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Avaliação e Melhoramento das Propriedades Anti-Soiling do Couro utilizado no Setor Automóvel

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POLITÉCNICO
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LEATHER FINISHING

EVALUATION AND IMPROVEMENT OF LEATHER'S ANTI-SOILING PROPERTIES FOR THE AUTOMOTIVE SECTOR

PRESENTED TO THE INSTITUTO SUPERIOR DE ENGENHARIA DO PORTO

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Orientation:
António Ribeiro Crispim

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Abstract

The present thesis was written at Stahl Holdings, B.V., in Waalwijk- Netherlands, in partial fulfillment of the requirements for the degree of master's in chemical engineering of the Instituto Superior de Engenharia do Porto (ISEP).

Stahl formulated the theme of the project, along with the interested company.

The results obtained from this project contributed to increase Stahl's internal knowledge and share it with the interested parties. This project started with the formulation of a coating system, followed by its application, consecutive tests and results evaluation.

This thesis regards the study of the anti-soiling properties of a Clean Top, by evaluating the impregnation resistance to indigo and pen ink. The tests were conducted according to the dye ingress standard of a specific OEM, soiling of a specific OEM and European VDA, using a Martindale abrasion tester, a Crockmeter and a Datacolor ™'s hardware and software. There were four samples tested, being two of them brown, two beige, and one of each color had Clean Top has the anti-soiling coat.

It was expected that the application of a last anti-soiling system would show better results to the soiling and dye ingress tests, and that its performance changed over time.

The worst results were shown by the dye ingress standard and lighter colors. The application of Clean Top improves greatly the anti-soiling properties, with small to no variation over time.

Key Words: Leather, Crust, Finishing, Indigo, Resin, Crosslinker, Impregnation, Abrasion, Standard, OEM, Formulation, Soiling, Cleanability.

Resumo

Esta tese foi escrita na Stahl Holdings, B.V., em Waalwijk- Holanda, como requisito parcial de finalização do mestrado em Engenharia Química, do Instituto Superior de Engenharia do Porto (ISEP).

A Stahl planeou o projeto, juntamente com a empresa interessada.

Os resultados obtidos contribuíram para aumentar o conhecimento interno da Stahl e partilhar com as partes interessadas. O projeto começou com a formulação de um acabamento, seguido pela sua aplicação, testes consecutivos e avaliação de resultados.

Esta tese apresenta o estudo das propriedades anti-mancha de um topcoat, testando a resistência à penetração de indigo e tinta de caneta. Os testes forem realizados de acordo com as normas de impregnação de corante de uma montadora específica, manchamento de uma montadora específica e a norma europeia VDA, utilizando o equipamento de abrasão de Martindale, um crockmeter e o equipamento e programa da Datacolor^{TM}.

Era esperado que a aplicação de uma última camada de anti-soiling mostrasse resultados substancialmente melhores ao manchamento e à penetração de corante, e a sua performance mudasse com o tempo.

Os piores resultados foram obtidos na norma do dye ingress e em cores claras. A aplicação do Clean Top melhora consideravelmente as propriedades anti-soiling, com pouca a nenhuma variação com o tempo.

Palavras-Chave: Couro, Semi-Acabado, Acabamento, Indigo, Resina, Catalisador, Impregnação, Abrasão, Normas, OEMs, Formulações, Manchar, limpeza.

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Glossary

Auxiliary- Levelling and penetrating agents.

Beamhouse- Section of the tannery where hides or skins are prepared for tanning, which includes, among other processes, the operations of soaking, unhairing, fleshing and deliming.

Chemical Resistance- Ability to withstand attacks from several products, keeping its visual properties and protective functions.

Coating- Compositions of polymeric film forming agents, pigments and additives.

Crosslinker- Additive that helps the cohesion and adhesion of resins, ensuring the necessary fastness properties of the leather surface.

Crust- Leather, which is tanned, dyed, fatliquored and dried, before finishing.

Embossing- Printing of artificial grain structure.

Finishing- Mechanical operations, followed by covering layers to the leather surface.

Ford Cup- Measures the time needed by a certain fluid to pass through an orifice located at the bottom.

Full Grain- Leather having kept its entire grain, with none of the surface removed by any corrective treatment.

Grain- Outer side of leather once the hair or wool and epidermis has been removed, characterized by specific patterns, depending on the animal species.

Hide- Pelt weighting over 15 Kg.

Leather- Hide or skin with its original fibrous structure more or less intact, tanned to be imputrescible.

Leuco Dye- Dye able to switch between two chemical forms, one of which colorless.

Resin- Film forming agent, that provides adhesion to a substrate, binds pigments and extenders together, determining the durability, gloss and flexibility of the leather.

Skin- Pelt weighting less than 15 Kg.

Texapon- Cleaning product, derived from natural fatty alcohols.

Thickener- Substance that increases the viscosity of a liquid without changing its properties.

Abbreviations

CT- Clean Top

GS- Gray Scale

MRSC- Manufacturing Restricted Substances List

PDMS- Polydimethylsiloxane

OEM- Original Equipment Manufacturer

WR- Water Repellent

XR- Crosslinker

ZDHC- Zero Discharge Hazardous Chemicals

1. Introduction

Man has exploited the unique properties of skin and leather for thousands of years, and almost every culture has developed exclusive techniques to use this promptly accessible material for a wide assortment of purposes. Tanning has been depicted as man´s first manufacturing process.

Leather is a material used in the assembling of various items, where it plays a major role, and is often the main material input. These may include shoes, bags, clothes, furniture, covering of cars, planes and boats, as numerous different other things of daily use. Different applications need a different kind of leather. At the core of the leather making process is the raw material, hides and skins[1].

1.1. Stahl

Stahl is a multinational company, running as a market leader in process chemicals for leather products. Stahl also produces polymers and performance coatings for several other industries, like textile, paper, plastics, rubber, metal and wood, and provides innumerous solutions for the automotive, apparel and home interior sectors, as well as for industrial applications[2].

In 2018, Stahl´s sales went over 850 million euros, and was present in 27 countries, with 2050 employees. Stahl has 38 application labs dedicated to investigation and development and 13 manufacturing sites. Stahl is the world leader in leather finishing products and is exploring high performance chemical coatings on other substrates.

Stahl has R&D departments across Europe, focusing on a wide range of areas. These laboratories explore the nearby raw materials. Stahl has also fashion departments, which are in Italy for upholstery and clothing items, and in Germany for automobile fashion.

Stahl is a material manufacturer, or Tier-3, that supplies chemicals for the leather production industry, Tier-2. Stahl's vision is to build partnerships with both the OEM and the Tier 2 industry, to develop and improve product solutions that is of interest for all parties. Stahl does this by offering prompt technical service and sales support anywhere in the world.

With sustainability being one of the most important themes of discussion, must of Stahl´s products comply not only with mandatory standards, such as Zero Discharge Hazardous Chemicals (ZDHC) and Manufacturing Restricted Substances List (MRSL), but also with internal standards targeting a wider range of chemical substances. The portfolio featuring these products is called Stahl Neo and is intended to comply with future international standards[3].

1.2. Theme

To get the most of such a luxury material, the leather finishing plays a crucial role, and is fair to say that the finishing is the part of the process that really adds value to the leather. Different applications require different properties from the leather.

The leather used in automotive industry, must be tough to be able to endure the constant wear, general dirt and chemicals used in cleaning, clothing (such as indigo dye) and present in the body, like sweat, moisturizers or self- tanners. These are problems that didn’t exist as much in the past and that the industry must adapt to and overcome them.

This project was fully dedicated to the study of a chemical solution applied during the finishing process that could potentially refine the level of resistance to indigo, which is a dyeing compound that bleeds from jeans.

The scope of the project was to evaluate the life cycle of the Stahl’s anti soil system after its application on leather. The performance of the finishing was assessed by testing the dye ingress and soiling, accordingly to three different standards and the pen ink cleanability. To assure the finishing performance in time, samples were evaluated, in a first phase only soiled and cleaned to see how the curing affects the soiling and then in cycles (soil, clean, repair- repeat).

After a few months of testing, it was decided to improve the finishing formulation, by optimizing the concentration of products that were already being used.

1.3. Objective

The purpose of the anti-soiling finishing on cars is to improve the practical use of the leather by protecting it from damage by water, soil and mechanical action, while keeping the handle, gloss and overall appearance of the finished leather.

The aim of this thesis is to test and evaluate the robustness and resistance performance of a leather anti-soiling finishing. This finishing must be capable of permanently change the material, making it resistant to a wide range of chemicals, especially indigo, and obtain good results when tested. Leather used in the seats of public transportation is exposed to rough use, and staining is often a problem, which must be overcome by the finishing.

In the automotive sector, the leather is exposed to an added number of factors, that upholstery and household items are not. These factors can be chemical or physical and are problems that car and public transportation manufactures simply can´t afford, since it is expected that the leather used lasts the entire useful life of the car, train, bus or commercial jet.

The automotive leather begins to stain over the constant use. This stain comes from the chemicals used in jeans, and can stay impregnated in part of the finishing, making it hard to remove without damaging the leather finishing properties. To find a solution to this problem it was made a formulation, and applied to the leather, that was then subjected to a series of trials to test its integrity.

1.4. Overview

The present thesis is organized in five main chapters. First the introduction gives an idea of the overall study, explaining what the purpose of the thesis is. Then follows the background that holds the review of the literature that describes the context of the problem, current perspectives, and the central aspects of theory and practice. It also provides the knowledge for the reader to understand and situate the work developed. In the body of the thesis, the context of the study is fully explained and sets up the current state of understanding in the field. The results chapter shows the entire outcomes of the tests made, as well as formulations and data treatment. In discussion, the results are analyzed and explained, followed by the conclusion and finally the appendix chapter, with all the extra data relevant to the study.

2. State of Art/ Technology

Although most of the basic operations in industry of leather production and transformation are still the same, it has undergone a series of fairly important changes, in order to make major improvements in the field of quality and environmental impact[4].

Skin is the largest organ of any animal, and being such a complex interface structure, it handles the protection, regulation and sensation of the organism. A close examination to the composition of a piece of skin proves that it has long thick filaments and fiber packs entwining in three dimensions within a jelly like ground substance (as shown in Figure 2.1). Different structures, for example, hairs and hair-roots, muscles, veins and fat cells can be found in skin, but it’s the three-dimensional woven structure that prevails and gives skin-based materials it´s exceptional physical qualities, such as flexibility, low bulk density, good heat isolation, water vapor transmission, resistance to tearing, puncturing, abrasion and shock loads. Leather is also a material easily moldable, stretched and compressed. All of these are qualities of great value in a wide range of applications[1].

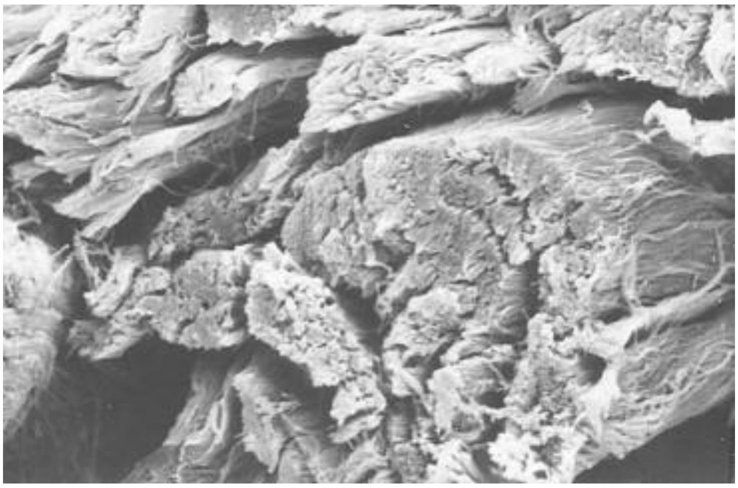

Figure 2. 1- Fibers and fiber bundles of collagen[1]

The tanning process aims to turn putrescible organic matter, into a product of greater value, with the necessary properties to be used by other industries. Preparing procedures and sophisticated treatment have a vital function in enhancing the competitiveness and environmental performance[4].

2.1. Global Industry

The worldwide leather production derives 95% from the processing of raw hides and skins of bovine, sheep and goats, 4% from pig skin, and the residual 1% comes from other animal typologies such as reptiles, kangaroos, fishes or deer. This data shows that 99% of the world leather production uses raw hides and skins of animals raised for milk production and/or meat production[5]. From this, it´s reasonable to assume that the leather production depends on the animal population, and rate at that they are slaughtered. On a global scale, 85% of the cattle inventory is found in India, Brazil, China, United States and European Union.

Cattle bred in Europe and in nations with comparable systems of animal farming, endure less skin damage than those kept under herding or ranching systems. For this reason, their hides offer higher yield of useful leather and are less prone to damage and contamination with unwanted chemicals, like prohibited pesticides or hormones.

The major raw skin production centers don´t necessarily coincide with main leather production centers, and subsequently there is a need for suitable means of transport and storage. Raw hides and skins are exchanged in a salted condition, but are progressively being trade as middle products, particularly in "wet blue" for bovine hides and the pickled state for ovine skins[6].

While European hides and skins are progressively being sent out, European tanners are facing hindrances to the entrance of their raw material from developing countries. These trade barriers consist on taxes and export-restrictions on raw hides, skins and "wet blue". From the globally available raw material, only 40% enters the free international market, which becomes susceptible to demand shortage and financial problems such as price volatility and dual pricing.

Developing countries have changed from exporters of hides and skins, to importers, reflection of the tannery capacity. Consequently, developed countries position towards the trading market has changed. In 2004 the European Union has become a net exporter of raw bovine hides. Being the main center of leather production in the world, the EU´s is starting to have serious competition in Asia and South America. EU´s is the world´s largest supplier of leather, and its top supplier of raw hides and skins is the United States.

Italy alone accounts for over 60% of the European leather production, and 15% worldwide, and is the most important leather location in Europe in terms of employment, establishments and production.[6].

The presence of the leather industry in some locations across Europe tend to make the entire region finances rely heavily on this sector´s activity. The increase in the use of imported intermediate materials, for example wet blues, means that some steps of the leather making process are done in other countries, particularly third world countries. This change, apart from the financial problems, has two environmental consequences. First it transfers the environmental impact to other countries, leading to a pollution unbalance. Secondly, chemicals that are banned in Europe, may appear in the effluents of finishing plants[4].

2.2. General Process

The whole goal of the tanning process is to keep the skin natural properties, stabilize its structure and to make it resistant to putrefaction. The protein fibers present in the skin can move when the skin is alive. When it dies, these fibers tend to shrivel and stick together, making a stiff substrate with a small useful life. The tanning process permanently fixes the fibers apart by chemical treatment and lubricates them so they can move in relation to one another, turning the leather into a flexible substrate.

In the slaughterhouse the hides and skins are temporarily treated/ preserved to keep their quality until further processing. The preservation protects the raw material from attacks by micro-organisms and makes it storable for a prolonged period. Although the most common method of preservation is salting, the hides and skins can be cured by drying, pickling or freezing[7].

At the entrance of the beamhouse, the raw materials are called hides and skins. At the entrance of the tanning process they are called limed hides and skins and leave as tanned leather. It enters in the finishing process as crust leather to finally become finished leather.

The leather production consists on the following steps:

Soaking- Restores the natural swollen condition of the skin and removes dirt, soluble proteins and curing agents.

Unhairing and Liming- The hides are immersed in a solution of alkali and sulphide, removing the hair and its root, along with the epidermis and altering the properties of the collagen. The collagen swollen, becoming thicker and opening its structure.

Splitting- While swollen, the grain is separated from the split.

Deliming- Removal of lime and correction of the pH.

Bating- Further loosening and peptizing of the fiber texture of the skin and elimination of alkali-swelling with the aid of specific enzymes.

Degreasing- Fats and grease are removed from the interfibrillar space with the use of lipases, detergents or solvents. Degreasing helps to make leather soft and pliable when used for other purposes.

Pickling- Acidification of the pelts to a low pH, destroying the microorganisms and suppressing their growth, making the hides and skins stable for tanning. Pickling is also used for conservation.

Tanning- Stabilizing the skin substance that is prone to putrefaction, by stabilizing it against enzymatic degrading and increase its resistance to chemicals, reduce or eliminate its ability to swell, enhance strength properties, reduce its deformability and enhance the porosity of its fiber texture. This is the most chemically complex step, and changes depending on the type of tanning.

Neutralizing- The free acids present in mineral tanned leather are removed.

Retanning- The leather is often retaned to give it a uniform fullness with selective filling of the structure and to give a tight and uniform grain surface.

Fat Liquoring- The fiber elements dehydrated by tanning are coated with a fat layer to give the desirable softness and handle. Fat liquoring influences the physical properties of the leather, such as permeability to water and air, tensile strength, extensibility and wetting properties.

Dyeing- The hides are soaked in a mixture of water and coloring substances, which helps the fibers to absorb the mixture.

Drying- The water is removed from the leather, and its chemical properties stabilized.

Finishing- A series of processes and operations that improve the properties and appearance of the leather and finally turn it into an exquisite material.

Grading- Before being dispatched the leather is graded according to color intensity and uniformity, feel, softness, visual appearance, thickness, design effects and defects.

Measurement- Nearly all leather is sold by area (usually square feet), measured by machine.

Leather production uses massive quantities of water and are being made efforts to reduce this impact. Leather-making is now a scientifically based industry but keeps some of the original craft. The leather industry has several types of processes, but it only changes some of the procedures[8].

2.3. Leather Finishing

Finishing determines the appearance. This step includes chemical processes like waterproofing, wax dressings, coloring, and mechanical processes such as ironing or leather embossing.

The finishing of a leather may vary depending on the final use for it. Skin usually have defects, and to correct the grain, these are buffed to remove the natural grain structure, and printed with a different pattern, depending on the final customer and use of leather. In this process, much of the natural look gets lost. Damaged leather requires thicker films, making the leather more plastic-like. To contradict this phenomenon, giving it a natural feel and look, the leather is embossed with an artificial grain and milled[9].

The purpose of the finishing is to improve the serviceability of the leather in general by protecting it from damage by water, soil and mechanical action, improving its physical properties such as rub fastness and lightfastness, modifying shade, handle, gloss, levelling out patches and grain faults and to apply an artificial grain printing.

To choose the best finishing it must be taken into account: the end use of the leather, the specifications required, the suitable crust for the purpose, the country where the leather will be sold, if it´s going to be full grain or corrected leather, the application equipment available and who is the customer.

The finishing basic process is described in the figure 2.2. Before applying a finish, the crust (leather without finishing) undergoes several mechanical processes to prepare it for even coating system. After the mechanical processes, is then applied a base coat, a color coat and finally a top coat[7].

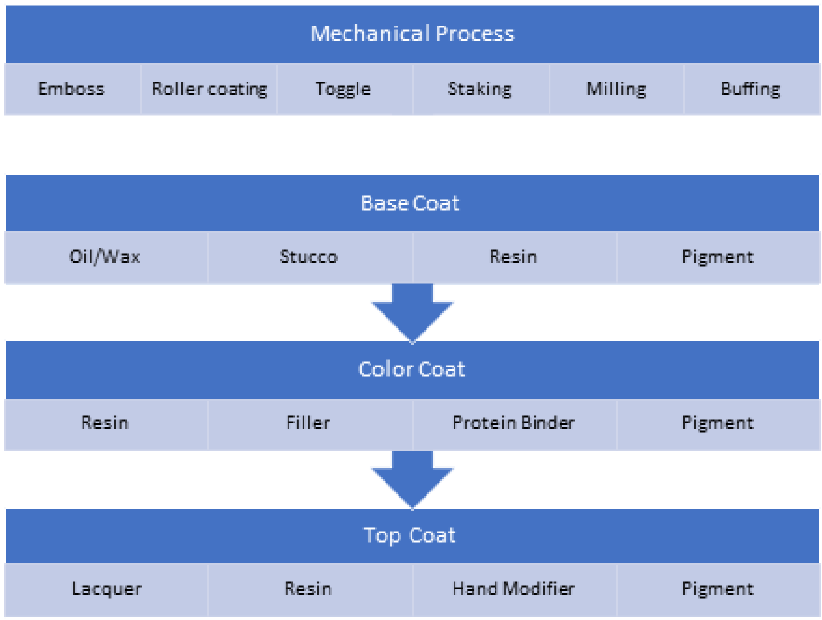

Figure 2. 2- Finishing Process[10]

Some mechanical processes, such as embossing, staking and milling may be done after the application of the base coat.

The finishing dictates most of the final requirements of the leather such as, flexes, abrasion resistance, adhesion, light fastness, water repellency, fogging resistance and heat resistance.

The finishing can be classified according to the main material used, the finishing effects or the application technique. These classifications are explained further.

2.3.1. Materials

The common structure of a conventional finishing can be divided into 5 sections. Firstly, the stain coat changes the color of the crust. Then the impregnation coat tightens the grain and impart a settled appearance and smoothness to the surface. The base coat consists of pigments, resins and auxiliaries to adhere the entire finish system. The color coat is to correct the color and imperfections. It confers the desired appearance and levels the leather surface. The last coat is the topcoat. It determines the ultimate appearance and the hand of the leather surface and helps improving chemical resistance and mechanical properties of the finish system[11].

The finishing system is made up of solvent-based or water-based products. The entire finish is built for properties since the base-coat, and it should be hard and compact, to provide the desired rub fastness, but as soft as necessary so that the leather may flex and stretch without breaking[11].

The three-coat system is shown in the figure 2.3. Aniline leather, is full grained leather with a finish addon less than or equal to 0,01mm[12],

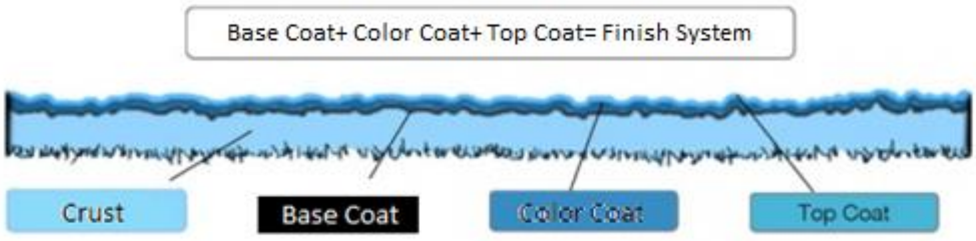

Figure 2. 3- Structure of the leather coloring and finishing[13]

It is desirable in all phases of leather finishing that the requisite resins may be applied in simple processes and ideally without solvents and with few crosslinking components, if any. The goal is that in general the final finishing operation should employ just a single resin. In the case of automotive leather, it is necessary to use additives to improve some properties due to severe exposure of the leather[11].

Resins are used extensively in leather finishing. The main components of a coat are organized in the figure 2.4 and explained further.

Pigments (used for coloring)	Cariers/ Resins	Fillers	Protein binders
•Organic •Inorganic	•Acrylic •Urethane •Butadiene •Compact •Hybrid	•Oil •Wax •Colloids	•Natural •Synthetic

Figure 2. 4- Main components of a finish system[10]

- Pigments

The most common additives are pigments, which are used to color the finishing and can be organic or inorganic.

Inorganic pigments are dull in color, have an exceptional light fastness, thermal stability, high opacity, resistance to bleeding and chemicals. Organic pigments, on the other hand, are brightly colored, variable heat stability and light fastness, poor opacity, inconstant resistance to chemicals and bleeding, and are difficult to disperse[9].

- Carriers/Resins

Overall, these components have a good adhesion, flexibility, cold and wet resistance, embossing and plating properties, UV resistance, pigment binding properties, fill and cover defects and aesthetic properties.

Acrylics have a natural feel and appearance, a good adhesion, flexibility, UV resistance and pigment binding properties and are solvent resistance. Their weaknesses are low filling properties and low wet fastness.

Urethanes have a high cold resistance, high flexing properties, good coverage, uniformity and filling, good abrasion and UV resistance, and good adhesion. They also have low wet resistance and a high grain coverage[10].

The strengths of butadienes are good cold and solvent resistance, good filling properties, good covering of defects, good flexibility and can make an elastic film. They have low adhesion, low UV resistance and low pigment binding ability.

Compact resins are simple to use, have a high performance but a low range of applications and need careful demand forecast.

Hybrids are used for their good defect coverage, plating-embossing properties, good flexes, cold properties and good filling properties. Their high grain recoatability and dry milling are their weaknesses. Hybrids are used as a general-purpose resin and in high-performance finishes. In foamed finishes, they upgrade lower grade corrected leather and have an excellent plate release, deep prints without cut-through. Can be used in high performance splits, for example for steering wheels[10].

- Fillers

Fillers are used to give leather peculiar features, such as softness, resistance to rubbing or abrasion.

Oil fillers softens the grain, gives the leather a pull-up effect and obstruct the dry film from going into the grain. Wax fillers give the leather a softening, natural finish, used to make soft products. Colloidal fillers are good for plating, piling and power use.

- Protein binders

Protein binders can be natural or synthetic. Natural proteins are mostly albumins from eggs and caseins from milk. They make a hard-glossy film. Synthetic proteins are hard or made soft in the laboratory and carry pigments. They are not thermoplastic.

- Water

Water make up for most water-based product composition. In case the penetration is not good enough, penetrator or alcohol are used. The use of pigment in the finishing will affect the color, make the mix thinner and will affect the pigment/resin ratio[10].

- Stucco/ Pre-base/ Upgrading

Leather has often a number of natural markings which require a mask to ensure their high quality. This is done by covering or filling them by hand or roller coating, with a white paste called “stucco” before removing the top part of the grain. After the stucco application, the upper part of the top grain is then removed using abrasive sandpaper to smooth the surface, removing most of the natural markings.

- Impregnation

When the fibers that make up the leather need to be arranged, it is used an impregnation resin that penetrates the loose areas and sticks the fibers together. Because of the heat and pressure, the layers will be thermoplastically glued together. Impregnation resin is exceptionally fine but sticky[10].

2.3.2. Application methods

The application of the leather finishing can be done using sprays, curtain coatings or roller coatings. The schemes for each of these applications are seen in figures 2.6 to 2.8. Coating can also be applied by pad coatings, but it’s an application method that is rarely used, where the finishing is applied with a push pad. This method, usually, involves the use of a wooden board covered with soft velvet cloth and is done by hand.

The most used method of finishing application is spray. Here, the finishing solution is fed through a fine jet to the atomizing zone of the spray gun and applied to the leather in a finely dispersed form. This application is conducted using a multi-spray gun machine supplied by compressed air. Figure 2.6 shows the schematic of a hand spraying gun.

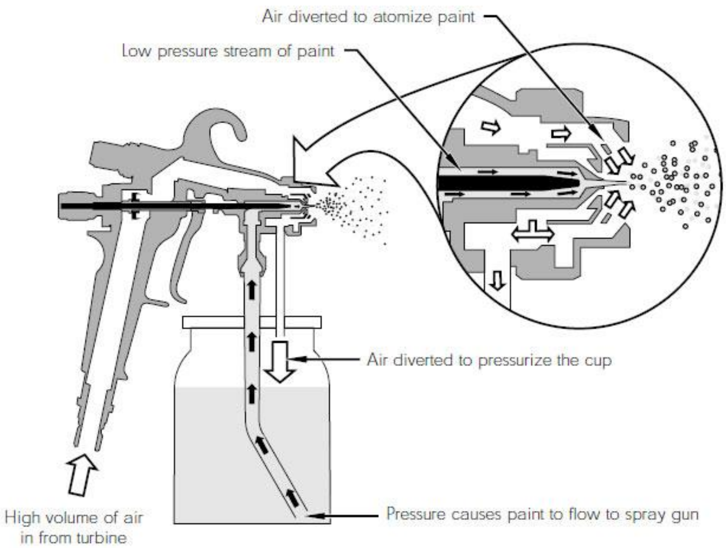

Figure 2. 5- Compressed Air Spraying Gun [7]

Curtain coating involves the application of the finishing in the form of a liquid curtain. This application is particularly useful for applying thick layers of coating, although their use in the industry is limited.

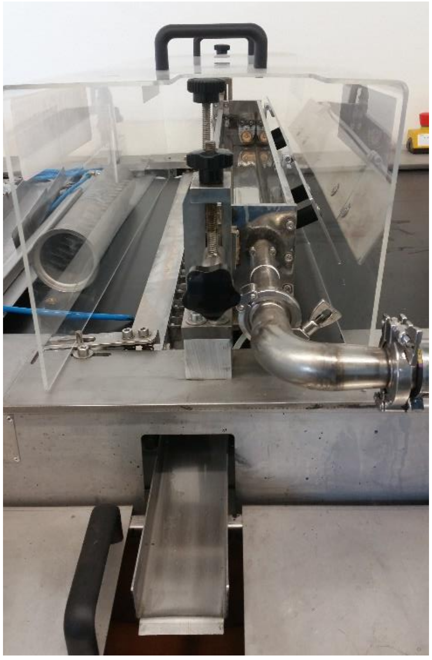

Figure 2. 6- Operating curtain coating [7]

Lastly, the roller application technique is applied by passing the leather between two cylinders, one of which is covered with the desired finishing that is then transferred to the leather[9].

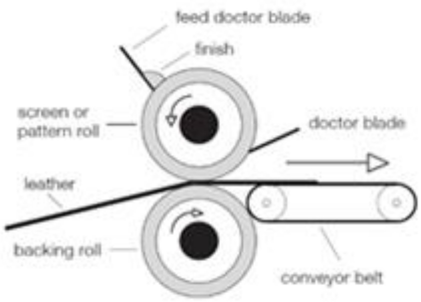

Figure 2. 7- Roll coater application [7]

The finishing should be worked from soft in the base to harder in the top, to give the best break in the grain, and avoid structural defects.

2.3.3. Finishing effects

Leather can have multiple finish effects, and although it has no real significance for the application, it has a fashion-oriented importance. The final effects or look of the leather offers it unique properties that gives the leather an added quality that customers might be looking for. The most common effects are the following:

Glaze finishes- There are based on protein binders, and their films are hard, not stretchy or water resistant. Only very thin films are applied, and the leather becomes brighter.

Pull-up or wax finish- Oils and/or waxes are applied on the full grain or corrected grain leather directly. It is followed by plating hot or polished. Surface becomes darker, and by flexing or pulling, the oil is pushed out of the grain and the color gets lighter.

Polishing- Closes the grain of soft leathers.

Rotopress/Plating smooth- The thermoplastic finish parts melts into the grain and form a soft and glossy film that follows the grain, improving the touch and the physical properties. Plating after the adhesion coat gives a better seal of the surface.

Embossing- It transfers a negative design, leaving a sort of a stamp on the leather. It is influenced by the humidity of the leather, temperature, pressure, time and speed.

2.4. Quality Assurance

Quality assurance involves the design, communication with customers for product development, purchasing and monitoring of raw materials, the manufacturing processes, testing and inspection of the finished product and finally customer satisfaction after delivery.

Leather quality is affected by the gender, age, nutrition, feeding and general care of the animal. Adding to this, the used given to the leather affects the quality and treatment needed by the skin. Skin quality tend to be better in younger animals, bred in harsh and cold climates with access to fresh forage and closed, controlled confinements. Animals bred in open fields are exposed to insect bites and sharp butches and sticks that increase the defects of the skin. The structure quality of the skin´s fiber is worst in older and female animals.

The leather used in furniture should be soft, warm and easy to maintain. Show leather is supposed to be robust, waterproof, soft and breathable. For cars, leather should be resistant to cold, heat, wear and non-reflectable of light. Independent from the application, leather must be easy to clean and durable. It should not bleach, tear, smell unpleasantly, or contain pollutants[13].

However, it can´t be expected that the leather is soft, robust and easy to keep all at the same time. It also can´t be ultra-thin, soft and tear-proof. It is often expected that expensive leather is easy to clean and maintain. Unfortunately, it is quite the opposite. Valuable leathers are very sensitive, and the regular use diminishes the beauty, while improper cleaning easily ruins the material.

The actual conditions of wear during the life of the automobile is not easy to simulate in laboratory, and each OEM has its own test methods. Added to this, the climacteric conditions around the world vary very significantly, and the test methods must take this into consideration. Car seat covers have high abrasion requirements, whereas parcel shelves and dashboards have the highest lightfastness and UV degradation resistance requirements[15].

2.4.1. Soiling and Cleanability

Soiling is the constant and regular exposure of leather to contaminants. The most common contaminants are dust, carbon compounds, oils and dyestuff from textiles. Staining is an accidental contamination of a leather product and can be dynamic such as the dye ingress and soiling tests, or static like pen ink staining, lipstick, sauce and coffee. Lighter colors have a higher tendency for soiling.

In the automotive industry, soiling and cleanability is of relevant importance due to the high wear and performance expected from the leather[16]. These factors are evaluated by applying on leather samples products that are likely to interact with a daily used car fabric. The procedures for testing differ from OEM and final application of the leather (steering wheel, seat, front panel, …).

The standards explain extensively the procedures, materials and equipment to be used, so everything is standardized.

Soiling and cleanability have a major effect in discoloration, which is one of the main sources of customer complaint. To evaluate the resistance to soiling, it is evaluated the change in color, usually using the greyscale.

Color fastness is usually assessed with respect to changes in color of the sample tested or staining of dyed material bleeding out color, which is in contact with the specimen during the test[17].

2.4.2. Automotive Articles

Car leather is known for being robust. To be used in cars leather must pass extremely tough tests, that include resistance to wear and daily-use chemicals (like sun lotion and moisturizers), be extremely durable and the leather gloss must be low. With all this, it is hard to produce leather warm and soft to the touch. The art of finishing plays a more key role in automotive leather than in any other type of leather.

To obtain the desirable qualities out of the leather, both the tanner and expert on the application should set up their own verifiable quality parameters. The tanner then makes the proper arrangements to have viable batches, which are prone to changes depending on the origin of the raw material, section of the skin and minor changes during the process. The degree of differences from on batch to another rest on the quality control limits[13].

Leather is no longer a material exclusively found in luxury vehicles, as buyers of mid-range vehicles are increasingly choosing a leather interior design. Leather can be used in steering-wheel covers, head rests, seat covers, gear lever, dashboards and doors panels.

When choosing a pigment, it must be considered the covering properties. In automotive leather it is requested that the grain defects are extensively corrected and that the leather have a high color consistency. These effects can be met by inorganic pigments, or organic pigments in a combination with inorganic pigments or special additives, such as pigment extenders or matting agents.

The fastness of the leather is especially important in the automotive leather, due to their organic structure, and tested for migration fastness. Lightfastness and heat resistance should be tested in advance. The VOC emissions should be low, and its value is dictated by the OEM and the country where it is produced.

2.4.3. Production of Automotive Leather

Leather used in economic cars are different from those used in executive vehicles. In economic the leather most be fully robust, and capable to withstand bad uses and treatments. On the other hand, executives are usually appreciated for the design, making the leather more elegant but with better touch and natural look.

For steering wheels and shift sticks is used splits. The requirements are often tougher, demanding a thicker finishing that make it harder to keep the hand/feel.

To withstand the tough tests required by manufactures, automotive leather has several key points that should be considered, as listed in figure 2.9.

Beamhouse

- No grain defects
- No neck folds
- No hair roots

Tannage

- Tendency to use Wet White tannage

Retannage/ Dyeing

- High perspiration strengh
- Fine and even break after miling
- High resistance to migration
- High tensile strengh and tear resistance
- High lightfastness and heat resistance
- High hiding power for grain defects
- Usually black, grey or beige shades

Fatliquoring

- Low-fogging products
- Neutral odour
- High resistance to high temperatures
- High tensile strengh and tear resistance
- Products with soft touch but not stretchy

Finishing

- High hiding power of grain defects
- Low-VOC finishes
- Low formaldehyde content
- High wear resistance
- High resistance to ageing

Figure 2. 8- Quality control factors for automotive leather production [7]

2.5. Current Knowledge and Methods

In the development of a finishing, there are several specific requirements that must be fulfilled. The technician starts by stating the problem and based on the requirements narrows down the products to use in the formulation. The formulation is then produced in a pilot scale and applied to a leather sample. The finished leather is then dried and cured, and taken to the test laboratory, and verified for the customer's required tests[20].

The lab results are compared to the specifications of the problem, and normally it must be optimized several times until it meets the final form. The formulation is a recipe, containing all the components and procedures for each layer of finishing, as well as a brief description of the process or product.

A formulation is nothing more than a mixture, being composed of two or more components. When the total weight of the product stays the same, then the component proportions are not independent. If the proportion of one increases, than the proportion of the rest will decrease[21].

In the formulation, there are some physical parameters that influence the properties of the finishing, like ratios and particles size. The chemical composition and physical-chemical interactions are also important for good adhesion and cohesion.

All components fulfill special functions in the liquid product and in the solid finishing film. After drying and curing the finishing, only the solid (non-volatile) content remains, so certain parameters such as ratio of resins, pigment or fillers are always referred to the solids content[20].

There are several factors contributing to soiling, being accelerated ageing one of them. To evaluate the weather resistance and curing effect, samples are tested during a long period of time in soiling and cleaning cycles.

2.6. Wrap up

The leather type is set up early in the production process, directed by the quality of the raw hide. Most of the times, the early steps of the process determine if the leather will end up as an aniline, semi-aniline, covered, grained or corrected grain leather. The following figures show the diverse types of top grain, in cross-sections.

Aniline leather is the most natural, soft and graceful of all leather types. It becomes more beautiful with age, with natural patina developing a deep character over time[19].

The surface coating does not contain pigment and is very thin, so they absorb moisture, but can last a lifetime if its cared correctly[12].

Figure 2. 9- Aniline Leather[19]

Semi aniline leather combines durability with the soft handle of natural leather. The coating layer helps to protect, smooth and create an even coloration while still letting it breathe. The pores remain open and it’s a good alternative to heavy duty applications[19]. The finishing of a semi-aniline leather contains a very small amount of pigment[12].

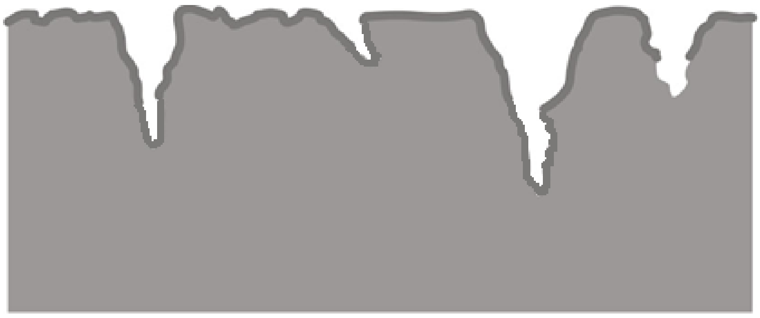

Figure 2. 10- Semi-aniline leather[19]

Pigmented leather is covered with a layer of colored pigment and provides a uniform appearance with no natural markings. Over the coloring layer, it´s applied a protective coating which gives greater control over the desired performance, such as resistance to scuffing or fading. Covered leather displays excellent lightfastness and is mostly used for commercial furniture upholstery and transport applications[19].

Figure 2. 11- Pigmented Leather[19]

The grained leather has the surface covered with resin and pigment and then embossed with a small grain plate, that gives the leather a uniform grain appearance[10].

Figure 2. 12- Grained Leather[19]

Corrected grain leathers are made from lower quality hides but requires more processing and intervention. The natural grain is completed removed by buffing the leather grain surface, which is then covered with multiple layers of pigment and protective finishing. It is then embossed with a uniform grain pattern that makes the leather lose softness, because the pores are closed[19]. The figure 2.14 shows corrected grain leather, where the grain is buffed and the surface printed with a negative pattern and finished.

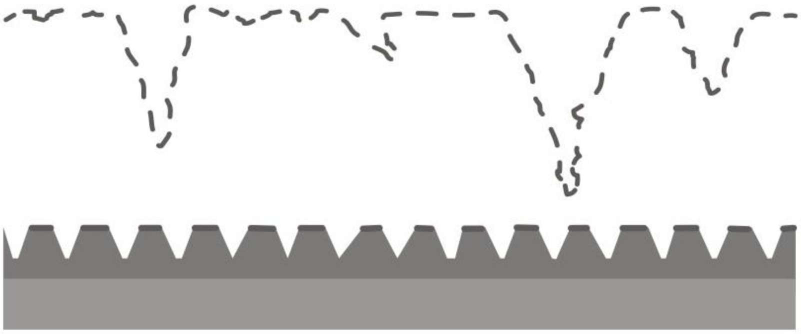

Figure 2. 13- Corrected grain Leather[19]

2.7. Vat dyes- Indigo

Vat dyes are derived from anthraquinone or indigo. Indigo is manufactured in mass production synthetically, and tends to dye the surface of the fiber, giving the textile the typical denim effect.

These dyes are water-insoluble and contain at least two carbonyl groups that enable the dyes to be converted by means of reduction under alkaline conditions into a corresponding water-soluble leuco dye.

Once dyeing is complete, the oxidation necessary for the development of the shade is achieved by washing in cold water or by treatment with an oxidizing agent such as hydrogen peroxide. The final process is soaping with a detergent at 100°C to remove any loose pigment and is essential to give both the true shade and best color fastness[18].

Indigo ($C_{16}H_{10}N_2O_2$) is used as a dye for cotton yarn, which is mainly for the production of the denim cloth for blue jeans. Indigo is insoluble in water, alcohol or ether, but soluble in DMSO, chloroform, nitrobenzene and concentrated sulfuric acid.

Indigo is an issue because nowadays lighter leathers are being used more often, and most of the persisting staining comes from this dye, which is not fixed in jeans cloth.

3. Methodology

The project hereby described, intends to study the performance of a solution to the ingress and soiling of dye present in jeans-Indigo- in time. Although there are no procedures, it was also studied the effect of pen ink in the leather, which might be a problem in leather used in public transportation. These problems were presented by an OEM to a Tier 2, which was then undertaken as a project by Stahl. Different OEM's require different standards. These soiling problems are more common in light colors.

To better understand the results showed by anti-soiling trials, it was decided to use light colors- light beige and brown, as shown in figures 3.1. To make these colors, it was mixed several pigments, which were then used in the formulations.

It will be described further the formulations used, procedures, equipment and tests made to the leather samples.

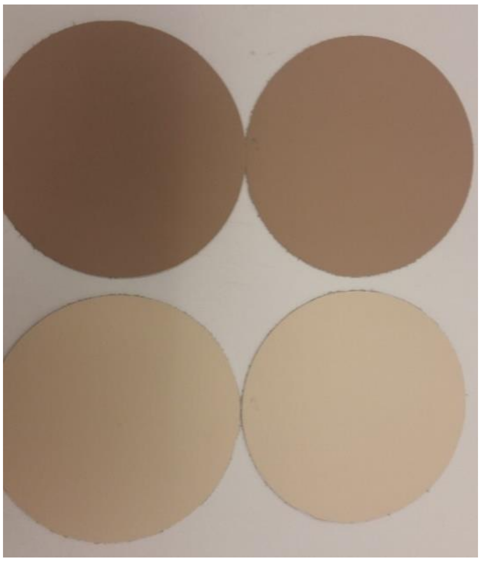

Figure 3. 1- Samples for testing (Samples with clean top on the right)

3.1. Formulation

To solve the problem of indigo transfer to the finish, it was used a typical formulation for base coat, color coat, top coat and added a last anti-soiling coat. There are several products in Stahl's catalogue, but to have a desirable finishing, the formulations must include products that will provide the required leather feel, look, physical resistance and chemical resistance. The formulations used are shown in the appendix A to D.

The relative strength between coats determinate the quality of the finishing, as it plays a key role in the print definition, adhesion, smoothness and appearance of defects such as bubbles or cracks. These parameters are met by the attractive forces that molecules exhibit between them and the substrate.

To make a formulation, first it is assessed how much of each material we need and how they interact with each other. The five general categories are pigments, resins, carriers (water-solvent), crosslinkers and additives. A great deal of experience with the products goes into a formulation, but there are overall rules that must be met to achieve a good result.

The base coat is meant to promote adhesion, levelling, coverage and print retention. The pigments and fillers are incapable of producing a film, so they must be mixed with a resin. The formulations of a finishing contain film forming agents and non-film forming agents and is expressed in a ratio. The resin and pigment-filler ratio depend on their functional group. In automotive is usually used acrylic or polyurethanes resins, which means that it is used a 3:1 and 2:1 ratio (film forming agents to non-film forming agents), respectively. Compact resins are a mixture of several resins and additives and are meant as “ready to use resins”. The ratio used is 4:1. The ratios applies to the solid content and is not related to the volume of product used.

For the shoe industry, the desirable ratio is usually 1:1 (film forming agents to non-film forming agents), for upholstery is 1,5-2:1 and for the automotive is 2,5-3:1. These values depend on the resistance and fastness required by the application, and automotive tend to be the most rigorous.

The hiding power and visual effect are properties required by the pigments and only achieved by pigments capable of scattering light. Figure 3.2 shows that the best particle diameter for hiding defects is between 400 and 600 nm.

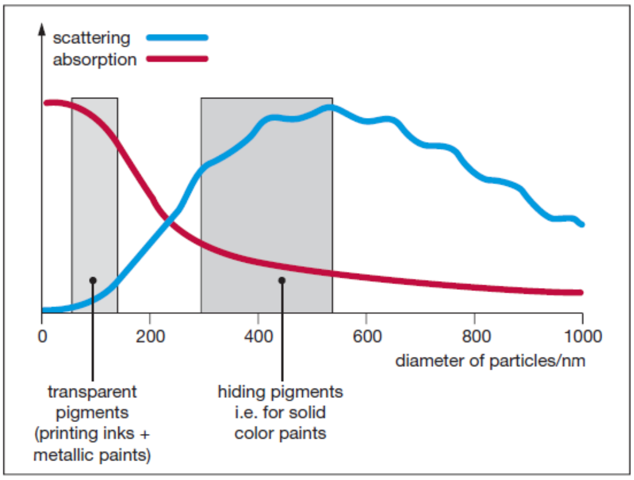

Figure 3. 2- Scattering and absorption of light to particle size of pigments[22]

Resins are film forming materials that hold the coating system together. Long chained resins in the polymer film improves elasticity, hardness and impact deformation, but also leads to higher solution viscosity of the resin[23].

In this formulation the solvent used was water and is used to stabilize and promote the compatibility of components, improve pigment coverage and dispersion, and control the viscosity of the mix. To avoid incompatibility problems, silicone emulsions must be diluted in water, before mixing with the other components.

Finishing additives are auxiliary products used to improve technical properties of the coating and are usually named in accordance to their mode of application. According to Stahl nomenclature, levelling agents (LA) promote the formation of a smooth and uniform surface, defoamers (DF) prevent the formation of foam, rheology modifiers (RM) increase the viscosity of the mix, thinners (DL) decrease the viscosity and crosslinkers (XR) are catalysts that accelerate drying and hardening and increase the molecular mass of resins. The crosslinkers used in the topcoat is a multifunctional polycarbodiimide, which is a very efficient catalyst for carboxylic groups, such as polyurethanes and polyacrylics (resins present in all the coatings). This catalyst forms an additional inter-polymer network (seen in figure 3.3), improving the chemical and abrasion resistance, as well as the inter-molecular strength[24]. The problem with carbodiimide crosslinkers is that they reduce the adhesion coating layers.

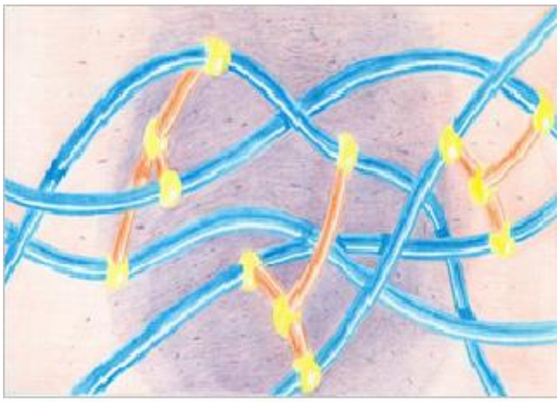

Figure 3. 3- Carbodiimide Crosslinking [25]

The base coat used in the study must have a very low tackiness, because after its application the leather was embossed, and tacky coats tend to be peeled off in the embossing roll. It is also necessary that the base coat has a high embossing retention and that the film does not get cut by the printing.

The color coat is designed to impart the desired appearance and levelling out the leather. This coat is made of pigments, fillers and resins, but can also be a combination between the products of the base coat and top coat.

The top coat has decisive appearance and fastness properties. To anti-soiling, this means that is composed by high performance, with resistance to abrasion, scuff, chemicals, dirt and handle improving products. There is no need to mix pigments in the formulation, although sometimes it is done in very low percentages to correct the color and prevent whitening. In the top coat applied were not used pigments.

The clean top (CT) was added to half of the samples, and the formulation is a highly complex mix, composed mostly of silicone, acrylic and polyurethane resins and other additives, diluted with water. The crosslinker used with the CT makes a very close network that helps preventing the impregnation of dyes, thus acting as a sort of anti-soiling agent. It has good aging resistance, so it is able to pass pretreatment tests and the data collected later after applications won't be affected by color changing. This crosslinking can only be used in top coats or CT because the adhesion strength of the following coats would be considerable diminish. A multifunctional carbodiimide crosslinker is normally only used in anti-soiling top coats, because it can diminish the flexion properties of the finished leather.

3.2. Application/ Procedures

The finishing coatings were applied to 20 sides (1 hide=2 sides), where half of them were colored brown and the other half beige. Half of the sides of each color, were coated with a final layer, called the CT. So, in the end of the application process, there were 4 different "batches" of 5 sides, where 1 was brown without CT, 1 was beige without CT, 1 brown with CT and 1 beige with CT. The table 3.1 summarizes the finishing applications.

Table 3. 1- Application Summary

20 Sides	5 Sides	Beige Without CT
	5 Sides	Brown Without CT
	5 Sides	Beige With CT
	5 Sides	Brown with CT

Before applying the coating, the viscosity must be checked, because it has a considerable influence in sagging, levelling, penetration and application properties.

The viscosity is measured using a Ford cup flow meter, as shown in figure 3.4. To adjust the viscosity, it was used a rheology modifier. A rheology modifier (or surfactant/ thickener) is an agent that changes the interfacial interactions, by associating with the resins and self-aligning the hydrophilic groups with the water and decreasing the viscosity. The use of rheology modifiers improves wetting, but permanently changes the coating even after the curing. The low surface energy will make them difficult to wet over, decreasing the adhesion of the following coats. To overcome this problem, it is used small amounts of a low potency surfactant, such as hydrocarbons [26].

Figure 3. 4- Ford Cups

The base coat is applied by the roller coater shown in figure 3.5, to improve the adhesion and levelling properties and to apply a thick layer of finishing. In this type of application, the viscosity must be around 550 cSt (centistoke), or 25 seconds measured with a Ford Cup 6. If the viscosity is too low, the mix will impregnate deeply in the crust, making it hard, loose and with low flexing. Before applying to the leather, the addon of the coat is adjusted, by cutting a sample of half a feet square of the leather, weighting it and applying the base coat. If the required weight is achieved ($110g/m^2$), the leather is trimmed to remove rough parts, and then passed through the roller coater and into the dryer conveyor.

Figure 3. 5- Roller Coater (Back View on the left and Front View on the right)

The day after the application of the base coat, all sides were embossed at 100°C with the haircell mold using the embossing machine shown in figure 3.6. It could also be used the ironing machine (figure 3.7), which produces better results, but in the industry the most common form of printing is embossing for being faster and easier to operate. The figure 3.8 shows the plates used in the ironing machine and forklift to move them.

Figure 3. 6- Embossing machine (back View on the left and Front View on the right)

Figure 3. 7- Ironing Machine and Plates

Figure 3. 8- Plates and Forklift

The color coat, top coat and CT were applied by the spraying machine shown in figure 3.9. For this application, a low viscosity at high shear rates is preferred, as it allows controlled atomization for a fine uniform spray and prevents the nozzles from blocking. To apply the color coat, the viscosity was set to 120 cSt, which means 30 seconds with the Ford Cup 4. Before applying the color coat, a square foot was passed throw to check the addon required (25g/m^2).

Figure 3. 9- Spraying Machine

The top coat was applied using the “in-line” method (Figure 3.10), which means that the crosslinker is mixed, using a helical twist bowtie mixer (also known as static mixer), with the coating right before the application. The percentage/total weight is set on the controller, and the in-line mixer checks the density of both mixes as it converts to percentage/volume. The regulator controls the amount of product sent to the spray nozzles. The addon of the top coat was of 8g/m^2 applied 3 times. When the product is changed, the spraying machine must be cleaned to avoid contamination. Starting with the cleaning of the in-line mixer tubes with 250mL of solvent and then water. After the in-line is cleaned, the head of the spraying machine is cleaned with water in close cycles (not with solvent, because paint crusted in the tubes would peel off and clog the nozzles). Then all the tubes are cleaned, and the nozzles are manually rinsed.

Figure 3. 10- In-Line Equipment

The CT was applied in half of the crusts, by spraying in "hot-pot" mode, which means that the crosslinker was mixed beforehand. The CT is a ready to use mix, so the viscosity is not checked, and the addon was of 2g/m^2.

3.3. Testing

The sampling of leather is done according to ISO 2418 and the conditioning to ISO 2419. To take the samples it is used the pressing machine shown in figure 3.11, along with the required cutting mold, which for determination of soiling and cleaning are specimens with 140mm of diameter.

Figure 3. 11- Pressing Machine

There are several standards to test the anti-soiling properties of the automotive leather finishing system. In this project it was decided that the standards used were the "VDA 230-212", a dye ingress of an OEM and soiling of another specific OEM. All these standards share the same principle, where the result evaluation consists in comparing the color change between the original sample and the sample after soiling, ageing and cleaning.

These three standards were applied to the four different leathers (brown, beige, brown with CT and beige with CT), with and without pre-treatment. The pre-treated samples were put into an oven for 72 hours, at 50°C and 95% humidity to artificially weather the samples, giving a better understanding of a real life application.

After the pre-treatment all the samples are preconditioned at 23°C and 50% humidity for 24 hours, then soiled using a Martindale-tester (figure 3.12) producing a Lissajous pattern, placed in a controlled environment for a certain amount of time and then cleaned. The test methods state that the color change must be analyzed by a spectrometer color computer after soiling, oven treatment and cleaning. The spectrometer model used was “Datacolor 600^{TM}” with the “DatacolorTools” software, and to soil the samples was used the “Nu-Martindale Abrasion and Pilling Tester”.

Figure 3. 12- Nu-Martindale Abrasion and Pilling Tester

The same trials were made on the first week after the application of the base coat, and then on the second, fourth, sixth, eighth, tenth and twelfth. The procedures declared in the standards are summarized as follows, as an overview of the main differences between them. Each revolution in the Martindale Abrasion Device takes about a second.

- **VDA 230-212, Evaluation of the soiling and cleaning behavior- process with soiling cloth**

The material to be tested is placed in a Martindale Abrasion Device facing up, with a felt underneath and clamped with the help of a standardized weight. After 1000 revolutions under the 90mm in diameter soiling cloth attached to a pilling holder, the samples are aged for 24 hours at 80°C in a dehumidifying chamber. Then they are removed and placed at room temperature for at least an hour, before cleaning with solvent (Texapon) by hand, on half of the sample (to be able to compare with the other side) until the cleaning cloth does not pick up any dirt. The samples are then placed in room temperature for at least 16 hours before being analyzed[27].

- **Soiling of a specific OEM**

The procedure until soiling is similar to the VDA 230-212 but using 500 cycles soiling instead of 1000. After the soiling, the samples are stored for 24 hours in a dark room, and then cleaned using a Veslic Tester, where the sample is stretched in a rubfastness tester (figure 3.13) and wet-cleaned 10 times with three felt pads previously dipped in a BMW-Foam-Leather-Cleaner solution until they are soaked. The samples are then dried with a paper towel and dry-cleaned 10 times with a single dry pelt. Finally the samples are ready for color testing[28].

Figure 3. 13- Crockmeter (Rubfastness tester)

- **Dye Ingress of a specific OEM**

The samples are soiled using a 38mm standard denim fabric, dipped in an alkaline perspiration solution for 5 minutes. After completing 1000 cycles place the samples in an oven at 80°C for 4 hours, and then at room temperature for 4 hours. The samples are cleaned the same way they are soiled but using a crock cloth dipped in Texapon. The samples are then analyzed in the spectrophotometer color computer[29].

The soiling, cleaning and repair cycles started on Monday of the ninth week and were done every day of that week. These cycles are important because they help to understand better the finishing behavior in real life applications. The cleaning and soiling were explained before and works the same way for this test. To repair, it is applied a standard leather protector after cleaning and left overnight. The next day the cycle starts again.

The anti-soiling system is used not only in automotive articles, but also in trains or airplanes. One of the main problems faced in public transportation are acts of vandalism, such as writing or scratching (figure 3.14). The application of the CT should help fight this problem by making it hard to write on the leather and making it easy to clean.

Figure 3. 14- Vandalism in non-leather bus seats [30]

3.4. Grayscale Color change & Grayscale Staining

The grayscale color change and the grayscale staining are standardized methods to evaluate and compare the performance of the finishing in several test procedures. The grayscale is a version of the color using a mix of black and white to represent the "value" of the colors. The value can be defined as the amount of light a color absorbs or reflects. A fully saturated light blue may have the same value as a desaturated purple[31]. This means, that the color is not tested for the quality of the difference, but for the size of the difference.

A grayscale to assess change in color, showed in figure 3.15 (a), consists of gray color fields with different saturation, according to five different degrees. The degree number five shows the lowest difference in lightness and the number one the greatest. Between these degrees there are the intermediate fields, summing up to nine different patches of different gray lightness. Every degree of the scale is paired up with a gray output color- degree 5- for easier assessment.

The grayscale for assessing staining, showed in figure 3.15 (b), is presented in the same way as the grayscale for assessing color, but evaluates lightness instead of saturation[32].

The leather samples subjected to soiling are evaluated based on the degree of color change, and are as follows:

Grade 1- Poor durability; Color strongly changed;

Grade 2- Mediocre durability; Color changed;

Grade 3- Average durability; Color slightly changed;

Grade 4- Good durability; Small color change;

Grade 5- Excellent durability; Color not changed.

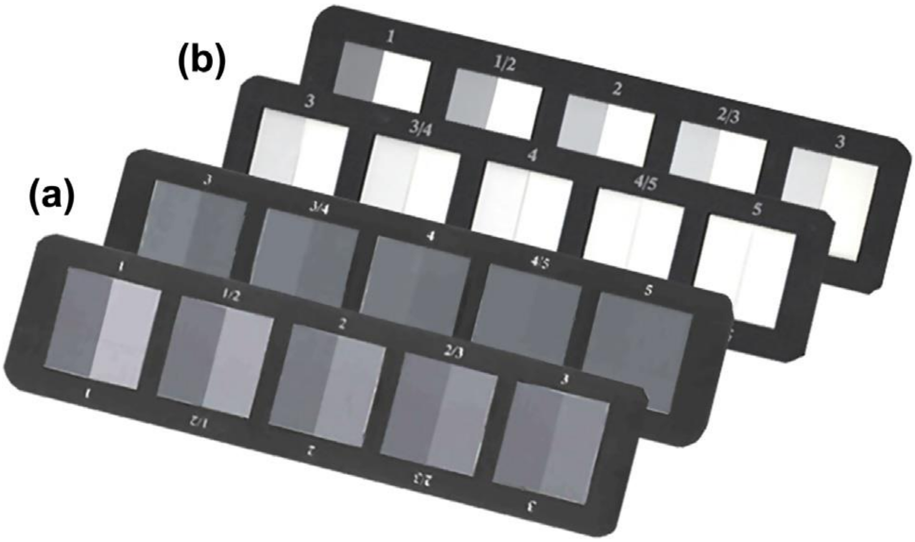

Figure 3. 15- Grayscale for assessing change in color (a) and staining (b) [32]

The color assessment is done using the spectrophotometer “Datacolor 600^{tm}” and the “Datacolor Tools” software, shown in figure 3.16. Firstly, it is made a standard for the untreated samples, and every time the samples are checked for color change, they are compared against this standard. The advantages of this system include speed, the ability to select for a measurement the most uniform area of a stain and the ability to assess multiple colors[32].

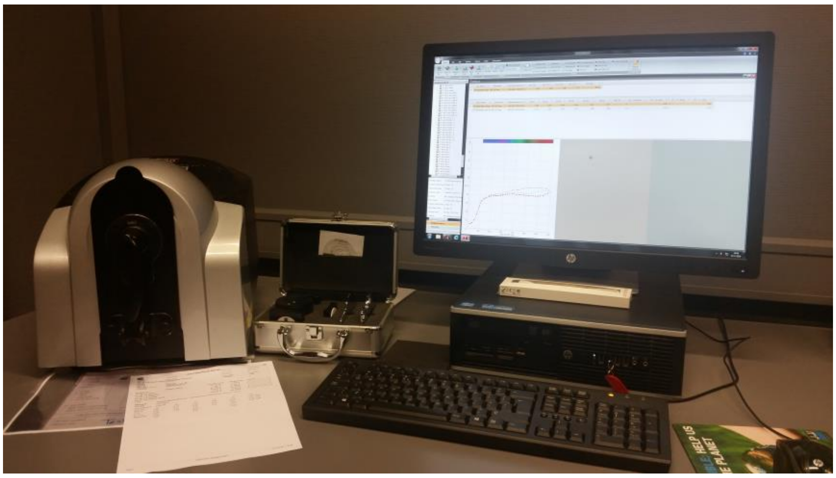

Figure 3. 16- Datacolor 600^{TM} Spectrophotometer and Datacolor Tools Software

3.5. Pigments

Pigments are insoluble particles used in finishing to hide the substrate, provide color, modify the application properties or performance and/or to reduce costs. The formulation to produce the color brown is in table 3.1, and to produce beige is shown in table 3.2.

Table 3. 2- Formulation for brown color

Color Brown	Quantity	Solids (%)	Pigment Type
Black	4	22	Carbon Black
Tan	9	57	Iron Oxide
Ochre	31	58	Iron Oxide
White	107	66	TiO_2
Total	151	62,7	

Table 3. 3- Formulation for beige color

Color Beige	Quantity	Solids (%)	Pigment Type
White	282	66	TiO_2
Black	1,3	20	Carbon Black
Lemon Yellow	2,7	17,5	Organic
Ochre	22	58	Iron Oxide
Violet	2,4	11	Organic
Total	310,4	64,4	

The pigments used in the automotive leather are produced to have high physical and chemical properties, such as light fastness, rub fastness, high coverage, temperature resistance, scuff resistance and others.

These pigments fall in the following two general categories:

- Organic

Are made of organic compounds, with no affinity to the substrate. Therefore, the fixation of the pigment to the substrate relies solely on the film-forming substances. They are bright colored and have high dispersion properties, but their coverage properties are relatively low.

- Inorganic

Inorganic pigments are bigger than the organic pigments and have lower gloss. These pigments are easier to disperse and usually have stronger physical properties.

3.6. Clean Top

The samples without CT, are finished with the anti-soiling formulation that is used in production, while the samples with CT have a last top coat formulation that should improve the anti-soiling properties.

The CT used over the top coat is a custom made, state of the art mixture. Unlike the resins used in the three-coat system, the CT is primarily designed to prevent the soiling and staining of the surface, by improving cleaning, dirt and dye resistance and "stick-slip" performance. It must also be resistance to abrasion, as the soiling tests are dynamic.

Soil repellency and stain resistance refers to the ability of the finishing to prevent soiling and dye adsorption and penetration. These properties are linked to oleophobic and hydrophobic functionalities, and may increase problems with static electricity, greying, stiffer handle, reduced permeability[33].

The repellency of both water and oil is related to the wetting behavior, which is determined and classified by the contact angle of the liquid on the finishing. Usually, hydrophobic surfaces have a contact angle of 90° or higher, and rough surfaces increase the contact angle. The scheme of drops on solid surfaces and angles of contact is seen is figure 3.18.

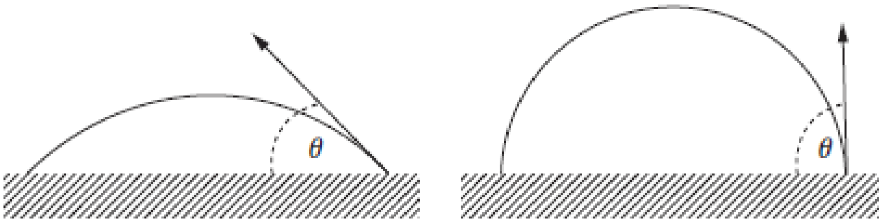

Figure 3. 17- Contact angles of drops on finishing[33]

The surface tension is a term used for estimating wetting properties and is related to the surface chemical composition. When the surface tension of the liquid is higher than the surface tension of the finish, the surface will not be wetted.

The anti-soiling and anti-staining properties of the CT is achieved by the presence of the hydrophobic functional group in the silicone molecule, the wetting capacity of the silicone, which allows it to distribute and fill the substrate and its high stability and resistance to chemicals and oxidative degeneration.

Silicone is a manmade polymer based on a framework of alternating silicon and oxygen bonds, with organic substituents attached to the silicon. The most common silicone has methyl groups as the organic substituent and is called polydimethylsiloxane (PDMS)[33].

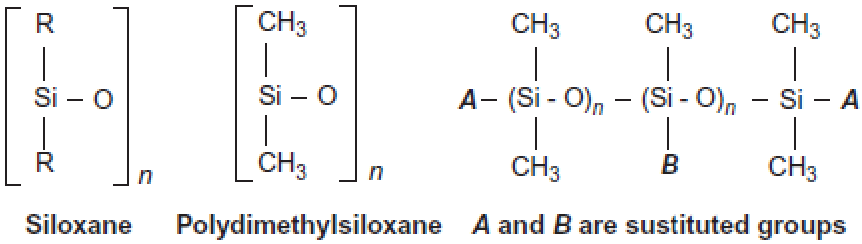

Figure 3. 18- Siloxane, polydimethylsiloxane and water repellency arrangement[33]

Silicone waterproofing agents are usually elastomeric polydimethylsiloxanes or penetrating water repellent chemicals. In the first, the elastomer adheres to the substrate and cures to form a flexible, protective membrane. In the second clusters reactive silanes and siloxanes resins react with crosslinkable side chains, which are materials with small molecules, capable of penetrating and bond with the substrate.

From figure 3.19, the presence of an alkyl group in the terminal position or side group position (A and B, respectively), makes the molecule unreactive and functioning as a water repellant.

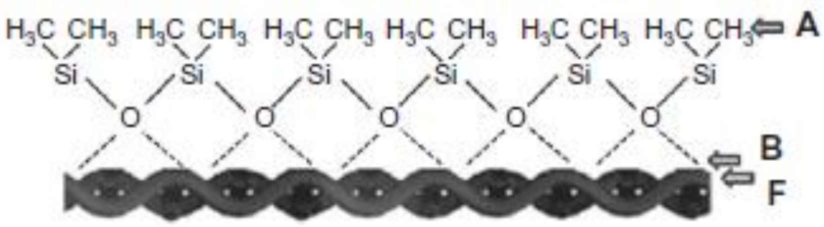

Figure 3. 19- Polydimethylsiloxane water repellency mechanism. A hydrophobic outer surface; B, polar hydrogen bonds; C, top coat [33]

As shown in figure 3.20, polydimethylsiloxanes (PDMS) allow the water-repelling methyl groups to face towards the surface, creating a waterproof "shield". Due to the electronegativity difference of oxygen and silicon atoms, hydrogen bonding occurs between the O-Si-O chain and the surface groups that carry electropositive hydrogen atoms. The weak intermolecular interaction enables reactive groups to be introduced in the siloxane chain. Although liquid water in unable to pass though the methyl barrier, gaseous water passes though the small pores of the silicone film[33].

In the silicon chain, the Si-H groups of the silane are the reactive groups, generating crosslinks or being oxidized by air or pretreated by water. Either directly or pretreated, the hydroxyl groups can undergo a reaction with crosslinkers such as polycarbodiimides. If many of hydroxyl groups stay unreacted, their hydrophilicity will decrease repellency. So, if excess amount of product is used, the water repellency capacity will be severely decreased.

Silicones have typically low intermolecular forces, low glass transition point temperature, and due to the high molecular distance, they have high gas permeability and high compressibility.

Water repellant agents based on silicon, to keep durability, must have a silanol, a silane and a catalyst. The catalyst promotes the orientation of the methyl groups towards the surface and joins the elastomer chains to prevent irreversible flow by unrestricted slippage of chains past each other. The film formed by CT is a very thin coat, and when the sheath cracks the durability is lost. Adsorption of hydrophilic substances found in cleaning products impairs the water repellency, through hydrolysis of siloxane and rupture of the film.

Water repellants based on silicone, although are not as strong or durable as fluorocarbon finishes, are a very environmentally friendly cheaper alternative to other waterproof agents. In addition, silicon-based finishes produce finishes with a soft feel, due to the flexibility of the polysiloxane structure, which is the most flexible chain in polymer chemistry[33].

A product exact formulation, like the CT used, is not usually known outside the R&D department, and it generally contains a lot of more active substances in addition to the main ingredient polydimethylsiloxane. Chemical modification of the PDMS chain can improve the oil and soil repellency of the finishing, by adding polyfluoroalkyl as a side chain. These modified types are called hybrid systems.

3.7. Crosslinker

Crosslinks are covalent chemical bonds that occur between macromolecules. The type and density of the crosslinker used has a big effect on the chemical and mechanical properties of the finishing. The density is controlled by the concentration of crosslinker in the mixture[34].

Lightly crosslinked materials tend to be soft and flexible, particularly above the glass transition temperature. By contrast, this behavior changes in highly crosslinked polymers, which become brittle and hard. This causes the highly crosslinked coating system to become weak to dynamic tests, such as flexion tests[35].

The crosslinker concentration in anti-soiling properties is important because if too much CT goes unreacted, the three-dimensional structure is more open and exposed to soil impregnation, making the surface harder to clean. By contrast, if the crosslinker concentration is too high, might make the surface easily soiled and harder to clean. The use of crosslinkers helps to bring permanency, durability and property improvement.

The evolution of the anti-soiling properties was studied to a concentration of 11% in solid weight of a carbodiimide. To find the optimal concentration of crosslinker, firstly it was used a carbodiimide at 5%, 7,5%, 10%, 11% (standard) and 16%. It was also made a sample with 9% of isocyanate. With this result, it was found that the best concentration of crosslinker, and then used several ratios of isocyanate and carbodiimide crosslinkers.

4. Results

All the tests and results were obtained on the first, second, fourth, sixth, eighth, tenth and twelfth week after the coating system application. The samples were tested for dye ingress and soiling resistance, following the standards required by VDA and two different OEMs and also for pen ink staining, that although there is no standard for this sort of test, special attention was taken for reproducibility and precision.

Later, the samples were also tested for repairing ability using a “protector” used to keep the leather from damage. To test the CT formulation for improvement possibility, it was changed the concentration of crosslinker and combinations of different crosslinkers and the results were compared with the first formulation.

The results organize all the data by standard (Dye Ingress OEM specific, Soiling OEM specific and VDA procedure), sample origin (1- Beige without CT, 2- Brown without CT, 3- Beige with Ct and 4- Brown with CT) and color after sample soiling, ageing (oven) and cleaning. The tests were conducted to samples without pretreatment and after being pretreated/ pretreated for 72 hours at 50°C and 95% relative humidity.

The dye ingress OEM specific standard states that the cleaned samples must be at least a 4 in the greyscale color change, while the soiling OEM specific standard expects a minimum of 4 after cleaning and 3 after ageing. The VDA standard procedure uses the greyscale staining to evaluate the results, and the soiled samples must be at least a 2 after soiling and 3-4 after cleaning. In each week, the first table shows the real values and the second the values accordingly to the standard. The values in green follow the standards, opposing to the red ones. Values in black are not regulated by the standards.

The table 4.1 shows the conversion of GS and CC values to GS rating.

Table 4. 1- GS and CC values to GS rating

GS/ CC Values	GS- Rating
0,00-1,25	1
1,26-1,75	1-2
1,76-2,26	2
2,27-2,76	2-3
2,77-3,26	3
3,27-3,76	3-4
3,77-4,26	4
4,27-4,76	4-5
4,77-5,00	5

Changes of soiling cloth batches showed a considerable influence in color, being that the first batch used had a darker color than the following cloths. Although its impact on color analysis is negligible, it could mean the difference between a pass and a fail.

The CT should also improve the pen ink staining, and although there is no standard procedure to follow, this test was conducted alongside the indigo staining tests.

It should be noted that the crust used has a very loose grain, that although it does not affect the results, the hand and look are not the greatest, and it is a defect that cannot be corrected by the finishing. The samples are all organized in a portfolio, to ease their presentation and results comparison.

A few months after the project started, to understand the importance of the right concentration of crosslinker and how it might affect the results, it was decided to repeat the application of the system, with several concentrations of crosslinker, but this time it was applied by hand with a spray gun. After analyzing the data and determining the optimal crosslinker concentration, it was then repeated the procedure for the optimal concentration, with a combination of isocyanate and carbodiimide, at different concentrations.

In appendix, it can be seen all the obtained results used for the result analysis, in the form of graphs.

4.1. First Week Results

Table 4. 2- First Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,15	3,22	3,14	3,67	0,68	2,05	2,19	2,75	2,17	3,34	3,56	4,23
	After Oven	2,38	4,45	3,42	3,93	0,73	2,26	2,53	2,88	2,18	3,34	3,38	4,39
	Cleaned	2,95	3,87	3,6	4,15	1,83	2,81	4,31	4,4	3,26	4,16	4,5	4,68
72h/50°C/95 %RH	Soiled	2,04	3,81	2,71	3,9	0,93	1,66	2,31	2,28	2,01	3,17	3,31	3,7
	After Oven	2,13	---	3,15	4,28	1,42	2,25	2,6	2,79	2,27	3,56	3,59	4,16
	Cleaned	2,6	3,9	3,92	4,42	2,1	2,87	4,25	4,45	3,01	4,22	4,36	4,6

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2	3	3	3-4	1	2	2	3	2	3-4	3-4	4
	After Oven	2-3	4-5	3-4	4	1	2-3	2-3	3	2	3-4	3-4	4-5
	Cleaned	3	4	3-4	4	2	3	4-5	4-5	3-4	4	4-5	4-5
72h/50°C/95 RH%	Soiled	2	4	2-3	4	1	1-2	2-3	2-3	2	3	3-4	3-4
	After Oven	2	---	3	4-5	1-2	2	2-3	3	2-3	3-5	3-4	4
	Cleaned	2-3	4	4	4-5	2	3	4,25	4-5	3	4	4-5	4-5

On the first week, the best results were obtained in the VDA standard, where only the pretreated beige sample failed the test. All the samples passed the test being that only the beige sample without CT and pretreated for 72 hours failed. The soiling OEM specific standard shows the poorest results, and so is the most demanding test, with the only passing samples being the brown with CT. The dye ingress OEM specific standard shows good results for the brown samples, with and without CT, as well as the pretreated beige with CT.

By looking at the soiling results, it is safe to assume that the pretreated samples are more easily soiled, but there is no consistency for the cleanability. The soiled samples after ageing/oven show overall a color closest to the initial color than before, with a more visible impact on the pretreated samples.

As it was expected, all the samples with CT show better results when compared to their peers.

4.2. Second Week Results

Table 4. 3- Second Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,51	3,56	3,59	3,55	0,97	2,07	2,59	3,04	2,21	3,59	4,04	4,12
	After Oven	2,42	3,52	3,69	3,6	1,06	2,25	2,6	2,97	2,31	3,62	4,19	4,29
	Cleaned	2,83	3,94	4,13	4,01	2,82	3,72	4,35	4,5	3,64	4,46	4,28	4,54
72h/50°C/95 RH%	Soiled	2,04	3,91	4,51	3,54	0,86	2,28	3,94	2,87	2,26	3,68	4,56	4,01
	After Oven	1,95	3,65	4,55	3,51	1,08	2,41	4,21	2,98	3,13	3,81	4,63	4,18
	Cleaned	2,43	3,99	4,63	4	2,9	3,79	4,56	4,27	3,54	4,62	4,86	4,66

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2-3	3-4	3-4	3-4	1	2	2-3	3	2	3-4	4	4
	After Oven	2-3	3-4	3-4	3-4	1	2-3	2-3	3	2-3	3-4	4	4-5
	Cleaned	3	4	4	4	3	3-4	4-5	4-5	3-4	4-5	4-5	4-5
72h/50°C/95 RH%	Soiled	2	4	3-4	4-5	1	2-3	4	3	2-3	3-4	4-5	4
	After Oven	22	3-4	3-4	4-5	1	2-3	4	3	3	4	4-5	4
	Cleaned	2-3	4	4	4-5	3	4	4-5	4-5	3-4	4-5	5	4-5

On the second week there are noticeable improvements of almost every value. All the samples passed the VDA standard and only the beige sample without CT failed the dye ingress of the dye ingress OEM specific standard. The soiling OEM specific standard continuous to show the worst results, but with a slight improvement.

4.3. Fourth Week Results

Table 4. 4- Fourth Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,63	3,6	2,99	3,93	1,35	2,67	3,03	3,57	2,7	3,84	4,28	4,45
	After Oven	2,85	4,18	3,27	4,16	1,32	2,51	3,48	3,44	2,87	4,1	4,48	4,55
	Cleaned	3,02	4,2	3,25	4,22	2,59	3,17	4,48	4,49	3,51	4,31	4,59	4,77
72h/50°C/95 RH%	Soiled	1,99	4,1	3,77	3,75	1,51	2,68	4,31	3,73	2,56	3,84	4,58	4,36
	After Oven	2,08	4,21	3,98	3,94	1,27	2,53	4,23	3,86	2,55	4	4,51	4,41
	Cleaned	2,48	4,16	3,59	4,02	2,29	3,2	4,59	4,67	3,28	4,19	4,75	4,63

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2-3	3-4	3	4	1-2	2-3	3	3-4	2-3	4	4-5	4-5
	After Oven	3	4	3-4	4	1-2	2-3	3-4	3-4	3	4	4-5	4-5
	Cleaned	3	4	3	4	2-3	3	4-5	4-5	3-4	4-5	4-5	5
72h/50°C/95 RH%	Soiled	2	4	4	3-4	1-2	2-3	4-5	3-4	2-3	4	4-5	4-5
	After Oven	2	4	4	4	1-2	2-3	4	4	2-3	4	4-5	4-5
	Cleaned	2-3	4	3-4	4	2-3	3	4-5	4-5	3-4	4	5	4-5

On the fourth week the samples without CT decreased their cleanability even though the soiling was not so stout. The beige with CT has significantly dropped its cleaned value in the Dye ingress test, which caused it to fail, but passed the soiling OEM specific and VDA standards. The brown with CT passed easily in all tests.

All the samples passed the VDA standard, although the beige without CT was just above the passing value. The soiling OEM specific standard results of the samples with CT have improves in contrast with the ones without CT, in both pretreated and not pretreated samples.

The pretreated samples with CT have shown better cleaning results than the ones without pretreatment, and it seems that pretreatment does not affect them as much as the ones without CT, both on soiling and cleaning.

4.4. Sixth Week Results

Table 4. 5- Sixth Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,01	3,08	2,66	3,33	1,2	2,24	2,75	3,57	2,46	3,72	4,36	4,4
	After Oven	2,2	3,53	2,81	3,89	1,23	2,28	2,73	3,5	2,89	4,04	4,49	4,6
	Cleaned	2,51	3,93	3,28	4,12	2,17	2,87	4,24	4,62	3,22	4,33	4,79	4,77
72h/50°C/95 RH%	Soiled	2,09	2,96	2,97	3,21	1,19	2,37	3,35	3,38	2,77	3,96	4,39	4,43
	After Oven	2,2	3,12	3,14	3,36	1,39	2,45	3,22	3,31	2,62	4,13	4,53	4,49
	Cleaned	2,49	3,47	3,63	3,69	1,96	3,11	4,43	4,62	3,18	4,37	4,81	4,76

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2	3	2-3	3-4	1	2-3	3	3-4	2-3	3-4	4-5	4-5
	After Oven	2	3-4	2-3	4	1	2-3	2-3	3-4	3	4	4-5	4-5
	Cleaned	2-3	4	3-4	4	2	3	4	4-5	3	4-5	5	5
72h/50°C/95 RH%	Soiled	2	3	3	3	1	2-3	3-4	3-4	3	4	4-5	4-5
	After Oven	2	3	3	3-4	1-2	2-3	3	3-4	2-3	4	4-5	4-5
	Cleaned	2-3	3-4	3-4	3-4	2	3	4-5	4-5	3	4-5	5	5

The dye ingress standard without pretreatment showed a decrease in cleanability in all samples, except the beige with CT. The soiling OEM specific standard decreased its values to the samples without CT and beige with CT, but the brown with CT slightly increased. The VDA results suffered very few changes, compared to the previous weeks.

As for the dye ingress OEM specific standard, after pretreatment, the beige without CT is showing some consistency, in opposition to the rest of the samples. After quite some decrease, the beige with CT got the same result as in the fourth week. The brown with and without CT, are showing some variation over time, although their results are close. As for the soiling OEM specific standard, every sample is keeping the same overall trend. The VDA standard, shows that the browns and the beige with CT have approximately the same values. The beige without CT is not showing a significant variation over time, but its results are much poorer than the rest of the samples.

4.5. Eighth Week Results

Table 4. 6- Eighth Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,18	3,24	2,49	3,40	1,11	2,38	2,58	3,33	2,52	3,8	3,96	4,23
	After Oven	2,15	3,93	3,22	3,78	1,26	2,52	3,01	3,46	2,74	4,02	4,38	4,31
	Cleaned	3,76	4,29	3,8	4,12	2,25	3,38	4,32	4,73	3,59	4,26	4,81	4,73
72h/50°C/95 RH%	Soiled	1,96	3,1	2,51	3,35	1,22	2,64	2,75	3,49	2,5	3,86	4,17	4,44
	After Oven	3,17	3,49	2,85	3,65	1,5	2,64	2,85	3,38	2,55	4,03	4,33	4,51
	Cleaned	2,54	3,97	3,23	4,04	2,49	3,55	4,43	4,67	3,64	4,23	4,71	4,73

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2	3	2-3	3-4	1	2-3	2-3	3-4	2-3	4	4	4
	After Oven	2	4	3	4	1-2	2-3	3	3-5	2-3	4	4-5	4-5
	Cleaned	3-4	4-5	4	4	2-3	3-4	4-5	4-5	3-4	4-5	5	4-5
72h/50°C/95 RH%	Soiled	2	3	2-3	3-4	1	2-3	2-3	3-4	2-3	4	4	4
	After Oven	2	4	3	4	1-2	2-3	3	3-5	2-3	4	4-5	4-5
	Cleaned	3-4	4-5	4	4	2-3	3-4	4-5	4-5	3-4	4-5	5	4-5

There was an overall improvement of every sample without pretreatment. For the dye ingress OEM specific standard, this was best shown by the beige without CT, which got near the beige with CT. Also, the brown without CT got better results than the brown with CT. As for the soiling OEM specific standard, the only major improvement was the brown without CT. Everything else stayed the same. The VDA standard shows that the apart from the beige without CT, that improved the cleanability, all the samples stayed the same.

The dye ingress OEM specific standard after pretreatment, is keeping the same trend over time. The beige without CT decreased its value, but the brown increased. Also, after pretreatment, the soiling OEM specific standard is showing that the CT is keeping its anti-soiling properties steady over time, with a slight increase of the samples without CT values. Lastly, the VDA standard, is not showing a significant change, apart from the beige without CT that showed the best results so far.

4.6. Tenth Week Results

Table 4. 7- Tenth Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	1,77	3	2,5	3,51	1,28	2,26	3,16	2,35	2,48	3,69	4,3	3,9
	After Oven	2,02	3,36	2,8	3,73	1,23	2,37	3,3	2,52	2,68	4,03	4,4	4,05
	Cleaned	2,43	3,87	3,23	4	1,97	3,09	4,6	4,31	3,43	4,26	4,69	4,54
72h/50°C/95 RH%	Soiled	1,97	3,26	2,62	3,45	1,28	2,47	3,48	2,41	2,64	3,85	4,45	3,99
	After Oven	2,16	3,48	2,89	3,64	1,19	2,55	3,55	2,43	2,83	4	4,43	4,09
	Cleaned	2,6	3,84	3,35	3,82	2,39	3,43	4,64	4,04	3,22	4,26	4,68	4,55

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2	3	2-3	3-4	1-2	2-3	2-3	3	2-3	3-4	4	4-5
	After Oven	2	3-4	3	3-4	1	2-3	2-3	3-4	2-3	4	4	4-5
	Cleaned	2-3	4	3	4	2	3	4-5	4-5	3-4	4-5	4-5	4-5
72h/50°C/95 RH%	Soiled	2	3	2-3	3-4	1-2	2-3	2-3	3-4	2-3	4	4	4-5
	After Oven	2	3-4	3	3-4	1	2-3	2-3	3-4	3	4	4	4-5
	Cleaned	2-3	4	3-4	4	2-3	3-4	4	4-5	3	4-5	4-5	4-5

In the tenth week, the samples were taken out of an unused side.

The samples tested with the dye ingress standard without pre-treatment suffered a slight decrease in cleanability, while the pretreated samples maintained their value. The beige samples did not pass the test. As for the soiling, all the values kept their values, except for the brown without pre-treatment that severely decreased its value.

The soiling OEM specific standard did not change its values in soiling in any of the samples. The cleaned samples kept all their values steady, except for the beige sample with CT, that decreased its value by 0,5 in the sample without pretreatment.

As for the VDA standard, the beige samples slightly decreased the cleanability, while the other values kept steady.

4.7. Twelfth Week Results

Table 4. 8-Twelfth Week Results

Pre-Treatment	Stage	Greyscale Color Change- CC Value								Greyscale Staining- St Value			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2,00	3,02	2,56	3,73	1,23	2,29	2,50	3,66	2,52	4,01	3,90	4,36
	After Oven	2,26	3,36	2,86	3,93	1,24	2,52	2,54	3,78	2,64	4,23	3,92	4,51
	Cleaned	2,42	3,85	3,22	4,16	1,89	3,26	3,90	4,61	3,47	4,36	4,58	4,74
72h/50°C/95 RH%	Soiled	1,93	2,99	2,64	3,61	1,09	2,39	2,38	3,43	2,64	4,05	3,72	4,29
	After Oven	2,10	3,27	2,93	3,80	1,14	2,57	2,71	3,52	2,80	4,17	3,96	4,40
	Cleaned	2,51	3,64	3,02	4,04	2,53	3,22	4,15	4,50	3,21	4,27	4,49	4,70

Pre-Treatment	Stage	Greyscale Color Change- CC Rating								Greyscale Staining- St Rating			
		Dye Ingress OEM Specific				Soiling OEM Specific				VDA Procedure			
		1	2	3	4	1	2	3	4	1	2	3	4
None	Soiled	2	3	2-3	3-4	1	2-3	2-3	3-4	2-3	4	4	4-5
	After Oven	2-3	3-4	3	4	1-2	2-3	2-3	4	2-3	4	4	4-5
	Cleaned	2-3	4	3	4	2	3-4	4	4-5	3-4	4-5	4-5	4-5
72h/50°C/95 RH%	Soiled	2	3	2-3	3-4	1	2-3	2-3	3-5	2-3	4	3-4	4-5
	After Oven	2	3-4	3	4	1	2-3	2-3	3-5	3	4	4	4-5
	Cleaned	2-3	3-4	3	4	2-3	3	4	4-5	3	4-5	4-5	4-5

In the twelfth week, the dye ingress OEM specific standard decreased all their values, except for the brown samples with CT, which are the only ones that passed the test. The soiling results suffered some changes, when compared with the tenth week, but nothing unusual.

The soiling OEM specific standard only showed a significantly decrease in the cleanability of the beige sample without CT and without treatment. Only the brown samples with CT passed these standard requirements.

The VDA standard tests showed that the samples without CT are keeping its values steady, whereas the samples with CT are decreasing their resistance to soiling.

4.8. Pen Ink Staining

To test the behavior of the finishing to pen and marker scratching, it was picked a pen amongst several to do the trials. On this trials, two small samples were cut from the original leathers, and one of them was pretreated at 50°C and 95% relative humidity for 72 hours. After that, the samples would be cooled to room temperature and then scratched two times with a rollerball pen- one as a standard, and another to clean off- as shown in figure 4.1.

After an hour, one of the scratches would then be cleaned off with a microfiber cloth soaked in a solution of 0,5% texapon.

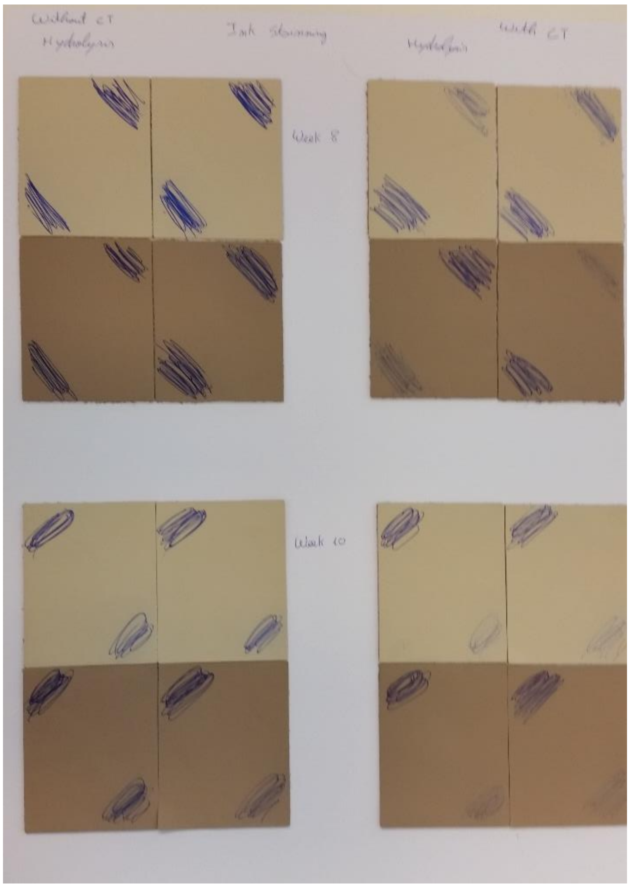

Figure 4. 1- Pen Ink test (On the left samples without Clean Top, and on the right with Clean Top)

The results were not very satisfying, and there were a lot a variation between tests. This led to change the way this test was being made. Three pens and two markers were then chosen, and a first scratch, without persisting, would be made on top of an A4 leather sample. Under that scratch, two lines and two scribbles would be made, even if the pen needed to change surface to write again. The line and the scribble on the bottom would then be cleaned with cleaning paper soaked in a solution of 0,5% texapon after one hour.

The pens picked were a roller ball pen as a standard to the earlier tests, a ballpoint, a common deskpen and two whiteboard markers- one red and one black. This test can be seen in figure 4.2.

Figure 4. 2- Pen Ink Staining, version 2- On the left a sample without CT and on the right with CT)

Overall, this test went well, although, as seen on the top left sample of figure 4.2, the rollball pen was scratching at the first try, but not in the place where persisting scratching was supposed to be. On the bottom left sample of the same figure, the rollball pen only scratched the place where it should be cleaned afterwards.

4.9. Soil, Clean and Repair Cycles

To make sure that the leather lasts the entire service life of a car, the leather most be cared for. Most of the times, car owners neglect the leather treatment, and only do something about the staining after mistreating the leather for several years. A good leather cleaning is supposed to remove the dirt, while protecting the finishing from further soiling.

The procedure to make this test, is following the standards, and after cleaning apply the cleaner/protector with a cloth soaked in the solution, leave it for 16 hours and then repeat everything again. The standards followed to make this test were the dye ingress OEM specific and the VDA, and only the beige samples with duplicates (A and B) were used.

The result of the soil, clean and repair cycles with protector are shown in table 4.9. The results of the test without protector are shown in the table 4.10.

Table 4. 9- Soil and Cleaning Cycles with Protector Results

Cycle	Stage	Greyscale Color Change- CC value				Greyscale Staining- St Value			
		Dye Ingress OEM specific				VDA Procedure			
		1-A	1-B	3-A	3-B	1-A	1-B	3-A	3-B
1	Soiled	2,10	2,12	2,63	2,75	2,67	2,67	3,71	3,58
	After Oven	2,84	2,44	3,12	3,46	2,96	2,95	4,23	4,13
	Cleaned	3,19	2,72	3,42	3,85	3,49	3,48	4,43	4,34
2	Soiled	1,99	1,79	2,58	2,73	2,12	2,14	2,88	2,99
	After Oven	2,38	2,09	2,89	3,14	2,14	2,11	3,11	2,98
	Cleaned	2,93	2,23	3,01	3,43	2,69	2,84	4,13	4,01
3	Soiled	2,03	1,76	2,58	2,67	2,12	2,09	2,79	2,74
	After Oven	2,32	1,91	2,83	2,91	2,10	2,15	2,92	2,79
	Cleaned	2,75	2,36	3,16	3,26	2,61	2,64	3,85	4,09
4	Soiled	1,97	1,73	2,56	2,62	1,74	1,95	2,89	2,76
	After Oven	2,22	1,94	2,85	2,90	2,04	2,01	3,05	3,04
	Cleaned	2,65	2,27	3,04	3,15	2,48	2,55	3,76	3,93
5	Soiled	1,94	1,68	2,57	2,56	2,13	2,01	2,80	2,41
	After Oven	2,15	1,85	2,73	2,77	2,22	1,94	3,13	3,43
	Cleaned	2,47	2,02	2,95	2,98	2,40	2,29	3,56	3,87

Table 4. 10- Soil and Cleaning Cycles Without Protector Results

Cycle	Stage	Greyscale Color Change- CC value				Greyscale Staining- St Value			
		Dye Ingress OEM specific				VDA Procedure			
		1-A	1-B	3-A	3-B	1-A	1-B	3-A	3-B
1	Soiled	1,83	1,78	2,39	2,54	2,61	2,52	3,61	3,61
	After Oven	2,15	2,01	3,87	3,90	2,93	2,62	4,04	4,09
	Cleaned	2,70	2,62	4,28	4,11	3,18	3,18	4,42	4,30
2	Soiled	1,52	1,44	2,46	2,46	2,04	2,31	3,03	2,77
	After Oven	1,82	1,68	3,30	3,10	2,16	2,44	3,32	3,10
	Cleaned	2,19	2,16	3,68	3,50	2,68	2,58	4,19	3,95
3	Soiled	1,40	1,35	2,24	2,22	2,04	1,76	2,66	2,46
	After Oven	1,67	1,61	2,82	2,68	1,94	1,88	2,76	2,57
	Cleaned	1,98	1,90	3,22	3,05	2,18	2,28	3,75	3,49
4	Soiled	1,31	1,27	2,22	2,11	1,59	1,54	2,33	2,24
	After Oven	1,53	1,46	2,61	2,45	1,72	1,62	2,46	2,34
	Cleaned	1,83	1,72	2,90	2,71	2,04	2,13	3,39	3,21
5	Soiled	1,18	1,09	1,96	1,93	1,44	1,41	2,07	2,02
	After Oven	1,39	1,30	2,33	2,31	1,55	1,53	2,20	2,16
	Cleaned	1,53	1,51	2,61	2,62	1,87	1,95	3,11	2,89

The table 4.9 and 4.10 provided the required data to produce the figures 4.3 and 4.4.

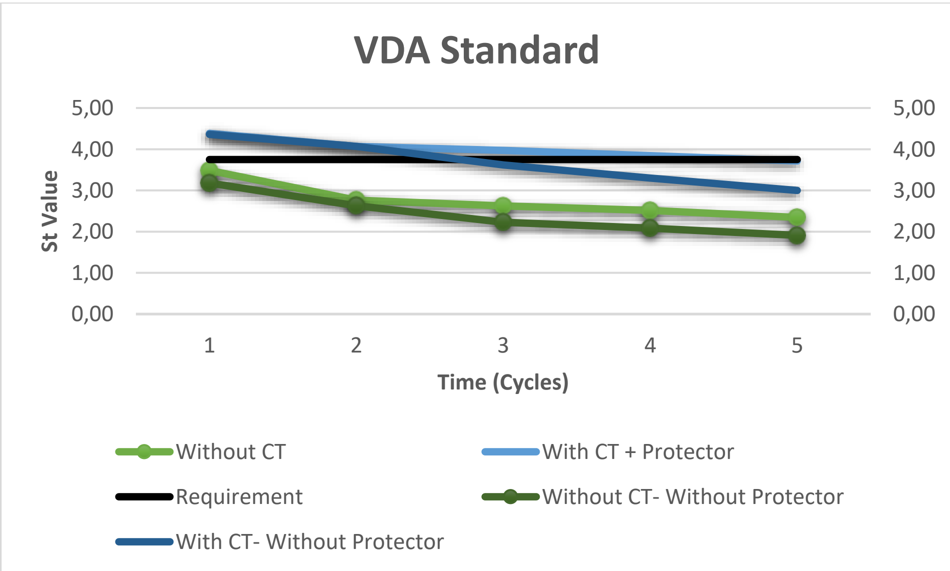

Figure 4. 3- Graphic with VDA Standard results of the soiling, cleaning and repair cycles

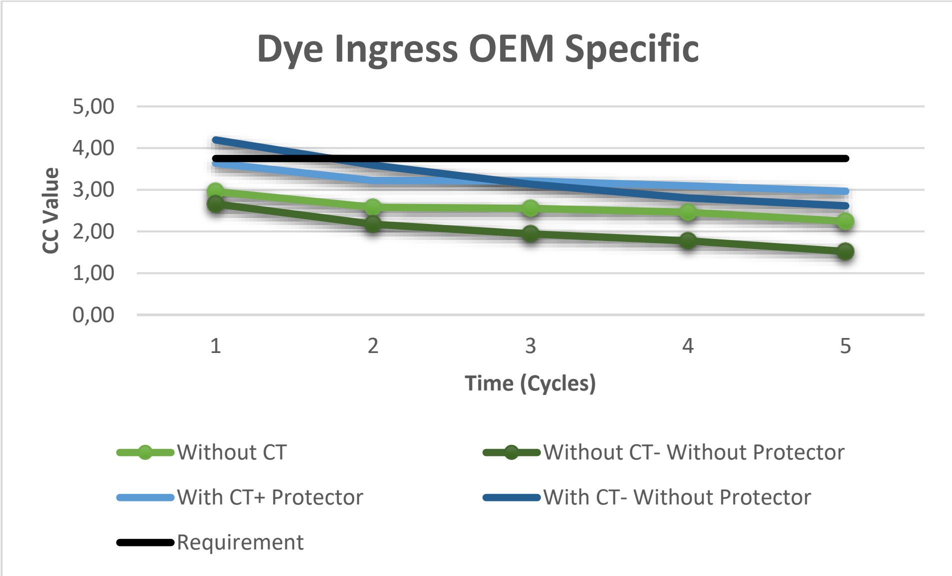

Figure 4. 4- Graph with Dye Ingress standard results of the soiling, cleaning and repair cycles

It is clear that the samples with CT show the best results in both standards, being that the Dye Ingress standard failed the test since the first day.

4.10. Clean Top Optimization

To find the best ratio of CT and crosslinker, firstly started by calculating the standard conditions. The solids percentage of the application was of 26% and the carbodiimide concentration was 11% of solid weight. While keeping the total solids percentage, the concentration of carbodiimide was increased and decreased around that value. It was also made a sample with isocyanate to have a base line for the combination of crosslinkers made afterwards. This was called the trial A, and its formulations are shown in table 4.11.

Table 4. 11- Formulations for crosslinker optimization (Trial A)

Formulation	Product	Volume (mL)	Solids (%)	Solids (g)	Solids (% WT)
A-1	***Water***	287,1	0	0	0
	Clean Top	742,9	0,35	260,01	95
	Carbodiimide	30	0,5	14,99	5
	Total	1060		275	
	Solids percentage			26%	
A-2	***Water***	292	0	0	0
	Clean Top	726,8	0,35	254,38	92,5
	Carbodiimide	41,3	0,5	20,63	7,5
	Total	1060		275	
	Solids percentage			26%	
A-3	***Water***	297,9	0	0	0
	Clean Top	707,1	0,35	247,5	90
	Carbodiimide	55	0,5	27,5	10
	Total	1060		275	
	Solids percentage			26%	
A-4 (Standard)	***Water***	300	0	0	0
	Clean Top	700	0,35	245	89
	Carbodiimide	60	0,5	30	11
	Total	1060		275	
	Solids percentage			26%	
A-5	***Water***	312	0	0	0
	Clean Top	660	0,35	231	84
	Carbodiimide	88	0,5	44	16
	Total	1060		275	
	Solids percentage			26%	
A-6	***Water***	308,7	0	0	0
	Clean Top	720,4	0,35	252,14	91
	Isocyanate	30,8	0,8	24,64	9
	Total	1059,9		276,78	
	Solids percentage			26%	

To apply the new Top Coat formulations, it was necessary to start the finishing application from scratch, since if they were applied on top of cured finishing there would be adhesion problems. So, starting from the color coat, all the formulations were applied by hand, as shown in figure 4.5, to a crust that had already a base coat and been embossed. Although the results cannot be directly compared to the initial project results, they can be compared against the standard, and the standard against the initial project results.

Although it is hard to achieve the required addon accuracy in hand spraying applications, it can be close very close to it. To do so, half of feet is sprayed first, and if the addon reached was close to the required value, the same movements and proximity would be repeated on the bigger piece.

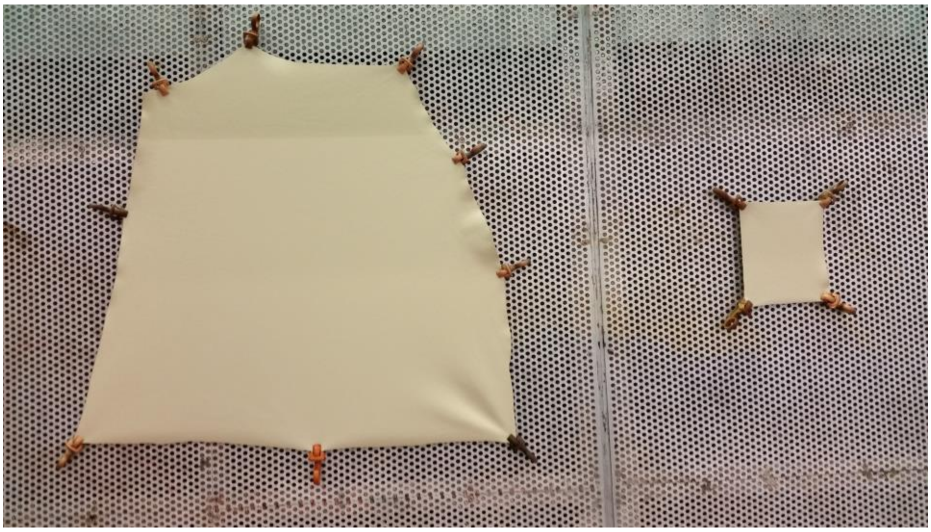

Figure 4. 5- Finishing application by hand

To these samples, only the dye ingress standard was tested, since it assesses the indigo impregnation in the finishing and to some extent the abrasion resistance. The soiling standards only test for abrasion.

The formulation number 6, was made with isocyanate. Usually, for the same crosslinking effect, it is used more isocyanate than carbodiimide. This is because carbodiimide reactions are stronger and therefore need less amount of crosslinking agents.

Table 4. 12- Results for different concentrations of Crosslinker (trial A)

Pre-Treatment	Stage	A-1	A-2	A-3	A-4	A-5	A-6
None	Soil	3,69	3,41	2,99	3,43	3,72	2,22
	Oven	4,33	4,18	3,96	4,16	4,63	2,78
	Clean	4,44	4,36	4,19	4,39	4,69	2,89
72h/ 50°C/ 95%	Soil	3,33	3,8	3,79	3,33	4,24	2,49
	Oven	4,25	4,27	4,14	3,99	4,48	3,07
	Clean	4,19	4,32	4,3	4,2	4,46	3,06

From the table 4.12 the sample pretreated doesn't show a big difference in cleanability (The pretreatment of sample number 1 got even better results). The blue graphic shows the values of the samples with pretreatment after cleaning and the green dot is the isocyanate sample. Since high concentrations of crosslinkers severely decrease the quality of the finishing and do not significantly improve the anti-soiling properties, the sample A-4 was discarded, producing the orange graph. From the function of this graph, it is possible to find the best concentration of crosslinker, by deriving this function and finding it is zero (appendix E).

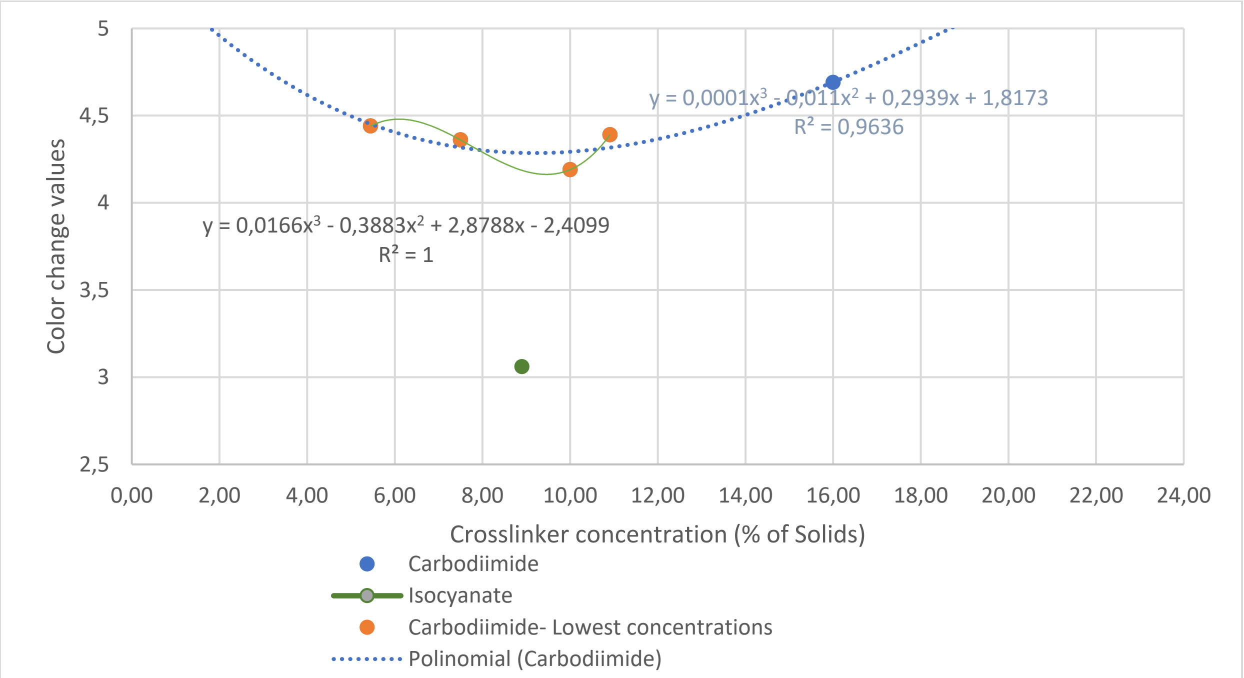

Figure 4. 6- Graphic with trial A results

It would seem from this test that the best carbodiimide crosslinker concentration would be 6,07% solids of carbodiimide. Although, the inaccuracy of tests that rely on color changing is around 0,20 to 0,25, and as such, there isn't nothing to conclude, besides that the carbodiimide is far better for anti-soiling systems than the isocyanate and low concentrations of carbodiimide are enough to produce good results.

It was decided to explore a little more the optimum concentration of carbodiimide. So, increasing the range and making duplicates, the same test was repeated. Pretreatment does not seem to have a severely negative effect on the results, so all the samples were tested without pre-treatment. The new formulations used can be seen in table 4.13.

Table 4. 13- Formulations for crosslinker optimization (Trial B)

Sample	Product	Volume (mL)	Solids (%)	Solids (g)	Solids (% WT)
B-1	Water	242,3	0,00	0,00	0,00
	Clean Top	700,0	0,35	245,00	100,00
	Carbodiimide	0,0	0,50	0,00	0,00
	Total	942,3		245,00	
	Solids percentage			26	
B-2	Water	251,5	0,78	0	0
	Clean Top	700	0,35	245	98
	Carbodiimide	10	0,5	5	2
	Total	961,5		250	
	Solids percentage			26	
B-3	Water	270	0,78	0	0
	Clean Top	700	0,35	245	94,23
	Carbodiimide	30	0,5	15	5,77
	Total	1000		260	
	Solids percentage			26	
B-4 (Standard)	Water	300	0	0	0
	Clean Top	700	0,35	245	89,09
	Carbodiimide	60	0,5	30	10,91
	Total	1060		275	
	Solids percentage			26	
B-5	Water	316,2	0,78	0	0
	Clean Top	700	0,35	245	85,96
	Carbodiimide	80	0,5	40	14,04
	Total	1096,2		285	
	Solids percentage			26	
B-6	Water	343,8	0,78	0	0
	Clean Top	700	0,35	245	81,67
	Carbodiimide	110	0,5	55	18,33
	Total	1153,8		300	
	Solids percentage			26	
B-7	Water	371,5	0,78	0	0
	Clean Top	700	0,35	245	77,78
	Carbodiimide	140	0,5	70	22,22
	Total	1211,5		315	
	Solids percentage			26	
B-8	Water	399,2	0,78	0	0
	Clean Top	700	0,35	245	74,24
	Carbodiimide	170	0,5	85	25,76
	Total	1269,2		330	
	Solids percentage			26	

This trial got the results showed in table 4.14.

Table 4. 14- Results of the trial B

Sample		Soil	Oven	Clean	Clean Average	
		GS	GS	GS	GS	|Carbodiimide|
B-1	A	3,95	4,06	4,71	4,70	0
	B	4,13	4,36	4,68		
B-2	A	4,4	4,49	4,6	4,62	2
	B	4,44	4,56	4,64		
B-3	A	4,62	4,73	4,81	4,80	5,5
	B	4,71	4,78	4,78		
B-4 (Standard)	A	4,4	4,51	4,58	4,67	10,91
	B	3,62	4,7	4,75		
B-5	A	4,7	4,78	4,79	4,79	14,04
	B	4,76	4,77	4,79		
B-6	A	4,48	4,52	4,6	4,58	18,33
	B	4,46	4,56	4,56		
B-7	A	4,54	4,64	4,65	4,66	22,22
	B	4,54	4,63	4,67		
B-8	A	4,38	4,47	4,52	4,52	25,76
	B	4,37	4,48	4,51		

From the table 4.13 it was possible to do the graphic showed in figure 4.5. Note that the VDA test requires a 3-4 (above 3,25) in greyscale staining to pass the test. The test B showed that minimal concentrations still have satisfactory results.

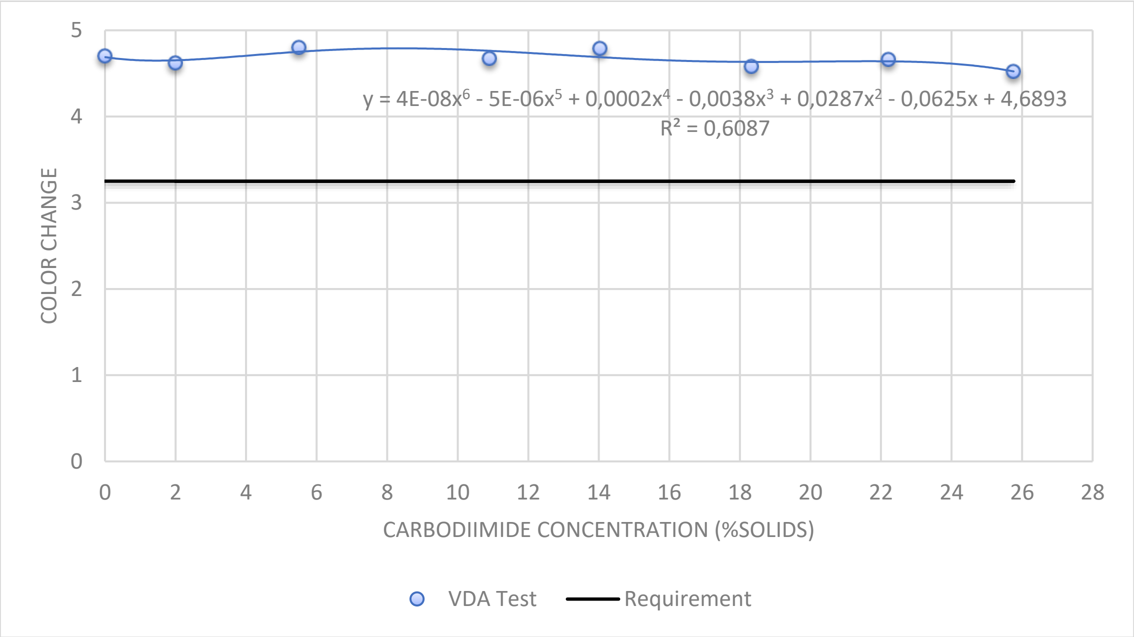

Figure 4. 7- Graphic with Trial B results

From the trial A and trial B results is seen that the carbodiimide crosslinker is not contributing a lot to anti-soiling properties, so the combination of crosslinkers was planned to sum up to 2% of solids in the mix. Note that the tests made only test the resistance to the tests itself, and not permanency of the anti-soiling over time (like the cycles test).

The combination of crosslinkers was made accordingly to several carbodiimide/ isocyanate ratios. The trial to verify the influence of isocyanate mixed with the carbodiimide crosslinker was called trial X and the formulations are shown in the table 4.15. The formulation X-1 has 100% carbodiimide (repetition of the previous trial), and the formulation X-7 has 100% isocyanate. In between, are the rest of the equally distributed ratios.

Note that although the isocyanate used has more solids, the formulation reference states that it is used the same volume, if either isocyanate or carbodiimide is used. For this reason, the formulations for the different ratios of crosslinker are made regarding the volume of carbodiimide at 2% of solids.

Table 4. 15- Formulations of crosslinkers at different concentrations (Trial X)

	Product	Volume (mL)	Solids (%)	Solids (g)	Solids (% WT)
X-1 100%	Water	251,5	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**98,0%**
	Carbodiimide	10,0	0,50	5,00	**2,0%**
	Isocyanate	0,0	0,80	0,00	**0,0%**
	Total	961,5		250,00	
	Solids percentage			0,26	
X-2 83%	Water	253,5	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**97,8%**
	Carbodiimide	8,3	0,50	4,15	**1,7%**
	Isocyanate	1,7	0,80	1,36	**0,5%**
	Total	963,5		250,51	
	Solids percentage			0,26	
X-3 67%	Water	255,3	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**97,6%**
	Carbodiimide	6,7	0,50	3,35	**1,3%**
	Isocyanate	3,3	0,80	2,64	**1,1%**
	Total	965,3		250,99	
	Solids percentage			0,26	
X-4 50%	Water	257,3	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**97,4%**
	Carbodiimide	5,0	0,50	2,50	**1,0%**
	Isocyanate	5,0	0,80	4,00	**1,6%**
	Total	967,3		251,50	
	Solids percentage			0,26	
X-5 33%	Water	259,3	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**97,2%**
	Carbodiimide	3,3	0,50	1,65	**0,7%**
	Isocyanate	6,7	0,80	5,36	**2,1%**
	Total	969,3		252,01	
	Solids percentage			0,26	
X-6 17%	Water	261,1	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**97,0%**
	Carbodiimide	1,7	0,50	0,85	**0,3%**
	Isocyanate	8,3	0,80	6,64	**2,6%**
	Total	971,1		252,49	
	Solids percentage			0,26	
X-7 0%	Water	263,1	0,00	0,00	**0,0%**
	Clean Top	700,0	0,35	245,00	**96,8%**
	Carbodiimide	0,0	0,50	0,00	**0,0%**
	Isocyanate	10,0	0,80	8,00	**3,2%**
	Total	973,1		253,00	**0,0%**
	Solids percentage			0,26	**98,0%**

The trial X produced the results showed in table 4.16 and figure 4.8.

Table 4. 16- Trial X results

Sample		Soil	Oven	Clean	Clean Average	Carbodiimide / Isocyanate
X-1	A	4,08	4,43	4,73	4,73	1
	B	4,28	4,35	4,72		
X-2	A	4,21	4,48	4,79	4,77	0,83
	B	4,25	4,22	4,75		
X-3	A	--	--	--	4,66	0,67
	B	4,18	4,21	4,66		
X-4	A	4,04	4,34	4,65	4,68	0,5
	B	3,81	4,2	4,71		
X-5	A	3,63	3,98	4,68	4,62	0,33
	B	3,8	3,97	4,55		
X-6	A	3,65	4,09	4,46	4,46	0,17
	B	3,68	3,83	4,46		
X-7	A	3,74	3,81	4,39	4,45	0
	B	3,73	4,06	4,5		

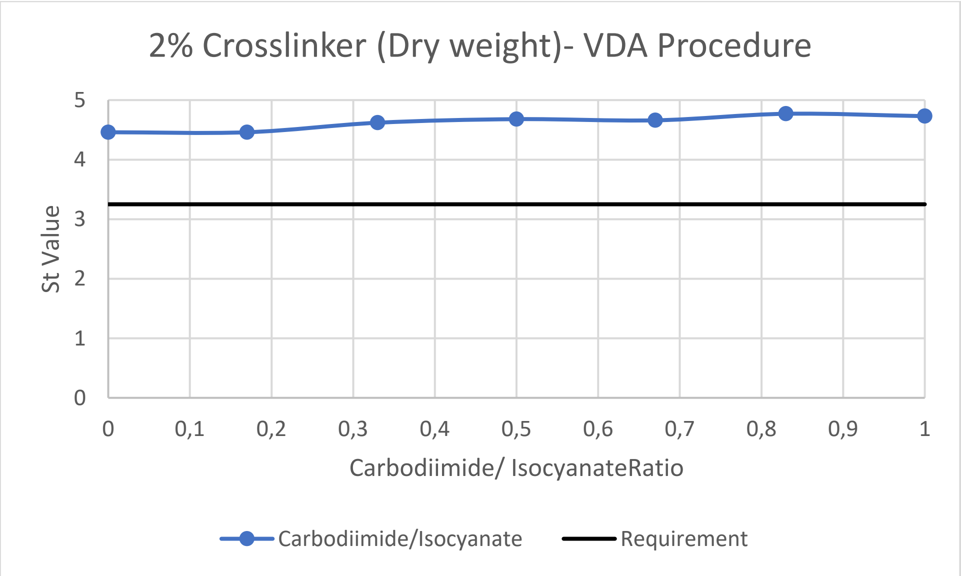

Figure 4. 8- Graphic with trial X results

From the results, it can be seen that higher carbodiimide content helps improving the results of the VDA standard, but even the samples with 100% isocyanate shows very good results.

4.11. Outlook

The break of the finished leather was not optimal. This might be caused by poor penetration of the base coat, crust with very loose grain and finish too heavy. This could somehow affect the results of dynamic tests, since the "hills" of the wrinkles are more exposed to the pilling holder than their "valleys".

At the eighth week, the results of the dye ingress OEM specific standard without CT got close, and even better than the results of the samples with CT. This might have happened because the sides that were being used were exposed to a lot of abrasion from sampling, and the CT could have been worn off. The sides were disposed, and new ones started being used.

In the optimization of the CT formulation, the application was made by hand spraying. For a uniform spread of the finishing, it's needed a lot of experience, and even then, the reproducibility wouldn't come near the application by spraying machine. In addition, the formulation was made to 200mL, which increases the error associated to the weight measurements.

There are no standards for the pen ink staining, so the results can have a lot of variables, such as ink, tip of the pen, force of application and/or angle of contact.

In practice, the CT can reduce the production soiling. During the manufacture of seats, steering wheels, dash boards, etc, and then while applying these products in the car, the leather suffers abrasion and eventually soiling, which causes most of the CT to wear off by the time the car leaves the Stand. Hence the importance of the protector.

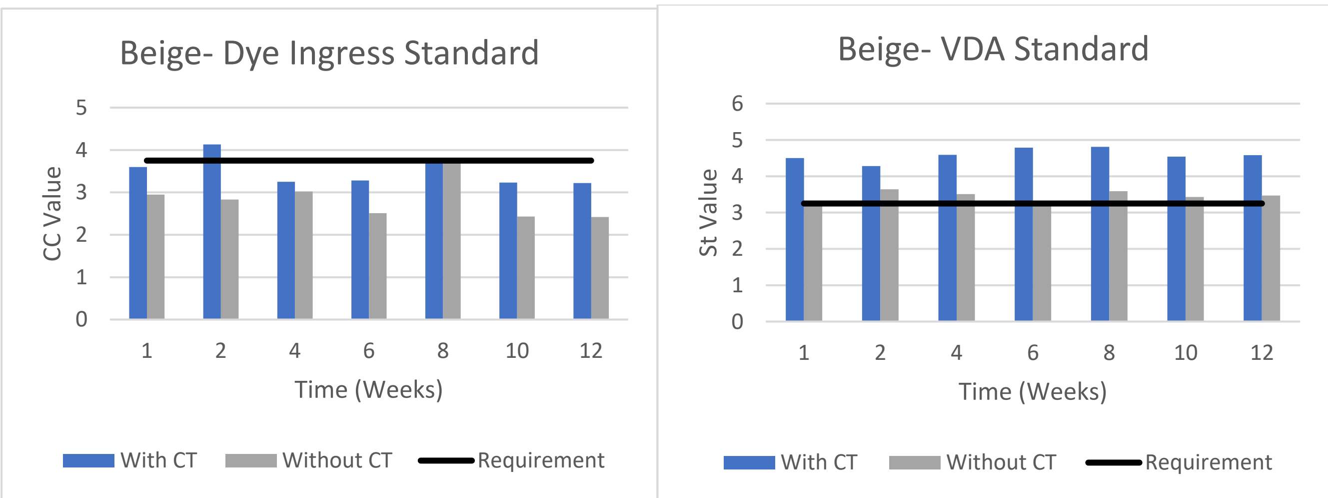

Figure 4. 9- Graphics with Results Overview

5. Discussion

On the course of the twelve weeks testing, all the samples were tested to indigo soiling resistance, following the standards used by a specific OEM and VDA, and dye ingress of a specific OEM, to pen ink staining and to repairing cycles with leather protector. In addition, the CT formulation was tested for room to improvement, by changing the crosslinker concentration and combining isocyanate with carbodiimide. The results obtained from these tests are discussed forward.

5.1. Indigo Soiling Resistance

The CT gives the leather repellency properties, increasing the resistance to chemicals, such as indigo or pen ink. However, the silicone based anti-soiling reduces the permeability, breathability and makes the handle oily. The shield made by polydimethylsiloxane has an open structure that enables air molecules to pass through, giving the finishing the ability to breath, but blocks the water due to the bigger size of water molecules.

The anti-soiling properties are reached by lowering the free energy at the fiber surface to a point where it is smaller than the surface tension of the liquid water or of the oil that is to be repelled. The surface tension of leather treated with CT has a surface tension of 24 to 30 mN/m, while liquid water is of 73 mN/m and oils between 20 to 30 mN/m. This means that the CT is capable to some extend repel the water but is easily wetted by oils or waxes.

To enhance oil and soil repellency, it is common in other textile substrates to combine the polydimethylsiloxane with perfluoroalkoxy alkanes, which enhances water repellency. Perfluoroalkoxy alkanes have a surface tension of 10-20 mN/m and show outstanding soiling and cleaning properties. Although fluorocarbons are not dangerous for the environment, their production is, due to the side-products perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are toxic, bio-accumulative and persistent in the environment. Compared to silicone-based repellents, fluorocarbons manufacture and application result in far more environmental issues[33].

The swelling of the leather fibers and hydrolysis of siloxane causes the rupture of the film and the anti-soiling properties are lost. This posts a big problem near needlework, because the water can easily penetrate the crust and destroy the anti-soiling system. This makes the leather prone to seam slippage, which is one of the most objectionable faults and degrades the quality of the product.

Finishes with anti-soiling properties usually increase the printing properties, drying velocity and chemical resistance. On the other hand, some problems such as poor soil removal, greying, stiffer handle and reduced permeability might become problems that need to be dealt with.

The crosslinker promotes better condensation conditions and the orientation of the film on the fiber surface, orientating the methyl groups outward, which generates the anti-soiling functionalities.

The addition of surface-active agents to the mix affects the tension at the air-water interface, and if enough surfactant is added, the critical micelle concentration is reached, and micelles of silicon particles are formed. Micelles are an aggregate of surfactant molecules and can bring several complications to the energetics of delivery to the substrate due to the presence and type of emulsifiers and the particle size of the silicone. For that reason, the mix of water, catalyst and CT was delivered without the addition of thickeners nor thinners.

The polycarboodiimide based crosslinker used with the CT has a second reactive group that creates an extra crosslinking network, closing even more the "anti-soiling shield", achieving a better performance.

To make a product such as CT, it takes sort of a perfect balance between resins able to be crosslinked and additives. The silicone alone is not what gives the finishing the anti-soiling properties. The CT is supposed to create a shield capable to resist both impregnation and soiling. The silicone present in the CT helps with the dye impregnation test and pen ink.

The soiling OEM specific standard showed the worst values throughout the study, and for the formulation to work, darker colors should be used, since lighter colors show poorer results.

The values obtained on the samples that were pretreated and the samples that weren't are relatively close, which leads to conclude that both the CT and the Top Coat have a thermal stability relatively high.

The transversal microscopic analysis shows that the application of CT stops indigo from penetrating the finishing. The figure 5.1 shows the samples performance to this problem.

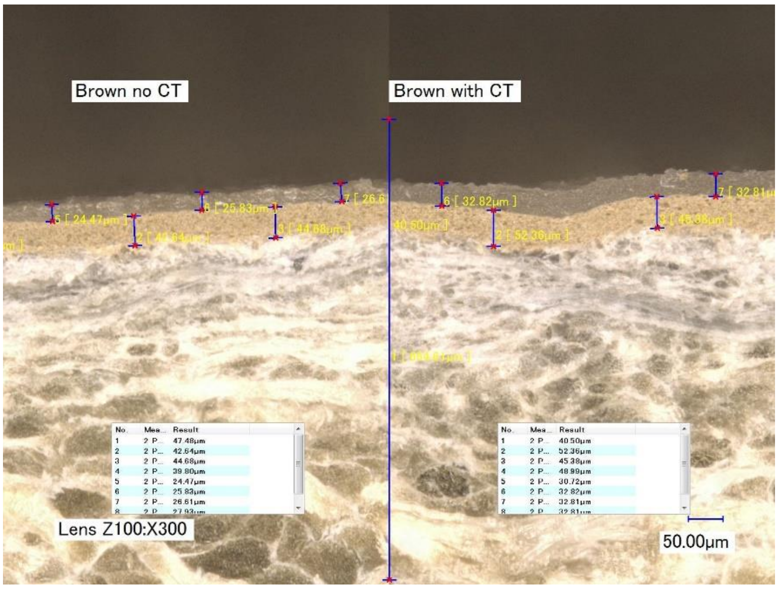

Figure 5. 1- Cross section of a sample without CT (left) and with CT (right) after Dye Ingress test

The standard that best relates to this behavior is the dye ingress OEM specific, and from the results, it is safe to assume that the application of CT improves the shielding to this dye. In practice, the impregnated indigo can only be “removed” by breaking down the indigo molecules with Ultra-Violet radiation.

All the standards show that the samples without CT ability to endure soiling, peaks between the first two to four weeks, and severely decreases until the eighth week, where it stabilizes. The same behavior is seen in the samples with CT pretreated. As for the samples with CT without pre-treatment, these are not as affected by soiling as the rest.

The pre-treatment of the samples does not seem to have much effect on the anti-soiling properties, either on the samples with or without CT. The application of CT has less variation over time, than the samples without it.

The samples without CT peak the anti-soiling properties at the second week after the application, decrease over the course of the next 4 weeks, only to peak again at the eighth week.

Time has the most visible effect on pretreated samples with CT, making the beige decrease around 2 values for the dye ingress and soiling OEM specific standards.

The CT greatly improves the resistance to indigo impregnation in the finishing. While the samples without CT are severely soiled by the dye impregnation standard and the cleaning is very ineffective, the samples with CT are more easily cleaned and the indigo does not stain as much.

The dye ingress and VDA standards require that the samples go to the oven at 80°C for 4 and 24 hours, respectively. This proved that the indigo stain is slightly “destroyed” at this temperature, because the stain actually got better values after the oven/ageing step. On the other hand, high temperatures make the stain harder to remove because the film is dried, and the soiling is fixed in the finishing.

It is important to mention, that these tests are subjected to a lot of variation that cannot be controlled, such as the color, Martindale tester, cloth batches, even spray application or pressure at which the sample is fixed during the dynamic tests.

5.2. Pen Ink Staining

From the pen ink staining, it could be concluded that the samples without CT are hard to scratch, but the cleaning is very ineffective. On the other hand, the sample with CT is much easier to scratch but is also quite easy to clean.

The pretreatment on the samples without CT seems to improve the anti-soiling properties, although the cleanability does not change. The pretreatment appears to damage the CT, making it easier to scratch.

The rollball pen is the most ineffective pen and poorly scratches any of the samples, only marking the leather after a lot of persistence. The ballpoint pens, although they scratch the leather easier than the rollpen, they also need a lot of persistence, especially on the leather without CT. The white board markers scratches on the samples with CT are easily cleaned with Texapon solution, and the samples without CT, although the cleaning shows a visible difference, it is highly ineffective.

The test done over the course of twelve weeks showed that the samples with CT are more easily cleaned and the pretreatment has no visible difference. Time on ink staining did not show any impact, so the results are roughly the same over time.

5.3. Repairing Cycles

Well cared leather is often cleaned and then shielded with a “after care” protector. The protector is important, because it helps keeping the anti-soiling properties of the leather, although changing its feel to a more plastic-like appearance and touch.

The results of these tests showed that there is a small step of 0,5 in color change from the first cycle to second, and after that there is a very slight decrease until the fifth and last cycle on both the samples tested. This shows that the protector is very efficient and affects the samples with CT and without CT the same way.

Although the cycles without the application of protector were not tested, the degree of cleanability would decrease to a point where the soiling stain would be uncleanable, with both the cleaning and soiling values decreasing at a much higher rate.

5.4. Clean Top Optimization

The tests with different concentrations of crosslinker, showed that even the smallest concentration of crosslinker is enough to pass the dye ingress OEM specific standard, that should be a 4 (above 3,75) after cleaning, which means that even if it was used half of the crosslinker used in the initial 12 weeks project, the results would still be satisfactory. More, however, the crosslinkers are not as environmentally friendly as the CT, so the less of it is used, the better.

Carbodiimide crosslinkers make a close network of crosslinked molecules that prevent it from being impregnated by indigo. This is seen in the first test, where the sample with isocyanate got a 3,06 CC value and the carbodiimide, with the same volume, got a 4,19- both samples were previously pretreated.

The sample with isocyanate pretreated before testing got a better result than the sample without pre-treatment. Some products behave differently do pretreatment than others. While some, such as the carbodiimide, is damaged by the heat and humidity, others are cured, and the pretreatment actually improves their properties. This is what is happening with the sample with isocyanate.

Both the tests A and B showed that small amounts of crosslinker are enough to pass the requirements of VDA and Dye Ingress standards. At only 2% of carbodiimide solids the greyscale staining value is at 4,62 while at the value of the crosslinker application, 11%, the greyscale staining value is at 4,66.

The best concentration of carbodiimide to pass the Dye ingress standard is 6% and, theoretically, would give a color change value (CC Value) of 4,47. The trail B indicated that, to pass the VDA standard, the CT doesn’t need to be crosslinked. Trial X showed that higher concentrations of carbodiimide improve the results of the VDA standard, but even at 100% isocyanate the CT can easily pass the test with a 4,45 St value, when 3,25 is enough.

The more crosslinker is used in the formulation, the more brittle the leather becomes, and that may cause problems in physical properties, such as flexion tests. It also makes the handle harder, which is something to avoid in automotive leather. So, there should be a perfect balance between the advantages and disadvantages of a crosslinker, and if the anti-soiling properties can be achieved at lower concentrations, than that is what it should be used.

The crosslinker gives the coat more permanency, and although it might not be needed the addition of crosslinker to pass the tests, it wouldn't be accepted by an OEM because the feel would be waxy, and the tackiness wouldn't be right.

The CT is a mixture of resins and additives. Since only the resins can be crosslinked, low concentrations of carbodiimide are enough to produce satisfactory effects.

Carbodiimide based crosslinkers cannot be recoated and its adhesion to the previous coats is weak. For that reason, the use of a mix of isocyanate and carbodiimide might be helpful. The optimization of a combination of crosslinkers lies in finding a perfect balance between advantages and problems of each crosslinker.

5.5. Quality and Testing

The application of the CT after the Top Coat does not negatively change the finished system, being that the more noticeable changes are in appearance and feel. The grain looks more closed due to the addition of another layer of finishing and the low viscosity of the mixture, which improves levelling, decreases wettability. As for the feel, or hand, the leather appears to be oilier with diminished slipping, most likely caused by the additives present in the CT.

The figure 5.2 shows the apparent addon of the finish. The CT accounts for around 5% of the total addon of the finish. The appendix I shows the calculations made to get these values.

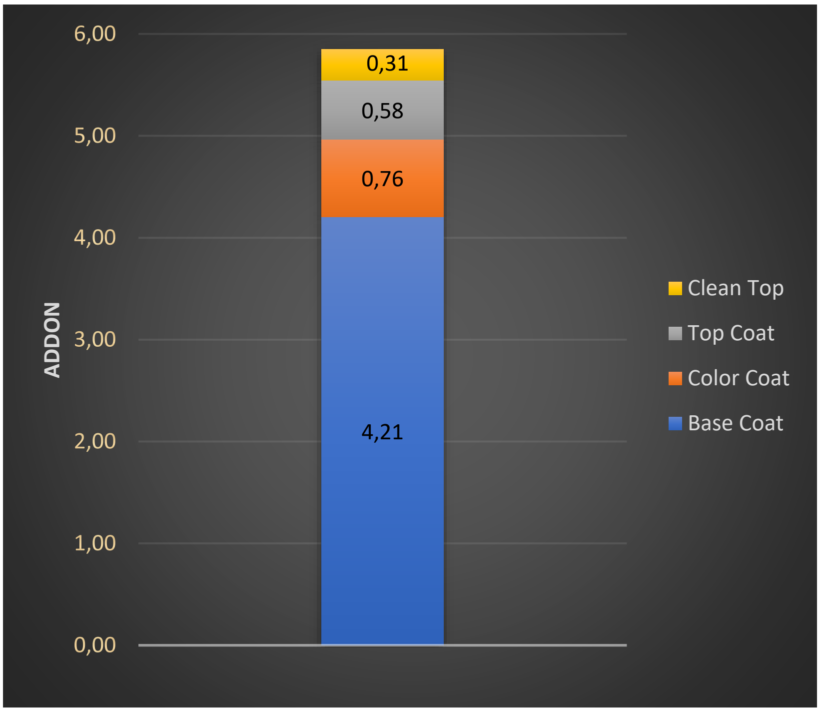

Figure 5. 2- Addon of the finishing, in grams (dry weight) per square foot

The CT has a very small impact on the finish addon, which has several advantages in physical tests. For this reason, the application of CT will still allow the leather to pass light fastness, abrasion resistance, taber abrasion, chemical resistance and flexion tests. The only variable that might diminish the leather strength is the concentration of crosslinker in the Clean Top formulation.

Conclusion

The application of the CT improves the anti-soiling properties, by increasing the resistance to soiling and dye impregnation. The brown samples with CT passed every test with fairly good results. The beige with CT, although it got much better results than the beige without CT, it only passed the Dye Ingress standard at the second week. The brown samples without CT were only able to repeatedly pass the VDA standard and the beige, also without CT, never passed the Dye Ingress standard and only passed 3 out of 7 weeks the VDA standard. The variation showed over time, is relatively low and might be associated to the test's accuracy.

Although the application of the CT improves the cleanability of pen ink stains, it is also easier to stain. For this reason, the CT showed the best results to marker staining, but its application makes it easier to scratch with common pens.

The optimization of the CT formulation showed that it is possible to significantly reduce the concentration of crosslinker, which might be desirable to reduce environmental impact and improve appeal. However, the crosslinker helps to pass several physical tests, so before changing the formulation, further testing is needed.

The CT offers a good non-soiling solution at no loss of aesthetics. On the other hand, it has only a moderate durability to cleaning, which might make the leather likely to be cleaned often, which in time removes the anti-soiling properties. Certain products found in cleaning agents, have hydrophilic substances that if used to clean the leather may cause its adsorption, impairing the anti-soiling properties.

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Appendices

Appendix A- Base Coat Formulation

Roller	1x 110 g/m2 4Kg x 2			
Viscosity	25" FC6			
Product	**Quantity (Kg)**	**Solids (%)**	**Functional Group**	**Description**
Pigment	150	63,5		
Thickener	*Xg to adjust viscosity*	21	Thickener	Non-Ionic; High Performance
Water	130	0	Solvent	Improves compatibility and solubility
Filler	100	28	Aqueous colloidal dispersion	Good Covering; Natural aspect- Duller
Resin A	75	20	Aromatic polyurethane	Improves adhesion without hardening; high wetting power; excellent levelling
Resin B	200	37	Aliphatic Polyurethane Resin	Excellent print retention, flexibility and cold/crack resistance
Resin C	100	35	Anionic polyester-polyurethane dispersion	Good film forming power; Excellent adhesion and ability to seal the surface
Resin D	100	25	Aliphatic polyurethane	Very tough; flexible; non-tacky; excellent lightfastness; Heat resistance; Good embossing; Excellent coverage;
Resin E	100	60	Polyurethane dispersion	Excellent fastness properties; Not tacky; High elasticity and water resistance; Medium elongation;
Leveler	10	98	Polyether Silicone	Prevents leveling problems; Improves Wettability;
Hand Modifier	15	68	Silicone Emulsion	High performance; Taber resistance; High wear; Resistance to wet and dry rubs
Crosslinker	45	39	Polycarbodiimide	Improves wet rub fastness and print retention; Resistance to accelerated ageing
Total	1025			

Leave overnight

Emboss- Haircell 100°C; 200bar

Appendix B- Color Coat Formulation

Spray Hot Pot	1x25g/m^2 12Kg x 2			
Viscosity	28-32" FC4			
Product	**Quantity (Kg)**	**Solids (%)**	**Functional Group**	**Description**
Pigment	150	63,5		
Thickener	*Xg to adjust viscosity*	21	Thickener	Non-Ionic; High Performance
Filler	75	28	Aqueous colloidal dispersion	Excellent print retention; Improves stacking; Good coverage, uniformity and filling; Warm, dry, pleasant feel
Water	250	0	Solvent	Improves compatibility and solubility
Resin A	75	20	Aromatic polyurethane	Improves adhesion without hardening; high wetting power; excellent levelling
Resin B	150	25	Aliphatic polyurethane	Very tough; flexible; non-tacky; excellent lightfastness; Heat resistance; Good embossing; Excellent coverage;
Resin C	100	35	Anionic polyester-polyurethane dispersion	Good film forming power; Excellent adhesion and ability to seal the surface
Resin D	100	60	Polyurethane dispersion	Excellent fastness properties; Not tacky; High elasticity and water resistance; Medium elongation;
Hand Modifier	15	68	Silicone Emulsion	High performance; Taber resistance; High wear; Resistance to wet and dry rubs
Water	50		Solvent	Dilutes Crosslinker
Crosslinker	30	39	Polycarbodiimide	Improves wet rub fastness and print retention; Resistance to accelerated ageing
Total	945			

Appendix C- Top Coat Formulation

Spray Inline	3x8g/m^2 24Kg			
Viscosity	28-32" FC4			
Product	**Quantity (Kg)**	**Solids (%)**	**Functional Group**	**Description**
Water	330	0	Solvent	Improves compatibility and solubility
Resin A	240	25	Aliphatic polyurethane dispersion	Zero bound duller; Non burnishing; good flexibility; Warm and feel
Resin B	140	19,5	Aliphatic polyurethane dispersion	High performance; Promotes abrasion and scuff resistance
Resin C	135	25	Polyurethane dispersion	Excellent fastness properties; Not tacky; High elasticity and water resistance; Medium elongation;
Leveler	10	98	Polyether Silicone	Prevents leveling problems; Improves Wettability;
Resin D	50	22	Acrylic resin	Use in pale, sensitive shades; Improves soiling resistance; Does not impair the fastness; Beneficial effect on the handle; Improves cleaning and wear resistance;
Hand Modifier	20	68	Silicone Emulsion	High Wear; Taber Resistance; Wet and dry rubs Resistance
Wax	20	30	Siloxane Resin	Heat resistance; Solvent rub fastness; Reduces repolishability; Enhances soiling resistance and cleaning; Improves abrasion resistance and taber rubfastness
Total	945			
Crosslinker	*100*	*80*	Polyurethane with isocyanate	Increases resistance to wet and dry rubs; Promotes abrasion and scuff resistance

Appendix D- Clean Top Formulation

Spray Hot Pot	1x2g sq.ft (wet) 8Kg			
Viscosity	As is			
Product	**Quantity (Kg)**	**Solids (%)**	**Functional Group**	
Water	300	0	Solvent	Improves compatibility and solubility
Clean Top	700	29	Acrylic/Polyurethane dispersion	Improve dirt and dye resistance; Maintains stick-slip performance; Warm, soft natural handle
Crosslinker	60	50	Polycarbodiimide	Improves wet rub fastness; Non yellowing; Excellent resistance to accelerated ageing
Total	1060			

Appendix E- Derivation of the Carbodiimide Concentration function

Derivation:

$$f(x) = y = 0{,}0166x^3 - 0{,}3883x^2 + 2{,}8788x - 2{,}4099$$

$$\frac{d}{dx}f(x) = \frac{d}{dx}[0{,}0166x^3 - 0{,}3883x^2 + 2{,}8788x - 2{,}4099] \Leftrightarrow$$

$$\Leftrightarrow \frac{d}{dx}f(x) = 0{,}0166 * \frac{d}{dx}x^3 - 0{,}3883 * \frac{d}{dx}x^2 + 2{,}8788 * \frac{d}{dx}x - \frac{d}{dx}2{,}4203 \Leftrightarrow$$

$$\Leftrightarrow \frac{d}{dx}f(x) = 0{,}0498 * x^2 - 0{,}7776 * x + 2{,}8788$$

Zero:

$$0 = 0{,}0498 * x^2 - 0{,}7776 * x + 2{,}8788 \Leftrightarrow$$

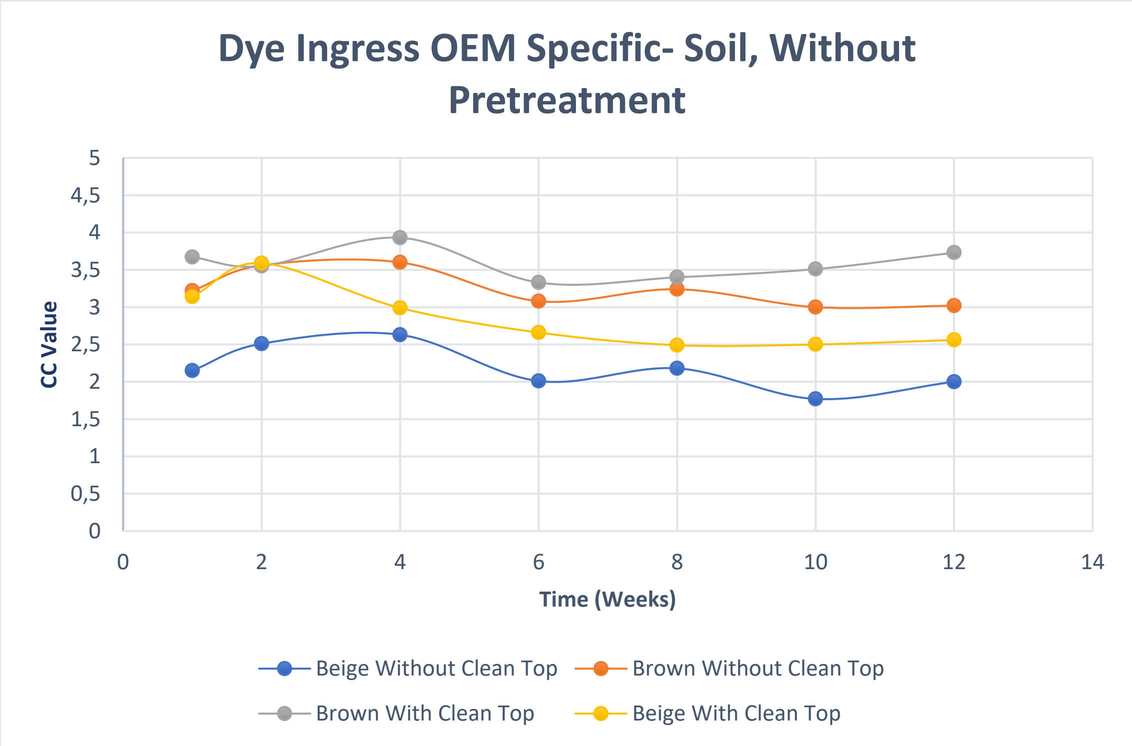
$$x = \frac{0.7776 \pm \sqrt{0{,}7776^2 - 4 * 0{,}0498 * 2.8788}}{2 * 0{,}0498}$$

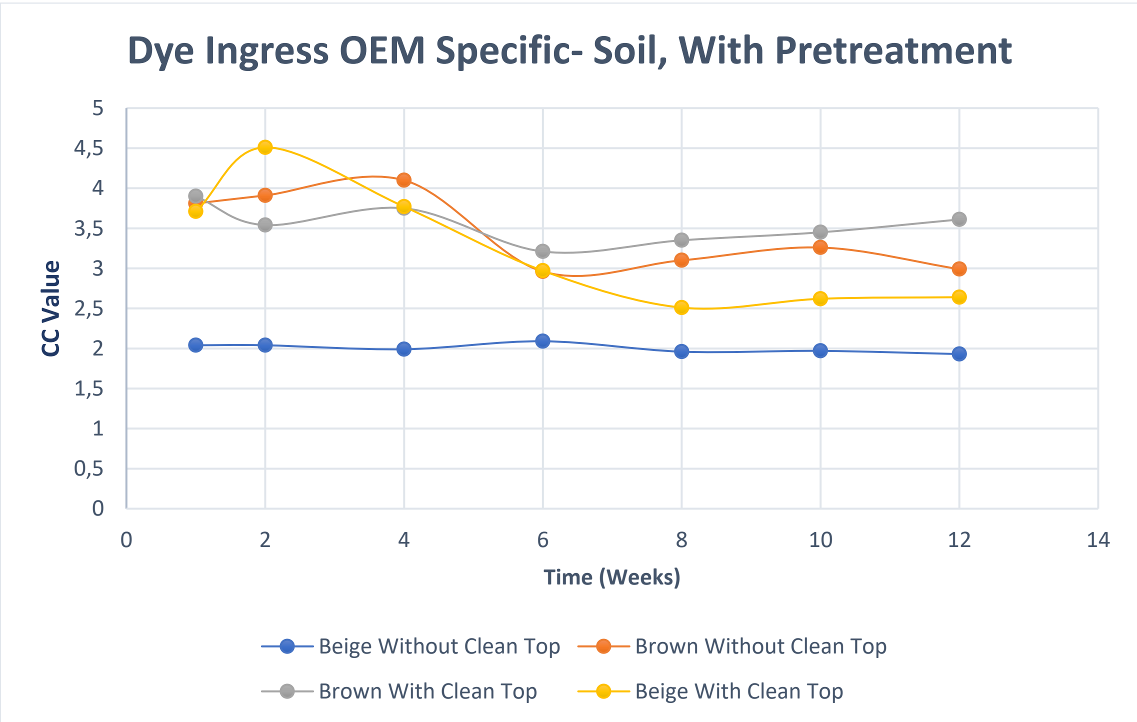
$$x = 6{,}07$$

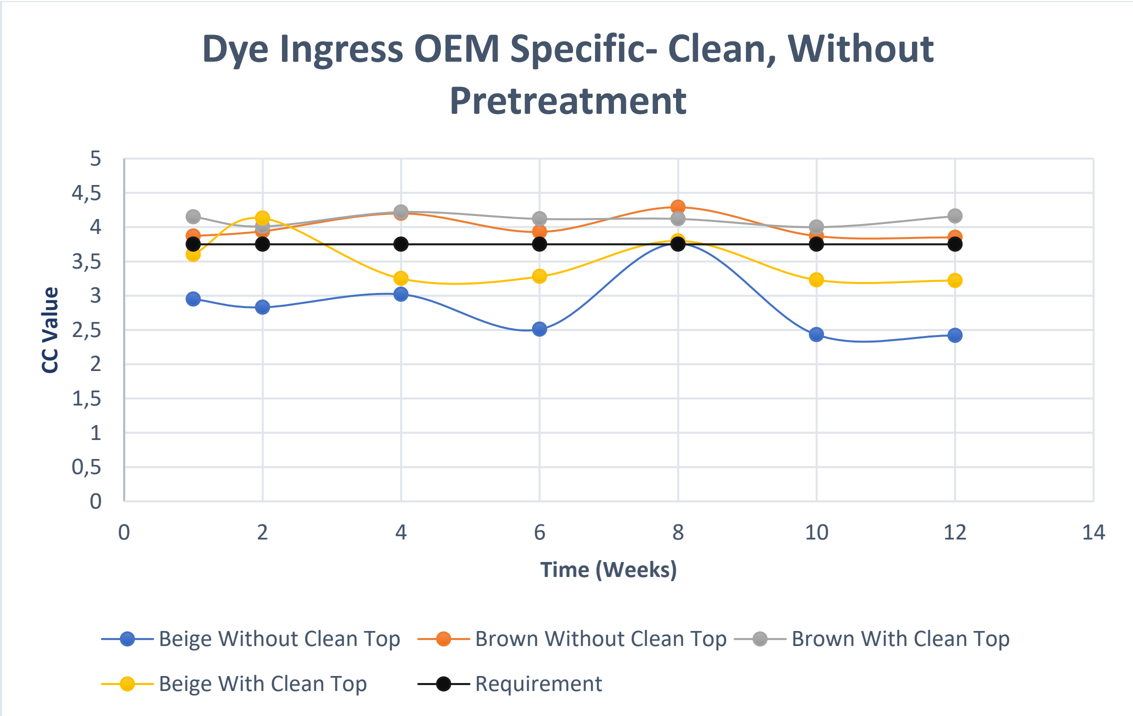
CC Value:

$f(6{,}07)$= CC value = $0{,}0166*6{,}07^3 - 0{,}3883*6{,}07^2 + 2{,}8788*6{,}06 - 2{,}4099 = 4{,}47$

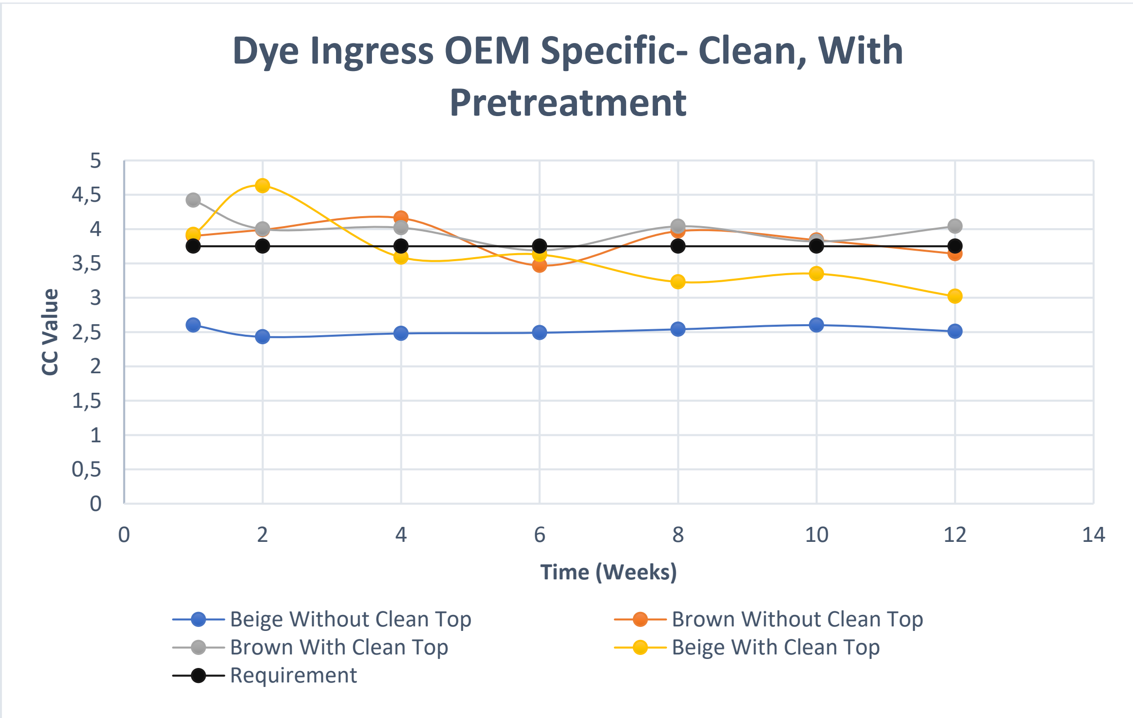
Appendix F- Dye Ingress OEM Specific Results





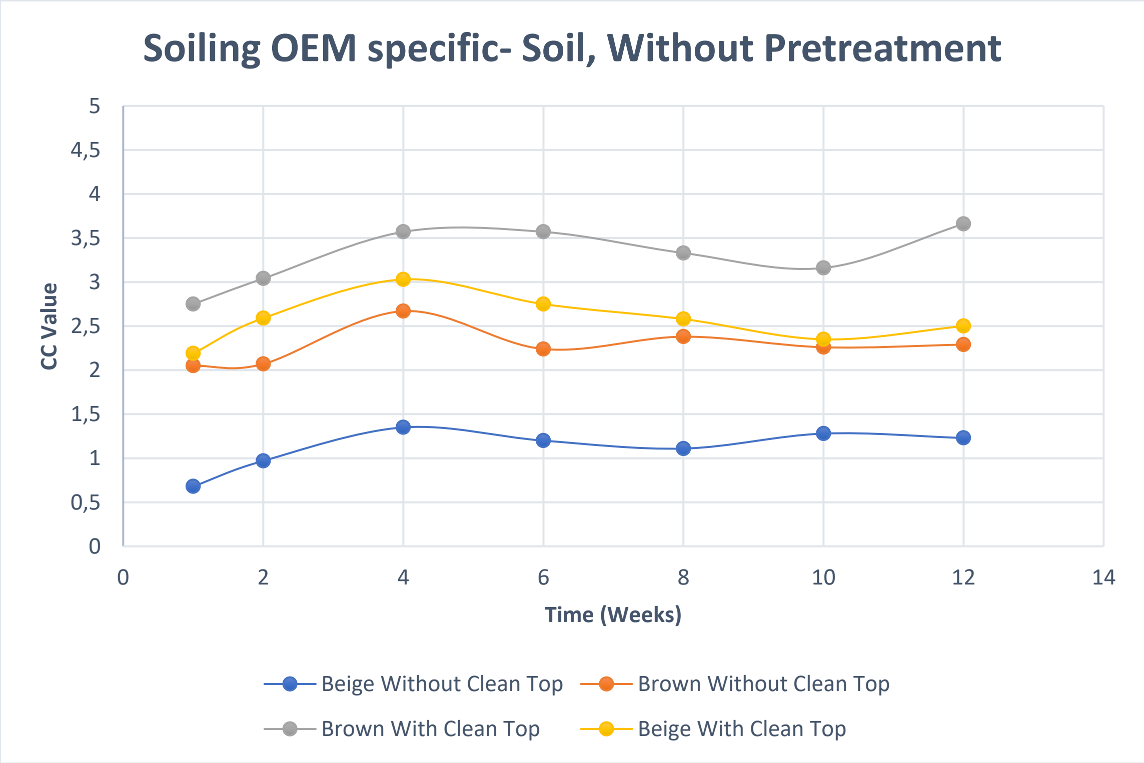


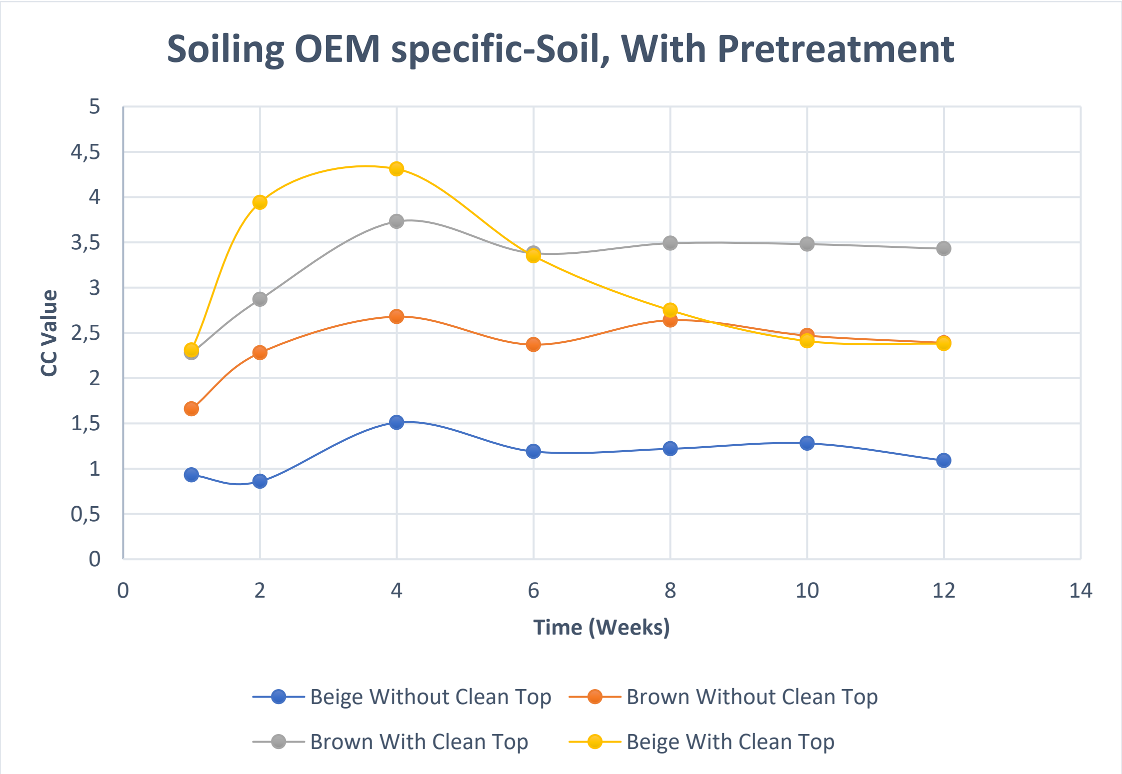
Dye Ingress OEM Specific- Clean, Without Pretreatment
CC Value
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0
2
4
6
8
10
12
14
Time (Weeks)
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement

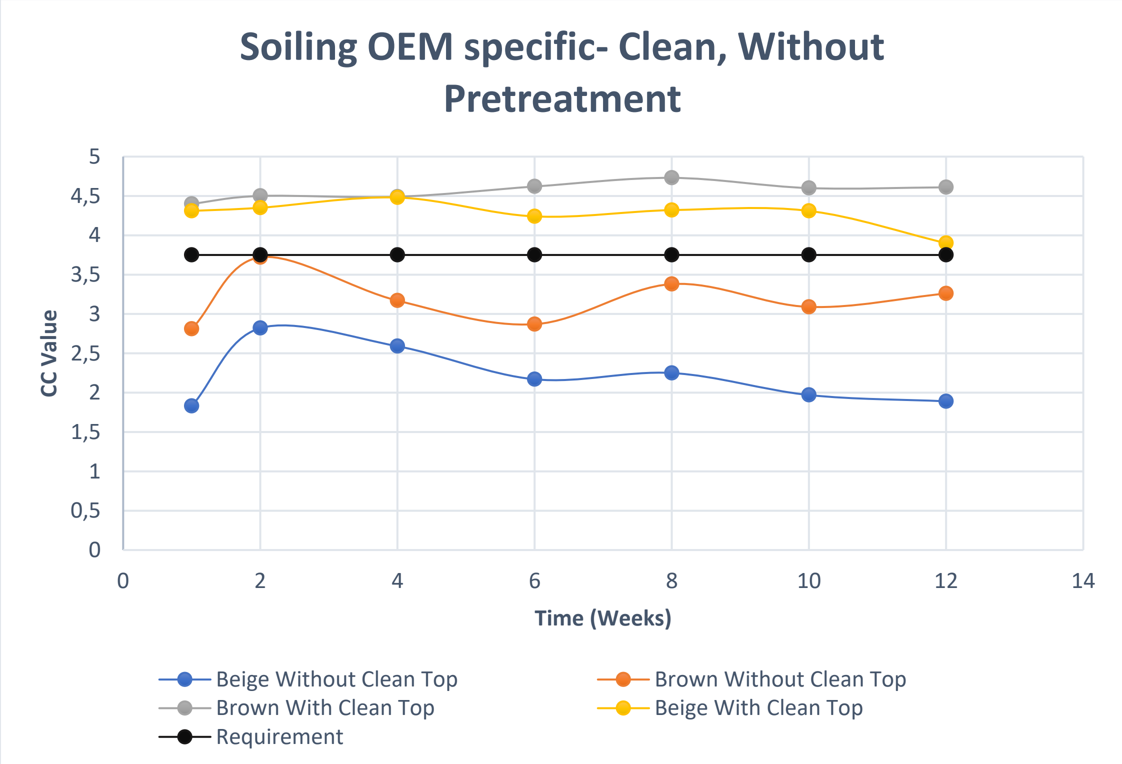


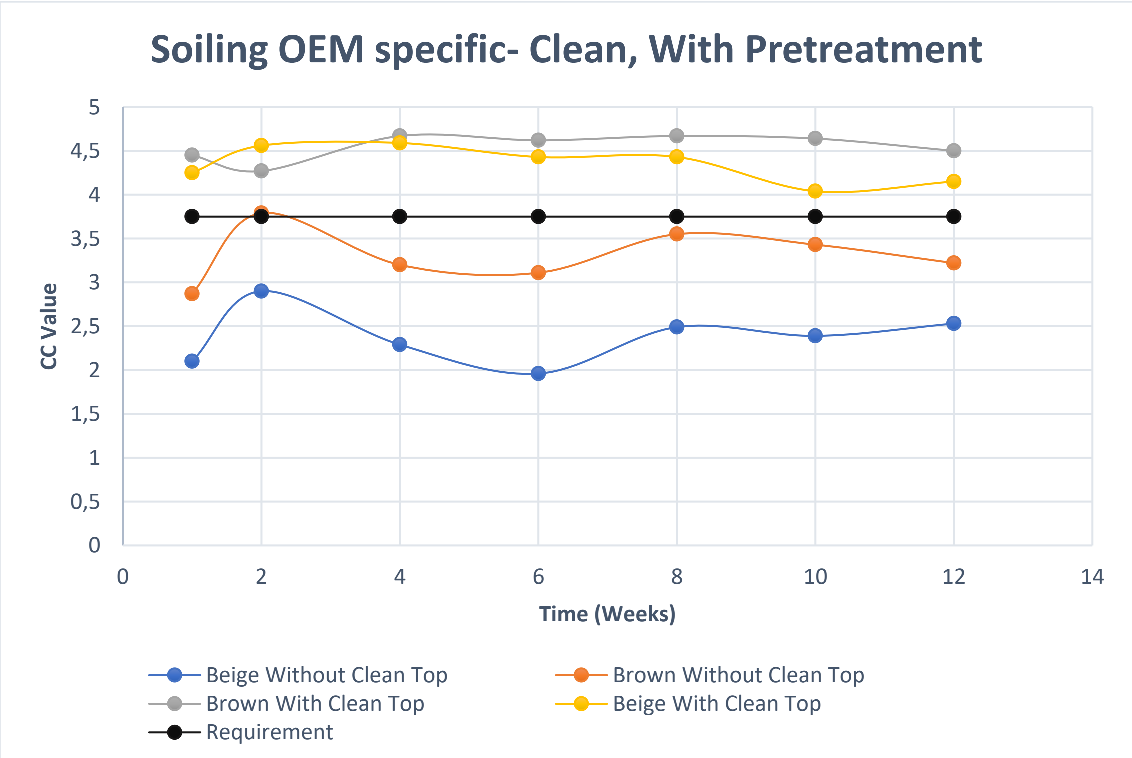
Dye Ingress OEM Specific- Clean, With Pretreatment
CC Value
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0
2
4
6
8
10
12
14
Time (Weeks)
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement

Appendix G- Soiling OEM specific Standard Results

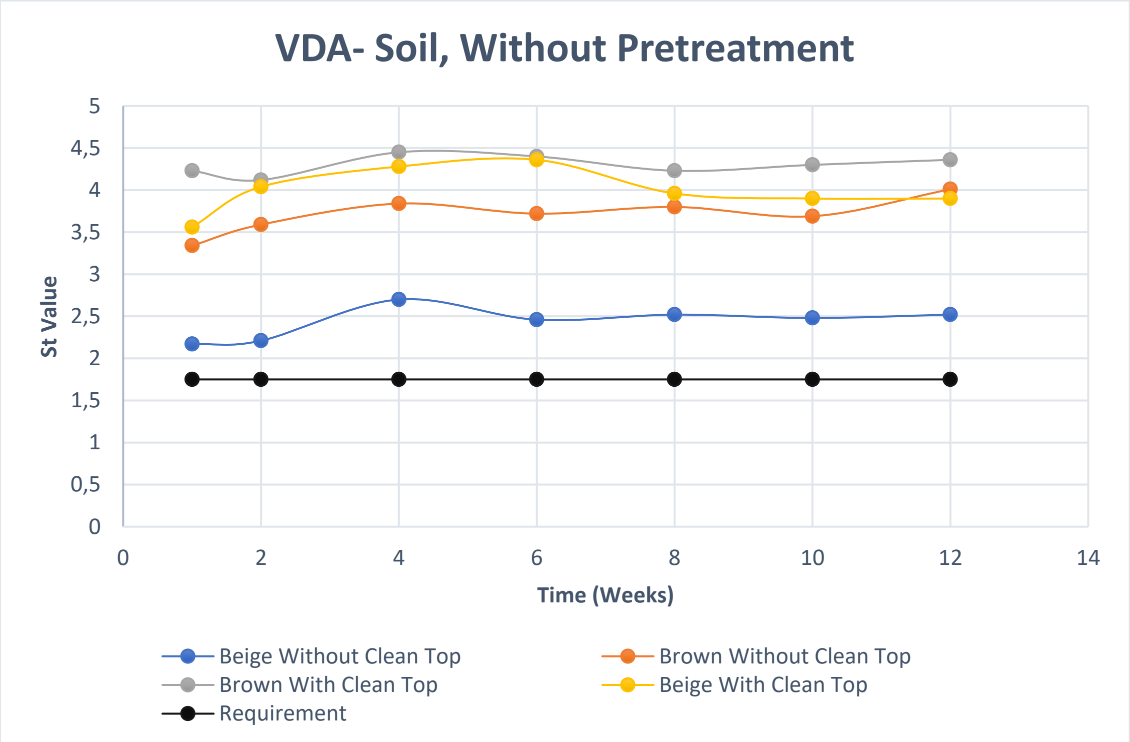


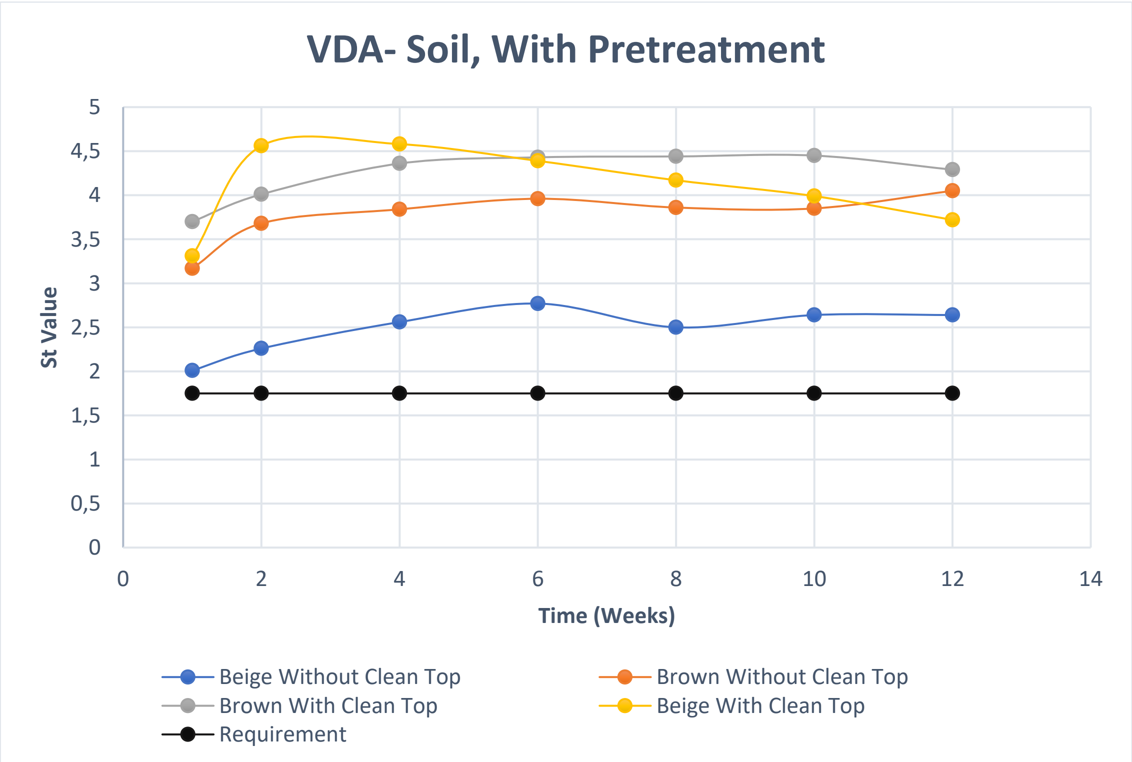


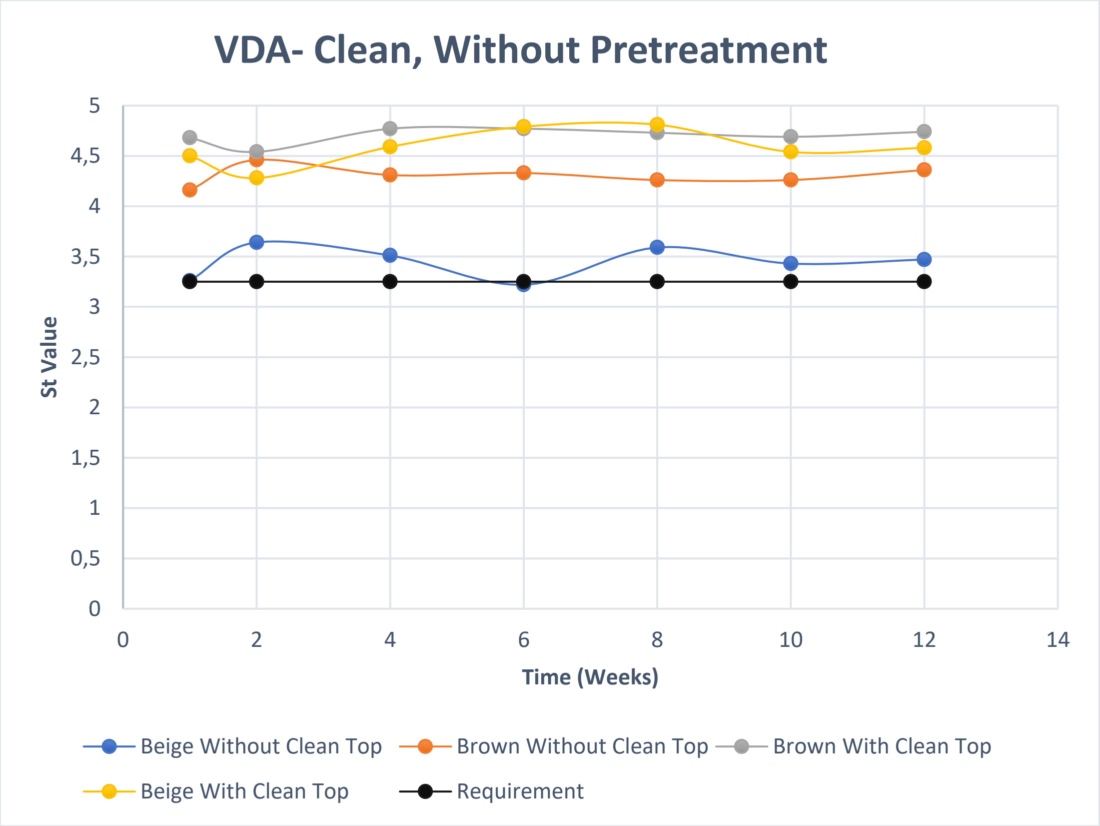

Soiling OEM specific- Clean, Without Pretreatment
CC Value
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0
2
4
6
8
10
12
14
Time (Weeks)
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement

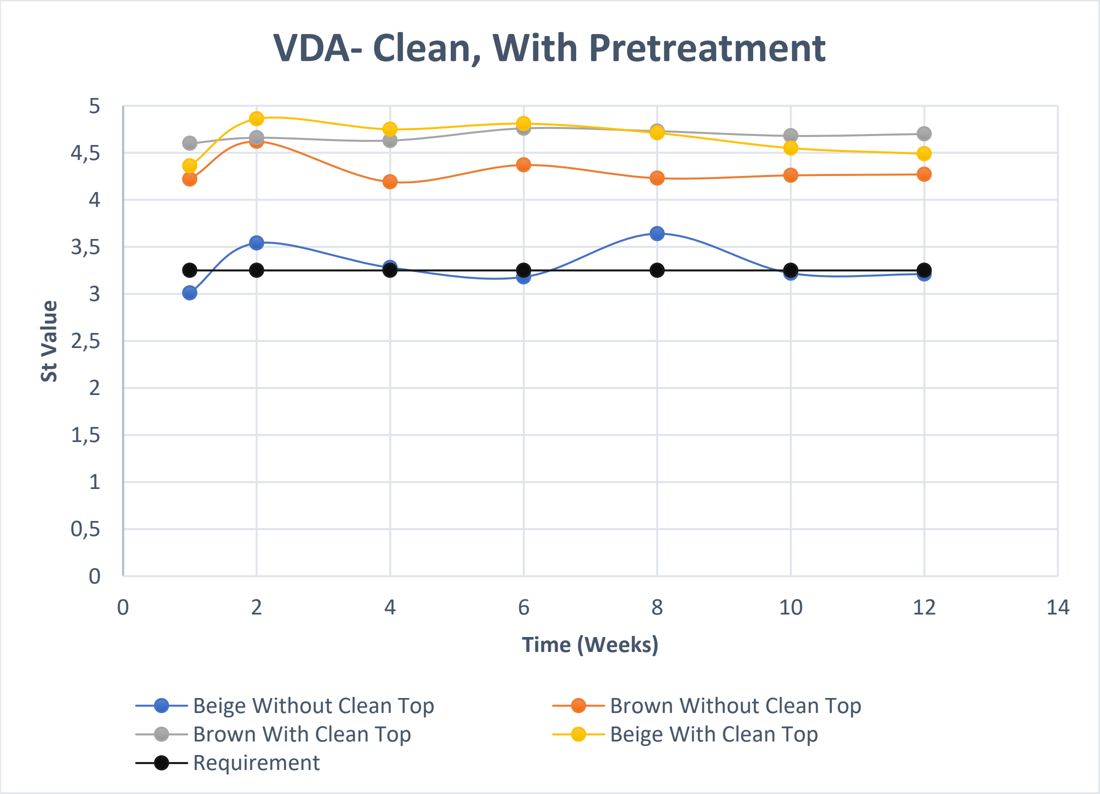

Soiling OEM specific- Clean, With Pretreatment
CC Value
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0
2
4
6
8
10
12
14
Time (Weeks)
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement

Appendix H- VDA Standard Results






VDA- Clean, Without Pretreatment
St Value
Time (Weeks)
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
0
2
4
6
8
10
12
14
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement


VDA- Clean, With Pretreatment
St Value
Time (Weeks)
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
0
2
4
6
8
10
12
14
Beige Without Clean Top
Brown Without Clean Top
Brown With Clean Top
Beige With Clean Top
Requirement

Appendix I- Finish Addon Calculations

	Formulations		Application		
	g Wet	g Dry	g Wet/ ft^2	g Dry/ ft^2	%
Base Coat	1025	369,8	11,7	4,21	71,89
Color Coat	995	285,7	2,7	0,76	13,00
Top Coat	1045	241,5	2,5	0,58	9,87
Clean Top	760	233	2	0,31	5,24
Total			18,81	5,85	100,00