked |
| **Coolant** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **FAM test fuel** | Strongly marked | Strongly marked | Marked | Strongly marked | Strongly marked |
| **Super unleaded fuel** | Marked | Strongly marked | Marked | Strongly marked | Strongly marked |
| **Engine oil** | Strongly marked | Marked | Marked | Unbranded | Unbranded |

Table 3. Chemical resistance obtained results using hardener 1

| Prototype / Solution | A | B | C | D | E |
|---|---|---|---|---|---|
| **Pancreatin** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Tree resin** | Marked | Strongly marked | Strongly marked | Strongly marked | Strongly marked |
| **Diesel fuel** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Biodiesel** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **Brake fluid** | Marked | Strongly marked | Marked | Strongly marked | Marked |
| **Coolant** | Unbranded | Unbranded | Unbranded | Unbranded | Unbranded |
| **FAM test fuel** | Strongly marked | Marked | Strongly marked | Strongly marked | Strongly marked |
| **Super unleaded fuel** | Marked | Unbranded | Marked | Strongly marked | Marked |
| **Engine oil** | Unbranded | Strongly marked | Marked | Strongly marked | Unbranded |

Table 4. Chemical resistance obtained results using hardener 2

# APPENDIX 2: COMPARATIVE TABLES

| Prototype | Detachment of the paint for Volkswagen rules | Detachment of the paint for PSA rules |
|---|---|---|
| A | 0,42 $cm^2$ | 3,50 $cm^2$ |
| C | 0 $cm^2$ | 1,7 $cm^2$ |
| J | 0 $cm^2$ | 0,13 $cm^2$ |
| K | 0$cm^2$ | 0,21 $cm^2$ |

Table 1. Comparison tests of adherence of water pressure according to the standards of Volkswagen and PSA of A, C, J and K prototypes using the hardener 2.

| Prototype | Resistance to scoring by abrasion according Renault specification | Resistance to scoring by abrasion according Ford specification | Resistance to scoring by abrasion according Ford specification 24 hours later |
|---|---|---|---|
| A | 69,9% | 61,0% | 62,2% |
| C | 57,3% | 86,7% | 88,3% |
| J | 22,4% | 78,1% | 81,1% |
| K | 22,5% | 71,7% | 78,8% |

Table 2 Comparison tests of resistance to scoring by abrasion according to the standards of Renault and Ford of A, C, J and K prototypes using hardener 2.