

Master in Chemical Engineering

***Evaluation of the performance of black coatings
for space applications***

Master's Thesis

by

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HPS Portugal

HPS

High Performance Structures
Gestão e Engenharia Lda.
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Abstract

Space environment and its extreme conditions can cause degradation of non-coated surfaces, reducing their life time and their capability to perform well during a mission. In space as the only way of heat transportation comes from radiation, these surfaces need to be able to resist against the problems associated with extreme temperatures, radiation UV and vacuum and for that there has been considerable investment in developing new materials and coatings. There is a number of black paints used to be able to resist and protect against these conditions, to help to maintain a desire temperature in space equipment and to avoid image degradation in optical equipment.

This work aims to test two black powder paints suggested by CIN (Maia, Portugal) because of their thermal and mechanical properties. For this, the influence of the three main steps of the painting process (pre-treatment, painting method and curing) on the painting adhesion properties of these paints in aluminium substrate was reviewed. Also a further study of the influence of different environments based on three standard tests was performed. The first test conducted was the hygroscopic test, where four specimens of each paint were placed in a water circulation system at 38 °C for 1 hour. The second test was the thermal shock, where in a first phase four specimens were immersed into liquid nitrogen (-195 °C) and in a second phase placed in an oven at 150 °C for 30 min in each environment. The final test was the UV degradation test, where four aluminium specimens painted with each paint were placed during 2 weeks under UV radiation, ca. 40 W/m². After all the performed tests, the specimens were subjected to an adhesion test and the paint adhesion to the substrate was classified.

The main conclusions withdrawn after the completion of this work are that both paints were able to resist to UV radiation, thermal shock with temperatures between -195 °C and 150 °C and to water, with no sign of any degradation on the surface. These leads also to the conclusion that the paint process is indicated for these paints that were able to withstand the same environments conditions tested during this work.

In other hand, these three tests are insufficient to conclude that both paints are suitable to be used in space applications because there are other tests (vacuum degradation test, outgassing test, etc.) mandatory for this industry.

Key Words (Theme): paint, thermal control, stray light, adhesion, thermal shock

Resumo

O ambiente espacial e as suas condições extremas podem causar em materiais não-revestidos degradação das suas propriedades, reduzindo o seu tempo de vida e a sua capacidade de realizar a sua missão obtendo os melhores resultados. Como o único meio de transporte de calor no espaço é através de radiação, estas superfícies precisam de ser capazes de resistir a problemas associados às temperaturas extremas, radiação UV e vácuo, e para isso tem havido um grande investimento no desenvolvimento de novas matérias e revestimentos. Existem inúmeras tintas pretas utilizadas para o controlo térmico de equipamentos espaciais e para evitar a degradação da imagem captada em equipamentos óticos.

Este trabalho visa testar duas tintas pretas em pó sugeridas pelas suas propriedades térmicas e mecânicas para serem usadas no espaço. Para isso, foram revistas as influências dos principais processos da pintura (pré-tratamento, o método de pintura e a secagem) nas propriedades de adesão destas duas tintas aplicadas num substrato de alumínio com a realização posterior de três testes padrão necessários para a indústria espacial. O primeiro teste foi o teste higroscópico, em que quatro amostras de cada tinta foram colocadas em água a 38 °C num sistema em recirculação durante 1 hora. O segundo teste foi o choque térmico seguido, em que numa primeira fase houve a imersão em nitrogénio líquido (-195 °C) de quatro amostras de alumínio pintadas e numa segunda fase colocadas numa estufa a 150 °C, durante 30 min em ambos os ambientes. O teste final foi o teste de degradação UV, onde quatro amostras de alumínio pintadas para cada uma das tintas foram colocadas durante 2 semanas sob radiação UV, aproximadamente 40 W/m².

As principais conclusões que se podem tirar após a realização deste trabalho são que ambas as tintas foram capazes de resistir à radiação UV, a choques térmicos com variações de temperatura entre -195 °C e 150 °C, sem sinais de qualquer degradação observados na superfície.

Por outro lado, estes três testes realizados são insuficientes para se concluir que estas tintas são indicadas para aplicações espaciais, porque existem outros testes (teste do vácuo, teste de outgassing, etc.) obrigatórios nesta indústria.

Statement

Declare, with honor, that this work is original and that all non-original contributions were properly referenced with the source identification.

Sign and date

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Notation and Glossary

List of Abbreviations

Feup	Faculdade de Engenharia da Universidade do Porto
HPS	High Performance Structures
UV	Ultraviolet
TCS	Thermal control systems
IR	Infrared
INEGI	Institute of Mechanical Engineering and Industrial Management
ESA	European Space Agency
SME	Small and Medium Enterprises
R & D	Research and development
DEMEGI	Department of Mechanical Engineering and Industrial Management
US \$	United States dollars
MLI	Multilayer insulation
LDEF	Long duration exposure facilities
TML	Total mass loss
CVCM	Collected volatile condensable materials
WVR	Water vapour regained
ASTM	American Society for Testing and Materials
DEQ	Department of Chemical Engineering
PVC	Poly(vinyl chloride)
ISO	International Organization for Standardization
ECSS	European Cooperation for Space Standardization

List of Symbols

a_s	Solar absorptance
a	Absorptance
ε	Emittance

1 Introduction

1.1 Background and Project Presentation

From planet Earth, the boundlessness of space may seem tranquil enough, yet this same environment represents a functional and durability challenge for both manned and unmanned equipment. Even before any exploration in the heaven, there was an idea that the sky was a harsh environment, prone to remarkable variations in radiation and temperature levels that can cause material degradation of their characteristics or even disable it over a period of time, or even instantaneously.

To protect critical subsystems against this harsh environment, there was always a crucial and difficult challenge to find efficient and cost effective ways (e.g., power supplies, life support systems, sensitive electronics, communications equipment and sensors), from an unforgiving and dynamic environment.

To protect spacecraft and their working components against the harmful effects of extreme temperatures are used thermal control systems (TCS). The most used form of thermal control for space environment is the passive subsystems that rely heavily on reflective coatings such as paints (e.g., black paints) and mirrors. Due to the varying amount and forms of thermal energy in space e.g., solar radiation, albedo (electromagnetic radiation reflected off of spacecraft surfaces), heat generated by on board equipment, and earth-emitted infrared (IR) rays is crucial to have a well-designed and properly operating TCS.

Besides the thermal regulation, the problem associated to optical instruments like telescope baffles and lens edges affected by stray light from the Sun, Earth limb, Moon as well as from its own housing that can degrade their image can be overwhelm by also the use of coatings.

1.2 HPS Portugal Company

This work was proposed by the company HPS with the goal of developing a low cost method of applying coatings for space applications.

HPS - High Performance Structures, Management and Engineering Ltd, a company based in Porto, on the premises of INEGI - Institute of Mechanical Engineering and Industrial Management, is focused on aerospace projects and activities, scientific and technological studies and various engineering services.

The company HPS was created with the intention of merging complementary capabilities between the German company HPS - High Performance Space Structure Systems, GmbH and INEGI on the areas of management, engineering and technology development. It is a company whose main business area are products and projects related to aerospace and other engineering-related services, and its activity linked with the development of MLI (multi-layer insulation) blankets, advanced composite materials and structures, design and analysis of complex mechanical structures and subsystems providing, always, competitive advantage in terms of quality and cost.

HPS Portugal belongs 70 % to HPS GmbH, 24% to INEGI and 6 % to private Portuguese investors and most part of its activity is directed towards R & D projects with ESA - European Space Agency. It is composed by a team of 12 people including engineers and production staff with a production area of 150 m² consisted by workshops and a cleaning room.



Figure 1: HPS Portugal Cleaning room

Regarding HPS-GmbH is an SME located in Munich and with offices in Braunschweig. HPS was originated from two German companies working in the space systems area (kayser-Threde) and in the composite structures for aeronautic and aerospace. It is also specialized in lightweight structures, thermal protection systems and smart structures. Was established in 2000 and has presented more than 100 research and development projects with the European Space Agency yielding new technologies and products to the market.

Concerning the INEGI is an institution that allows the connection between the University and Industry. It focuses on the realization of activity for Innovation and Technology Transfer oriented to industrial tissue. It was originated in 1986 in the Department of Mechanical Engineering and Industrial Management (DEMEGI) in the Faculty of Engineering, University of Porto (FEUP), which still maintains that connection, providing a major source of knowledge, scientific and technological ability.

1.3 Work Contributions

The complexity of future spacecraft, their long-term missions, and flight exposure to harsh environments require identification of new materials and coatings for spacecraft use, because no one coating can meet the criteria for all applications.

At present, due to the problem of the stray light affecting the properties of optical instruments and the need to maintain a constant temperature there has been a great financial investment in research and in the development of black coatings because of their durability and their acceptable thermo-optical properties.

This work aims to analyse, characterize and evaluate the performance some black powder paints to evaluate if they are suitable to be used in space applications following all the standard test methods and the safety specifications required for this area.

In the evaluation of these methods, we intend to evaluate the performance in terms of the coating adhesion to the aluminium substrate, hygroscopic, resistance to UV radiation, to thermal shock and to obtain the ideal conditions to apply them.

1.4 Thesis Organization

This present dissertation is organized in 4 chapters including this introductory chapter.

The second chapter is subdivided into subchapters, which initially begin by defining in general terms what is a coating and their material structure. Following is given a historical perspective of the coatings in the world. Next will be described all the process technology of the manufacture and processing of coatings, most precisely substrate and their pre-treatment, and posteriorly all the application and curing process existing for coatings. Lastly will be explained the main problems associated to the space environment and why the need for coatings in space applications and the most used ones for this purpose.

In the chapter 3 are presented and discussed all the results obtained from the experiments performed, where it is intended primarily to describe all procedures, such as the materials used. Finally are represented all the results obtained, with its consequent analysis.

Ends with Chapter 4, which represents the conclusions and limitations of the study, such as the proposed future work.

2 Context and State of the Art

2.1 Coatings

2.1.1 Classification and material structure of coatings

“Coatings” is a designation term used to describe a wide variety of products in order to decorate and/or provide surface protection. There are two separate groups of coatings [1]:

Non-curing coatings - a term used for coatings which harden by “natural” chemical reactions once applied to a surface eg., linseed oil. These coatings are the less produced.

Curing Coatings - these coatings are formed by a solvent, binder, and sometimes solids and its curing process occurs through the solvent evaporation, allowing the binder (a resin) to harden to a solid. This makes the resultant film tougher, one of the characteristics that make them preferred.

“Coatings” is not only a synonymous for paint, the layer on the coated products, but also the painting process. Paints can be liquid, paste or powder coating materials that provides protective, decorative and also specific technical properties. They can be classified according to [2]:

- its function (clearcoat, metallic paint, solid paint);
- layer type in the coating system (primer, primer surface, topcoat);
- purpose (car paint, decorative paint, industrial paint);
- degree of environment compatibility (water based paint, high solids paint, radiation curable systems, powder coatings);
- chemistry of the film forming agent (alkyd resin paint, acrylic resin paint, cellulose nitrate lacquer);
- processing conditions (baking enamel, oxidatively curable coating material).

All coatings materials can be based on the structure shown in the table 1, but this does not necessarily mean that they contain all these components.

Table 1: Coating materials structure [2]

Coating material	
Non-volatile matter	Volatile matter
Pigments	Solvents or dispersants
Fillers	Volatile additives
Film-formers	(any elimination products from stoving)
Non-volatile additives	

Pigments

These powders are finely dispersed substances, insoluble in substrate used to give colour or to protect against corrosion.

Examples: Titanium dioxide, carbon black, pearlescent pigments and zinc phosphate.

Fillers

Fillers are granular solids used to give toughness, texture or to improve technological properties and to give a larger volume to the coating material.

Examples: Chalk, talcum, cellulose fibres.

Film formers

They are responsible for the film formation and can be macromolecular substances.

Examples: Chlorine rubber, alkyd resin, polyester/polyisocyanate blends (two-component systems), polyester acrylate (radiation-curable).

Additives

Substances with desired chemical or technological properties, like additives to improve flow properties, improve pigment stability, etc.

Examples: Hardening accelerators (catalysts), thickeners, dispersants, flow control agents, flatting agents, preservatives.

Solvents

Liquids used to dissolve the polymer and adjust the viscosity of the paint.

Examples: Butyl acetate, butyl glycol, white spirit, water.

Dispersants

Liquids incapable to dissolve the film formers but instead hold them in a fine, micro heterogeneous dispersion (or emulsion).

Examples: Water and, in non-aqueous dispersions, hydrocarbons.

The selection of the right coating materials for an optimum performance depends equally on the quality requirements, the specified application conditions, the curing process, the design features and the various materials of the object to be painted. However, all coatings materials should have the same properties of wetting substrates, transforming into a closed film, flowing and then solidifying to make the desired mechanical and chemical protection.

2.1.2 Coatings technology [2]

Coating technology covers all the process technology of the manufacture and processing of coatings, where processing can be subdivided into processes of application (spraying, dipping, brushing, etc.) and of drying or curing (air drying, stoving, radiation curing). The object to be paint, its pre-treatment and the actual painting process itself have to be optimally coordinated with each other.

In the industry, the object to be painted passes through a high number of units in order to achieve a permanently decorative and protective skin. Firstly, the substrate receives the right pre-treatment method to make him capable of being painted. This pre-treatment consist of physical and chemical cleaning methods and on the application of thin, inorganic conversion layers.

After the material receives their pre-treatment, follows the processes of application, drying and curing of the coating material. In the painting application that can be done in the form of brush, roller, dip, flood, curtain or spray coating, the liquid or, in the case of powder coating, solid coating material can be transformed there into a uniformly thin, mechanically strong film.

Figure 2 shows the sequential steps followed when an object is subjected to painting process.

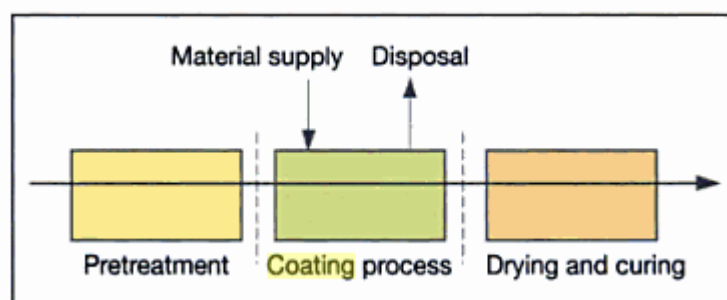


Figure 2: Process steps of coating lines [2]

One of the main problems related to coating technology is to obtain a uniform surface after a coating has been applied. Any irregularities formed during this process such as brush strokes, build-up of droplets from spraying or rollers marks should disappear naturally.

2.1.3 Substrates and pre-treatments

Coating materials are an intermediate product and not a final product. The end product is the finished, cured coating and this is consisted of the coating itself and the coated substrate. The cured coating can be used to serve several purposes, e.g., protect the coated object from environmental damage, decorative and improve special physical or functional surface characteristics. This only can be accomplished if there is a strong coating-substrate adhesion.

To determine if there is a good adhesion to the substrate, not only the coating material alone has to be taken in count but also the properties of the coated substrate. As pre-requisite for a perfect adhesion, firstly the substrate before being coated must go through a pre-treatment or preparation process, and secondly the coating material must be matched to the substrate in terms of specific film properties, e.g., hardness or thermal expansion behaviour. Furthermore, the method of application and the possible curing methods are determined by the substrate, thought its heat resistance and its dimensions.

Table 2 shows the surface pre-treatments that can be applied to each substrate. [3]

Table 2: Surface pre-treatment of several substrates [3]

Substrate	Contaminants	Cleaning	Preparation/Pre-treatment
Metals	Metal filings, oils, greases, scale, rust, oxides, rust film, dust, silicones, lapping, paste, paint, residues, old coatings	Mechanical: wiping, grinding, polishing, brushing, blasting	Activating, pickling (Al), phosphatising, chromating, chromate-free processes, secondary passivating
		Thermal: flame treatment	
		Chemical: pickling, cleaning with solvents or aqueous cleaning agents	
Plastics	Greases, oils, release agents, dust, perspiration from hands	Mechanical: abrading, blowing off, rinsing	Flame treatment, plasma treatment, corona discharge, fluorination, chromic acid process, satinising, benzophenone/UV
		Chemical: solvents or aqueous cleaning agents	
Wood	Sanding residues, dust, moisture, wood constituents, paint residues	Mechanical only: sanding, polishing, brushing	Impregnating, sealing, priming
Mineral substrates	Dust, salts, greases, tyre marks, old coatings	Mechanical: blasting	Impregnating, sealing, hydrophobing
		Chemical: solvents or aqueous cleaning agents	

2.1.4 Application and Curing

Any coating process has to satisfy as far as possible the three criteria of:

- Cost-effectiveness
- Quality (in regard to performance and appearance) and
- Environmental compatibility, health and safety

, all three are important factors that can influence the choice of a given method of application.

A coating is only considered a finished product if it has been successfully applied to a substrate and cured. Environmental conditions are the main causes that can influence the performance of a coating, like temperature, relative humidity, etc. resulting in defects, premature failure or reduced service life, if not controlled.

After the substrate pre-treatment and the right environmental conditions achieved, the material is ready for painting. There are many processes depending on the type of the material and surface to transfer the coating into the substrate.

Table 3 shows a simple and clear system for classifying painting processes.

Table 3: Important coating processes [4]

Object to Paint	Paint to Object
Conventional dipping <ul style="list-style-type: none"> • Solventborne paints • Waterborne paints 	Direct processes <ul style="list-style-type: none"> • Brushing • Scrolling, rolling • Flooding, pouring
Electrodeposition <ul style="list-style-type: none"> • Anodic • cathodic 	Indirect processes <ul style="list-style-type: none"> • High pressure atomization <ul style="list-style-type: none"> • Airless atomization • High rotation bell application • Electrostatical atomization

In conventional dip coating processes or those assisted by electrochemical coagulation the object is transported to the coating material. Such processes also include fluidized-bed coating for processing powder coatings. For the rest of the processing methods the object is painted by means of manual or mechanical roller, curtain or flood coating with only low

material spill or indirectly by means of atomization and spray coating, albeit with at times considerably lower material yields. Despite this disadvantage, the latter processes are the most commonly used industrial application techniques.

The following is a description of the application equipment and methods [4]:

- **Brush** - Generally there are two types of brushes: wall and sash. Depending on the substrate and their area, they can have different sizes, shapes and bristle types. For example, on steel substrates, wall brushes are used for small areas, repair areas, and crevices or gaps. Wall or oval brushes are preferred for stripe coatings irregular surfaces such as edges, corners and similar areas. On the other hand, sash brushes are better for coating narrow areas.
- **Roller** - They are constituted by a cover and a core. The cover is the part of the roller used to apply the coating and can have different diameters, length and fabric types. Rollers are used for large areas that are too big for brush applications or where overspray cannot be accepted.
- **Conventional Spray** - For this spray technique its necessary an air compressor, oil and water separator, a pressure tank or pump, air and fluid hoses, and a spray gun. For hot spray, a heater is needed to heat the material.

In this method the compressed air is mixed with the paint forming a finely atomized coating with a more uniform film. Can paint large areas relatively fast but on the other hand, this method consume large amounts of air, transfer efficiency is low due to material loss and it is not generally suitable for high-build coating materials without excessive thinning. Striping can be accomplished by this method and for hot spray applications, the viscosity is lowered to improve application or to meet minimum material temperature.

- **Airless Spray** - To perform this technique is needed a power source (electric motor or air compressor), a hydraulic pressure pump, a high-pressure fluid hose, and an airless spray gun with a safety extension tip.

During this method, the material is forced to pass through a small orifice using hydraulic pressure rather than air pressure. The spray gun has a fixed orifice size and various fixed angles to allow several spray fan patterns and thicknesses to be applied with the same amount of material. This provides greater capacity for applying high build coatings, greater surfaces penetration because of high application pressures, high coverage or production rates, the capacity to atomize high viscosity materials, reduced overspray and bounce back and the potential for reduced oil and water

contamination. On the other hand, this method does not produce the finely atomized coating particles that are produced by conventional spray, and it is not suited for high quality finishes. The operator has less control of the spray gun than with the conventional spray method, and there is a higher potential for application defects than with the conventional spray method.

Electrostatic Spray - This method is similar to the conventional airless spray, except that an electrostatic, high-voltage supply is required. The coating material can be positively or negatively charged and is attracted by the substrate that is negatively or positively charged and then cured with heat that will fluidize and harden. This method can be applied to any shapes and in corners. Has a high transfer efficiency rate and produces a uniform film. On the other hand, the wind can provoke loss of material. This method only allows one thin coat, is unsuitable for large structures and presents a potential electrical shock hazard.

After the coating has been applied, is necessary an ideal combination of temperature and humidity to allow the coating to complete the chemical reaction and to achieve structural integrity, called the Curing process. These factors and others like excessive moisture can influence the curing process. [4]

2.1.5 Coatings historical evolution [3]

The earliest known use of paint dates back around 30,000 years. People used mixtures of coloured earth, soot, grease and other natural substances to paint their bodies and to decorate their homes and places of worship, one such example being the cave paintings discovered in southern France and northern Spain.

The advanced civilisations of the Egyptians (from 4000 years B.C.), Greeks and Romans used sophisticated painting techniques to decorate or to identify vessels, statues, tools and buildings. Raw materials included vegetable, gums, starches, hide glue, milk (products), beeswax, charcoal and various minerals. Natural dyes such as indigo, purple and madder were used to dye textiles, fibres, wood, paper and leather.

In contrast to the decorative or colour-giving use of paints described so far, the art of lacquer work was developed in china from around 2000 years before Christ, to produce smooth and glossy surfaces. The lacquers were based on the sap of the of the Chinese rhus tree and, in addition to their decorative effect, they also had a protective function. Raw materials such as balsams and resins, vermilion and ultramarine, came predominantly from

India. The word “lacquer” itself stems from the term “Laksha”, from the pre-Christian, sacred Indian language Sanskrit, and originally referred to shellac, a resin produced by special insects (“lac insects”) from the sap of an Indian fig tree.

Seafaring brought with it another important area of application for coatings. The fourth century before Christ saw a wave of migration spreading from Asia Minor as far as England and Scandinavia - some of it by land and some by sea. The wooden ships that carried the migrants were made water light with mixtures of non-drying (non-curing) oils and tree resins or rock asphalt.

Leaping further forward in time, around the year AD 1100 the German goldsmith and monk Roger von Helmarshausen (Theophilus) described the manufacture of a coating by boiling linseed oil with molten amber. This process, known as paint boiling, continued to develop and by the 17th century there were numerous recipes for coatings made from a variety of natural resins, linseed oil and spirit.

Around the 18th century, the Industrial Revolution brought about a dramatic rise in the demand for paints and coatings. In particular, the increasing numbers of goods and buildings produced from rust-prone iron needed to be treated to protect them against weathering. Furthermore, countries with a strong seafaring economy required large quantities of marine paints. The first paint factories, which appeared in England in 1790, grew out of the larger paint workshops. They were followed by factories in Holland and later in Germany and other countries.

With the exception of a few synthetic pigments already produced on an industrial scale (Berlin blue, cobalt blue, mineral green, and chromium yellow), the raw materials for coatings were all of natural origin even in the 19th century. A distinction was made between “volatile paints”, “varnishes” and “long-oil paints”. This last group were manufactured by boiling resins with drying oils in “brewing kettles”, adding pigments if required. The addition of pigments became increasingly mechanised - first using cone mills then, from the early 20th century, cylinder mills. One weak point of these products was their extended drying time; it could take several weeks to paint an entire coach or car.

Around the 20th century, in terms of coatings technology, the following advances were particularly important:

- the development of polymer chemistry
- the invention of the production line by Henry Ford (1913) and the mass production of cars arising from it.

In the response to the demand for faster coatings technologies, the spraying of coatings based on cellulose nitrate (nitrocellulose) was introduced.

In 1907, the first entirely synthetic resins, phenol-formaldehyde condensates (“Bakelite”) were launched on the market. These were followed in rapid succession by vinyl resins, urea resins and, from the 1930s onwards, alkyd resins, acrylic resins, polyurethanes and melamine resin. Epoxy resins were introduced in the late 1940s. Titanium dioxide established itself as the leading white pigment when it went into mass production in 1919.

These developments in coating chemistry were paralleled (finally) by advances in coating technology. The various methods of brush application and spraying were supplemented by electrodeposition, electrostatic coating and powder coating techniques. Ambient air drying was joined by infrared and radiation drying methods (UV, electron beam), and automation of coating processes continued to advance. It is also worth mentioning environmental technologies for the control of air and water pollution and for waste reduction.

Measuring techniques for coatings can be regarded as the pillar supporting modern coating technology. The reproducibility of flow properties, optical characteristics, drying behaviour, adhesion, anti-corrosion action and many other properties of coating materials and/or coatings is the precondition for selective product development and the practical usage of products.

2.1.6 Market and fields of application [2]

The coating industry is classified as a medium-size sector with a growing tendency towards internationalisation, but it is more highly developed, for example, in North America, Europe and South East Asia, because the economic development is the most important factor that determines the growth in coating consumption. For these regions the per capita consumption is ca. 4.5 kg.

Due to their high value and great benefits, coatings have a broad field of applications and the fact that there are few objects which do not require coatings is an indication of the enormous importance of coating technology. In terms of the quantity, 23.6 million tonnes of coatings materials were manufactured annually worldwide in 2000 with a value of some 70 billion euros (Fig. 3).

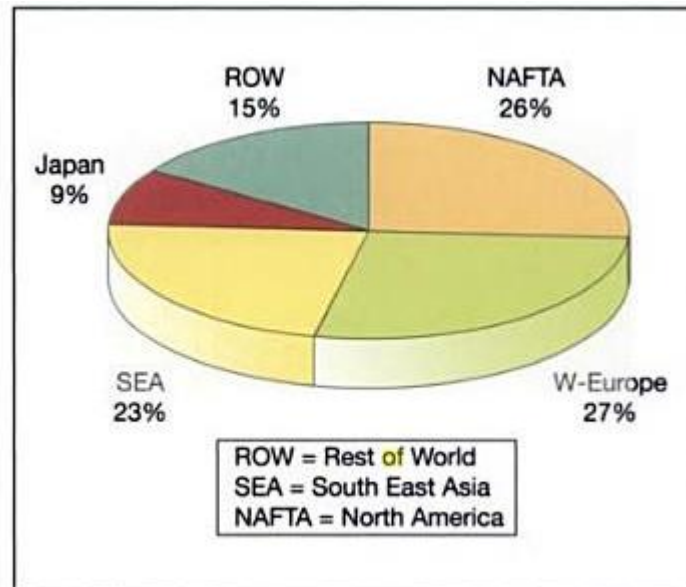


Figure 3: World coatings market of 23.6 million tonnes in 2000 by regions. [2]

Quantifying the coating materials does not give a real indication of the added value of industrial commodities but it does permit to calculate the area which can be protected or decorated by means of coating materials, taking into account the film thickness to be applied. To get an idea of the area that can be coated with the quantity produced in 2000 and if we assume an annual production quantity of 23.6 million tonnes and a wet film thickness of 100 μm (0.1 mm), a surface area of some 260,000 km^2 can be coated. This equals to about 2/3 of the surface area of Germany.

The coating market can be divided into branches or segments, such as:

- Decorative paints: approx. 60 %
- Industrial coatings: approx. 29 %
- Printing inks: approx. 4 %
- Automotive paints: approx. 7 %

In Europe the market size was 6.4 million tonnes in 2000, being Germany the leader with a consumption of approx. 1.9 million tonnes ahead of Italy, France, the UK and Spain, which are all in the range between 0.7 and 0.8 million tonnes. In concern to the North American market, in 2002, was 21.2 Bio. US \$ covering about 835 companies.

Figure 4 gives the most important branches for industrial coatings in the world.

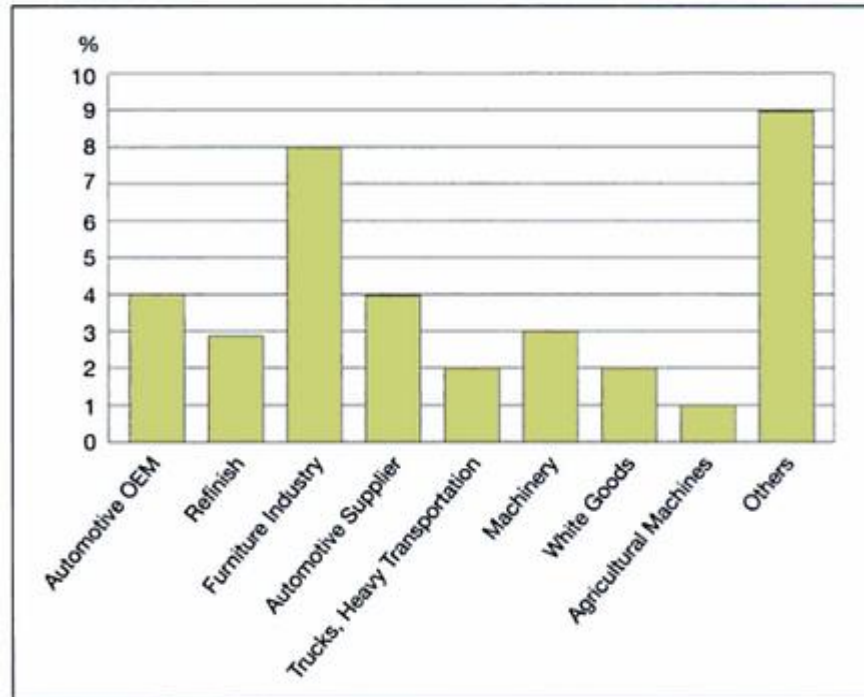


Figure 4: Important branches for industrial coatings of the worldwide coatings market. [2]

One of the biggest features of coating technology is the high energy consumption which is estimated at approx. 200 billion kWh annually worldwide, equivalent of the energy content of approx. 30 million tonnes of crude oil.

With the growing concern about the environment resulted in greater use of appropriate coating materials in the last 20 years. These include, in particular, solvent free powder coatings, waterborne paints, in which organic solvents are replaced in whole or in part by water, high solids paints and radiation curable paints, which are processed either in an aqueous solution or completely without conventional solvents with the aid of low molecular reactive thinners. Results from the German Paint Industry (VdL) show that these coatings had the greatest growth, with a 10 % annual increase in the last 10 years.

Coating technology is therefore a combination of chemical, physical, process-engineering, environmental, toxic and economic variables that is constantly progressing due to legislative requirements making companies to find new features and solutions.

Space applications

In the past, coatings had different uses, primarily for oxidation, corrosion and erosion resistance, decoration, and in some cases to camouflage aircraft and ground support vehicles. Since the complexity of future spacecraft, their long-term missions, and flight exposure to harsh environments, these uses take secondary considerations and require identification of new materials and coatings.

All materials designed for space missions, whether their mission is Earth observation, astronomy, space exploration, or future human settlement on planets, they are all subjected to a very harsh environment. The natural and sometimes self-induced environment of a space system consists of high vacuum, extreme temperatures and thermal cycling, charged particles fluxes, atomic gas species, volatile materials as contaminants, electromagnetic radiations, debris, and micrometeoroids which can separately, or in combination, degrade a mission or lead to its loss.

For more than 50 years of experience acquired in space vehicles development and use has clearly demonstrated the vast importance of using adequate coatings. Coatings now take a new role as overall temperature control, to increase the efficiency of heat sinks or radiators, for thermal insulation and for selective solar energy collection, requiring for this different coatings.

Coatings for temperature control in space vehicles [5]

In space, heat can come from several sources that contribute to space vehicle temperature, being the sun the most important one. Figure 5 shows the thermal forces charge for the heat of a space vehicle.

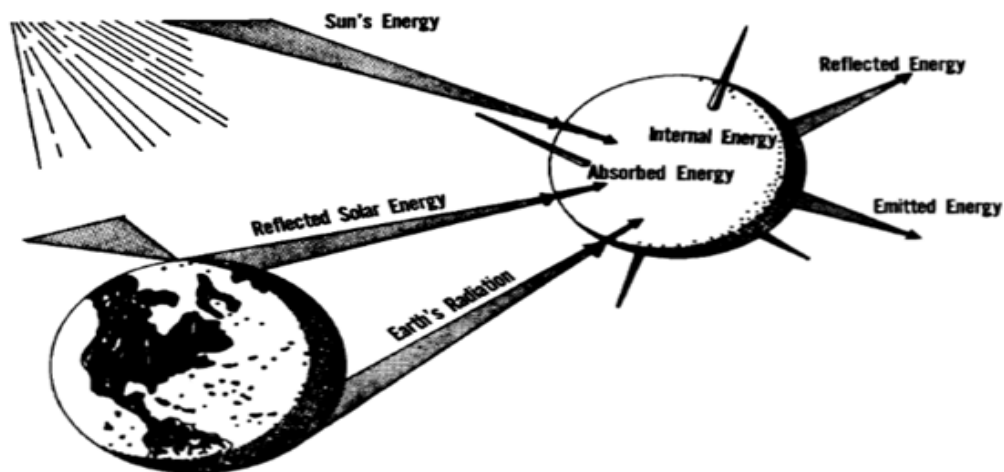


Figure 5: Space vehicle energy balance. [5]

One of the minor sources of heat but still can contribute to the space vehicle temperature balance is the internal energy caused by the electrical resistance and mechanical friction. Other sources are the energy coming from the earth, consisting of the earth's own radiation and the solar energy reflected from the earth, the latter quantity, called albedo and the prime source of heat, the solar energy absorbed by the space vehicle.

For thermal control of satellites are mainly used passive and active methods. Active thermal control systems such as resistive heaters, thermo-electric coolers, sterling or peltier cycle coolers, and heat pipes although they can manage the temperature in localized areas of spacecraft, they consume valuable electrical power and in cooling systems the thermal energy is concentrated in a small volume that must still be passively radiated into space. For this reason they are less used. In the other hand, passive methods are the most used and are based in the optical properties of specifically prepared surface coatings, e.g., paints (black and white), multilayer insulation (MLI) and radiators to achieve the required control action.

Low thermal conductive materials although they can reduce significantly the heat transferred, they are either bulky, heavy, or both which in space applications is an important factor. On the other hand, selective coatings can reduce heat transfer while at the same time govern energy absorption adding only a small amount of weight and volume to the overall system. This may be explained by a brief analysis of the basic optical properties of materials.

One of the ways to control radiant heat transfer is to use materials with selective optical properties to obtain the desired temperatures by the balance of the three basic optical properties:

- Reflectance
- Absorptance
- Emittance

The incident radiation in space vehicles surfaces can be either reflected or absorbed. If the energy is reflected there is no rise on the temperature of the vehicle, but if the energy is absorbed, it must be reradiated. The radiation of the absorbed heat is dependent upon the emittance of the exterior surface and the exposed area of the space vehicle, being the temperature a function of the ratio of the absorption coefficient and the emittance. For example a white coating have an absorptance very low but can efficiently radiate heat making a very cold surface. In other hand a black coating have a high absorptance in the visible and near infrared

To protect from extreme temperature differentials, maintaining a constant temperature there is techniques such as painting, polishing and shuttering.

There have been many types of inorganic and organic coatings used successfully in designing specific heat balances within the various spacecraft which have been launched to date. Metallic coatings like aluminium and stainless steel generally absorb little solar energy, but absorb infrared energy even to a less extent, resulting in a high solar a/ε ratios and high surface temperature. There is techniques like sandblasting the metal surface to reduce the

temperature, reducing the infrared reflectance more rapidly than the short wavelength reflectance, decreasing the solar a/ϵ ratios or it can be coated with a material which is transparent to solar energy but black or emissive in the infrared. This is true for many lacquers and inorganic coatings such as silica.

Organic coatings

Organic coatings due to their high emittance are the recommended and more stable for long heating exposure periods. The short wavelength absorption can overcome by the use of organic, inorganic pigmentation and other formulations using rutile, carbon black, red iron oxide and chrome oxide green, depending on the ratio desired. This coatings having a/ϵ ratios of 1 or less and can be used to give cool or cold surfaces in space.

Inorganic coatings

These coatings have less absorption than most organic coatings and are generally absorptive in the infrared. Ceramic coatings are more efficient when used as a pigment in organic coatings, increasing their reflectance. These coatings have a high temperature stability combined with their chemical structure that can be controlled to suitably deter diffusion, and consequently contamination of the reflective metal.

Black coatings [6]

A black surface is spectrally selective surface for which spectral absorptance is maximized over a range of wavelengths and angles of incidence. There is no material on Earth that absorbs 100 % of light at all angles and over all wavelengths, so an ideal black object does not exist, there is always some light that is reflected.

Due to the extreme and constant changes of temperature in Space, thermal regulation of satellites is extremely important and this is passively managed by radiative exchange between its external surfaces and the environment. For this purpose surfaces with certain thermo-optical properties are used i.e. surfaces having convenient solar absorptance (a_s) and emittance (ϵ). Thus, the utility of black coatings is their a/ϵ ratio close to one, which allow passive thermal control of equipment.

In addition to being used for temperature control in space vehicles, black coatings are also useful in the management of stray radiation issues in space optical systems.

Black coatings for space optical systems [7]

The performance of infrared and submillimeter systems can be severely degraded by stray light. In general terms, stray radiation is any radiation that degrades the performance of the system (i.e., degrades the signal to noise ratio). A useful dichotomy is to consider that two forms of types of electromagnetic radiation are propagating through the system, the “wanted” part and the “unwanted” part. The “wanted” radiation comes from the objects of interest (the target of observation) and is often imaged on the detector or coherently detected. The “unwanted” radiation can come from the Sun, Earth, limb, Moon as well generated by the actual optical system. It includes radiation that is diffracted, scattered due to microroughness and contamination of optical surfaces optical surfaces, or scattered from homogeneities in transmissive elements. All this radiation will affect the system performance level, so not only the “wanted” radiation need to be taken in consideration, but also the “unwanted”.

To avoid stray light in optical instruments, black coatings are useful and normally used in telescope baffles and lens edges. There are many different types of black surfaces and they can take many different physical forms. They can consist of painted surfaces, tapes, fabrics, metal surfaces, anodized surfaces, ion beam sputtered surfaces (sputter etched, sputter deposited, and sputter textured), electrodeposited surfaces, plasma sprayed surfaces, chemical vapour deposited surfaces, and surfaces with black optical thin film multilayer systems (produced via electron beam gun deposition, sputter deposition, ion vapour deposition, etc.).The mostly used are the black anodic films including inorganic dyes because of their low cost, their corrosive and wear resistances during storage, as well as the low risk of contaminating the spacecraft’s instruments, especially by outgassing.

In annex 1, table 14, 15 and 16 list anodized surfaces, paints, other forms of surfaces and processes and black surfaces already used on space-borne instruments, respectively.

There are many other black surfaces not included in the tables because they are either not studied for suitability for space use yet, or else known to be unsuitable primarily because of problems related to outgassing, environmental stability, and particulate contamination.

For space applications the most used black surfaces are the Aeroglaze paints (particularly Aeroglaze Z306), and the patented anodized processes from the Martin Marietta Astronautics Group (Martin Black, Infrablack, Enhanced Martin Black, and Post-treated Martin Black). Martin Black is known to be the blackest (i.e., lowest BRDF) of the conventional diffuse black surfaces. However black optical thin film multilayers (table 16) can be produced which are blacker, and can exhibit a low reflectance over a small range of wavelengths and angles of incidence.

Environment degradation of black surfaces in space [7]

Space is a harsh environment, subjected to extreme variations in radiation and temperature levels that can cause material degradation of their characteristics or even disable it. For this reason contamination control for space-borne systems are in a rapidly developing. It is an area very important and its detection, removal and prevention should be revised in the early stages on the design of these systems.

Three areas very important for space-borne systems are the effects of atomic oxygen, the outgassing effects, and particle generation by surfaces. There are other effects that can contribute to the performance of surfaces, or of the systems where those surfaces are installed, including adhesion of coatings, radiation effects on coatings, thermal cycling effects, vacuum ultraviolet effects and electrostatic charging effects, humidity, among others.

The contaminations of a black surface as well as aging effects are the most causes that contribute to the degradation of the optical properties. These effects will destroy the surface and not only reduces the ability of the surface to absorb stray radiation, but often also creates a contaminating of particles that can negatively affect the optical systems.

Atomic oxygen effects [7]

In the past, spacecraft surfaces showed significant weight loss and aging effects, like for example, on STS-1 the forward bulkhead camera blanket was milky yellow after the flight and the white paints on the Shuttle exhibited exposure-related degradation effects. Other flights, surfaces such Kapton showed significant mass losses and these effects were related to the interaction with the atomic oxygen present in low Earth orbit. Atomic oxygen attacks the binder in painted surfaces, causing the release of carbon particles, removing mass and causing glossy surfaces to become more lambertian. The weight is explained by both chemical and erosional (kinetic energy) processes.

Other problem associated is originated in many surfaces making them to glow when exposed to the atomic oxygen. Both of these phenomena undermine the effectiveness of baffle surfaces on space instruments.

Tests were already made on many surfaces to understand the effects of the exposure to atomic oxygen, like for example anodized black surfaces (Martin Black and Enhanced Martin Black) and on Chemglaze (now called Aeroglaze) Z-306 paint. These tests showed that carbon-black-based paint can be significantly affect over time while anodized surfaces exhibited only small changes in their surface morphologies or in their visible and near-

infrared reflectances. In general, long exposure time and high atomic oxygen flux levels can degrade the optical properties of surfaces. Some surfaces were tested in a Long Duration Exposure Facility (LDEF), and for the Chemglaze Z3-306 paint, this exposure has led to a loss of the binder material (Golden, 1991) and to loss of pigment.

Outgassing [7]

For space applications, the amount of outgassed material and its composition are of great importance. One of the principal effects is the formation of a film with undesirable properties on optical components and its particularly relevant for cooled systems. The continued outgassing of materials and the condensation of volatile materials on optical components can lead to catastrophic system failure.

To understand better the outgassing effects, two primary measures are made during these tests and they are the total mass loss (TML) and the percent collected volatile condensable materials (CVCM). An American Society for Testing and Materials (ASTM) Standard Test Method was developed and is called E 595-77/84.

A third measure of outgassing is the water vapour regained (WVR), relates to the water content of the material or surface and is a measure of the amount of water reabsorbed/reabsorbed in 24 hours while the sample is exposed to 25 °C and 50 percent relative humidity. This is done after the vacuum test for TML and CVCM.

Particle Generation [7]

Materials capable to withstand launch vibrations without generating excessive number of particles are one of the requisites for these materials to be able to be used in Space applications. This is not only a coating or surface problem but also a dynamic and a substrate problem. One of the sources that can produce particles is the abrasion between coated baffles surfaces. Also these surfaces should be able to resist to thermal cycling without generating particles. There are many cleaning techniques or procedures that can be applied to baffles systems already in space, among which are laser cleaning, plasma or ion cleaning, and jet snow cleaning.

3 Technical description

The present work has as main objectives the performance of several standard tests in two available black paints applied in aluminium substrates in order to quantify them and its method of application for use in space applications.

This work was divided in 2 essential parts:

- In a first phase, the paint was selected based in several restrictions/criteria. The restrictions/criteria for this choice were the coating performance in extreme temperatures (thermal stability), the substrate to be painted, the paint had to be black and available and the availability of the application means, since the pre-treatment step to the final coating application in the aluminum surface.
As these common black paints are used in terrestrial materials, they are not tested for negative temperature (-150 °C) like we find in the space. For this reason, these paints were subjected to a nitrogen environment (-195 °C) and their thermal stability was analysed.
- In a second phase, once the paints were tested and chosen, the aluminium specimens painted with the black paints were subjected to several standard tests in order to quantify them for use in space applications. The tests performed were the ISO-2409:2007 adhesion test, ASTM D870 - 09 to test water resistance of coatings using water immersion, thermal shock test where thermal stability of coatings were tested in a nitrogen environment (-195 °C) and at 150 °C and the UV test.

The application process was realised in the company CIN (Maia, Portugal) with his resources and the test phase was realised in the DEQ/FEUP.

3.1 Material and equipment

3.1.1 Surfaces

The surfaces used in this experimental work were provided by the company CIN (Maia, Portugal). These surfaces were in aluminium (14 x 6 mm²) provided already pre-treated and coated with the powder black paints, an essential part for this work due to the lack of the means for the paint application in the substrate. Each of these aluminium surfaces had to be cut in specimens of 20 x 20 mm², the measures indicated in the standard tests procedure.

In Figure 6 are represented the aluminium surfaces already pre-treated and painted used to perform the tests.

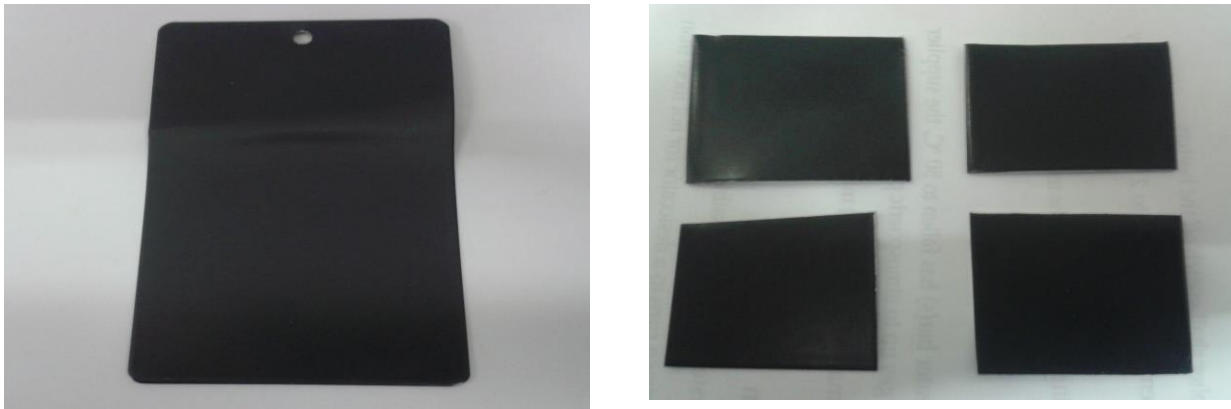


Figure 6: Aluminium surfaces coated and pre-treated.

3.1.2 Black paints

Although have been tested gray and black paints, only the black ones were chosen for this work. During this work were used two types of powder black paints provided by the company CIN (Maia, Portugal).

3.2 Work description and experimental procedures

3.2.1 Black paints thermal stability test

In space, satellites are directly lighted by the sun and then pass into the shadow of Earth, causing thousands of thermal cycles during their lifetime. Because of this, a spacecraft can be subjected to external temperature swings from about $-150\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ and the need of a coating that can resist to these extreme temperatures without degrading or detaching from the surface is very important. So the first part of this project was to search and find paints that can resist at least to temperatures between $-150\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$.

The common paints found in the market are normally used in terrestrial materials, and because in hearth $-150\text{ }^{\circ}\text{C}$ is impossible to happen, these paints are not tested for these temperatures.

Thanks to CIN (Maia, Portugal), some painted metal surfaces were provided and in a first phase were tested in a nitrogen environment ($-195\text{ }^{\circ}\text{C}$) and placed in a oven for 30 min, to understand if they can resist to $-150\text{ }^{\circ}\text{C}$ and to $150\text{ }^{\circ}\text{C}$.

Figure 7 shows the painted surfaces given by CIN (Maia, Portugal).



Figure 7: Aluminium surfaces painted supplied by CIN (Maia, Portugal).

3.2.2 Adhesion test

Significance and use [8]

For any purpose that the coating is designed, whether it is to protect or decorate a substrate, or whether it is for terrestrial materials or space materials, it must adhere to it for the expected service life. Because the adhesion is dependent of the substrate and its surface preparation (or lack of it), there is methods to evaluate the adhesion of a coating to different substrates or surface treatments, or of different coatings to the same substrate and treatment.

The methods normally used and required for space products are the ECSS-Q-ST-70-13 - Measurement of the peel and pull - off strength of coatings and finishes using pressure-sensitive tapes, clause 5.1.2, ISO-2409:2007 - Paints and varnishes - Cross-cut test and ASTM D 3359 - Standard Test Methods for Measuring Adhesion by Tape Test.

For this present work the method used was the ISO-2409:2007 - Paints and varnishes - Cross-cut test. It's a method similar to the others, but was preferred in relation to others because its procedure has more information available in the literature and is just used for coatings of total thickness smaller than 250 μm , the thickness observed. This test was conducted on the two powder black paints applied to the aluminium substrate. Four test samples for each of the two paints were tested.

Means [8]

- **Cutting tool**

A single-blade cutting tool with a defined shape and the cutting edges in a good condition was preferred and used in the adhesion test. The cutting tool was a X-Acto with a 30° edge and a blade thickness of 0,46 mm recommended in the standard adhesion test. [8]

Figure 28 in annex. 2 shows the single-blade cutting tool used to perform the adhesion test.

- **Pressure-sensitive adhesive tape [9]**

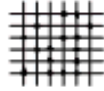



A *tesa*[®] transparent adhesive tape with an adhesive strength of 6 N per 25 mm (determined in accordance with IEC 60454-2) was used. It's based on stable PVC backing coated with a natural rubber adhesive.

Figure 29 in annex 2 shows the pressure sensitive tape used to perform the adhesion test.

Procedure [8]

The adhesion test was carried out at a temperature of 23 °C in a relative humidity of 50 %. The aluminium specimens of 20 x 20 mm² were placed on a rigid and flat surface to prevent any deformations of the panel during the test. With the cutting blade, six cuts in each direction with a spacing of 2 mm were made, penetrating to the substrate surface. The operation was repeated, making further parallel cuts of equal number, crossing the original cuts at 90°. After the cuts were made, the aluminium specimens were brushed with a soft brush several times forwards along each of the diagonals of the lattice pattern. A piece of tape approximately 75 mm was placed over the specimens in a direction parallel to one set of cuts. To ensure good contact with the coating, the tape was firmly pressured with a fingertip. After 5 min of applying the tape, the tape was removed by grasping the free end and pulled off steadily in 0.5 s to 1.0 s at an angle close as possible to 60°. In the end, the aluminium specimens were evaluated and rated according to the Table 7. This procedure was made in 4 specimens, each one representing a different zone of the same surface tested.

Table 7: Classification of the adhesion test results. [8]

Classification	Description	Appearance of surface of cross-cut area from which flaking has occurred (Example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	—
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 %, is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 %, but not greater than 35 %, is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35 %, but not greater than 65 %, is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	—

3.2.3 Hygroscopic test [10]

Significance and use

Water is an important factor that can cause the degradation of coatings and its submersion in water is helpful to predict if the coating is resistant to water exposure and if it protects the substrate from corrosion.

The method used for this present work was the ASTM D870-09 - Standard Practice for Testing Water Resistance of Coatings Using Water Immersion and was performed on the two powder black paints applied to the aluminium substrate. Four test samples of each of the two paints were tested. After the submersion test, the specimens were subjected to the adhesion and were evaluated and classified according to table 7.

Means

- 2 Flask
- Distillate water
- 4 aluminium specimens of each paint (20 x 20 mm²)
- 2 Magnetic stirrer and 1 heating plate with magnetic agitation

Figure 30 in annex 2 shows the experimental installation used for the hygroscopic test.

Procedure

The tank was filled with water such that the test specimens were immersed at least to approximately three-quarters of their length. The water was heated to 38 °C with the circulating system in operation. The test specimens were placed in the tank so that the planes of the specimens were parallel to the flow of water in the tank. The test was completed after 1 hour.

3.2.4 Thermal shock test [11]

Significance and use

In space, satellites are directly lighted by the sun and then pass into the shadow of Earth, causing thousands of thermal cycles during their lifetime. To simulate the space environment, the ESA Standard (ESA ECSS-Q-70-04A, 1999) recommends performing 100 cycles between -150 °C and 150 °C under vacuum with dwells times of 5 min minimum and a slope of 10 °C per minute to evaluate the paint resistance to these extreme temperatures. This test was conducted on the two powder black paints applied to the aluminium substrate. Four test samples for each of the two paints were tested. After the thermal sock test, the specimens were subjected to the adhesion test and were evaluated and classified according to table 7.

Means

In the thermal shock test were used:

- Oven and liquid nitrogen
- Protective gloves
- Plastic container
- 4 aluminium specimens of each paint (20 x 20 mm²)

Figure 31 in annex 2 shows the experimental installation used for thermal shock test.

Procedure

The painted specimens were subjected to a nitrogen environment (-195 °C) during 30 min and then put in rest at the ambient temperature (21 °C). After some rest time, specimens were clean and put in an oven at 150 °C, during 30 min. Past 30 min, the specimens were placed at the room temperature and after some time the coating adhesion test was performed and the coating adhesion to the aluminium substrate was analysed and classified according to table 7.

3.2.5 UV degradation test

Significance and use

UV radiation is one of the main degrading components which have to be taken in account when evaluating the degradation of materials placed in Low Earth Orbit environment. This radiation can have many effects in paints causing cracking because it has energy content sufficient to break chemical bounds that can be irreversible for polymers, organic and some inorganic paints.

There are no standard tests required to evaluate the combined effects of UV of the space in the physical properties of the paints like there is for the adhesion test and the thermal shock test, and what is done is to simulate an accelerated UV environment leading to several hours of exposure to these conditions.

Means

In the UV degradation test were used:

- UV light
- 4 aluminium specimens of each paint (20 x 20 mm²)

Procedure

In order to understand the effects of space ultraviolet radiation on black paints used in space instruments an ultraviolet degradation test was performed on both of the black powder paints. In a first phase, 4 specimens of each black powder paint have been exposed to UV radiation (40 W/m²) for two weeks and his appearance was visually analysed. In a second phase the same specimens were subjected to the adhesion test and their adhesion was rated using table 7.

3.3 Results and discussion

3.3.1 Black paints thermal stability test

With this test it was intended to see which paint was stable and capable of withstand extreme temperatures, more precisely temperatures between $-150\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ without degrading or detaching from the substrate applied, to evaluate which of them can be tested to be used in space applications. For this, all paints were subjected to a nitrogen environment ($-195\text{ }^{\circ}\text{C}$) and placed at $150\text{ }^{\circ}\text{C}$ in a heater and the results were visually analysed.

The results obtained for the stability test for paint 1 are presented in figure 8.



Figure 8: Comparative results before and after the thermal stability test for paint 1.

a) Before thermal stability test, b) after thermal stability test

As we can see from the images that show the before and after the thermal stability test for black powder paint 1, there was not a single change in the quality of the paint, no cracks or flaking were observed on the surface, so we can conclude that this paint can resist to extreme temperatures between $-195\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ and can be subjected to the remaining standard tests needed for the space industry.

The results obtained for the thermal stability test for paint 2 are presented in figure 9.



Figure 9: Comparative results before and after the thermal stability test for paint 2.

a) Before thermal stability test, b) after thermal stability test

As it happened to the first black powder paint, when this second paint was subjected to the thermal stability test, there was not a single change observed in the quality of the paint. No cracks or flaking were observed on the surface meaning that there wasn't thermal expansion either in the substrate or in the paint after the thermal stability test.

We can conclude that this paint can resist to extreme temperatures between $-195\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ and can be used to perform the entire standard test to be evaluated if it can be applied in space applications.

The results obtained for the stability test for paint 3 are presented in figure 10.



a)

b)

Figure 10: Comparative results before and after the thermal stability test for paint 3.

a) Before thermal stability test, b) after thermal stability test

Same results from the first and second black powder paint were observed in the third paint, meaning that no changes in the mechanical properties of paint were observed. No cracks or flaking were formed during this test and we can conclude that this paint is stable between temperature ranges of $-195\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$. This paint can be used in the remaining standard test to evaluate his performance in extreme environment like space.

The results obtained for the stability test for paint 4 are presented in figure 11.



a)



b)

Figure 11: Comparative results before and after the thermal stability test for paint 4.

a) Before thermal stability test, b) after thermal stability test

As we can see from the images that show the before and after the thermal stability test for black powder paint 4, this substrate shows no changes in its appearance and no flaking or cracking were observed. This paint can resist temperatures between $-195\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ and can be used to perform the rest of the standard test needed to be qualified to use in space applications.

All paints passed the stability test, but only the black paints were chosen and preferred to perform the rest of the standard test.

3.3.2 Adhesion test

With this test it was intended to know if the application method of the two types of powder black paints used and the pre-treatment given to the aluminium surface could produce an excellent adhesion between the substrate and the paint, verifying if there is no detachment before applying the adhesion test.

The results obtained before and after the adhesion test for paint 1 for two specimens, are shown in figure 12 and 13, respectively. For other specimens the results are in annex. 3.

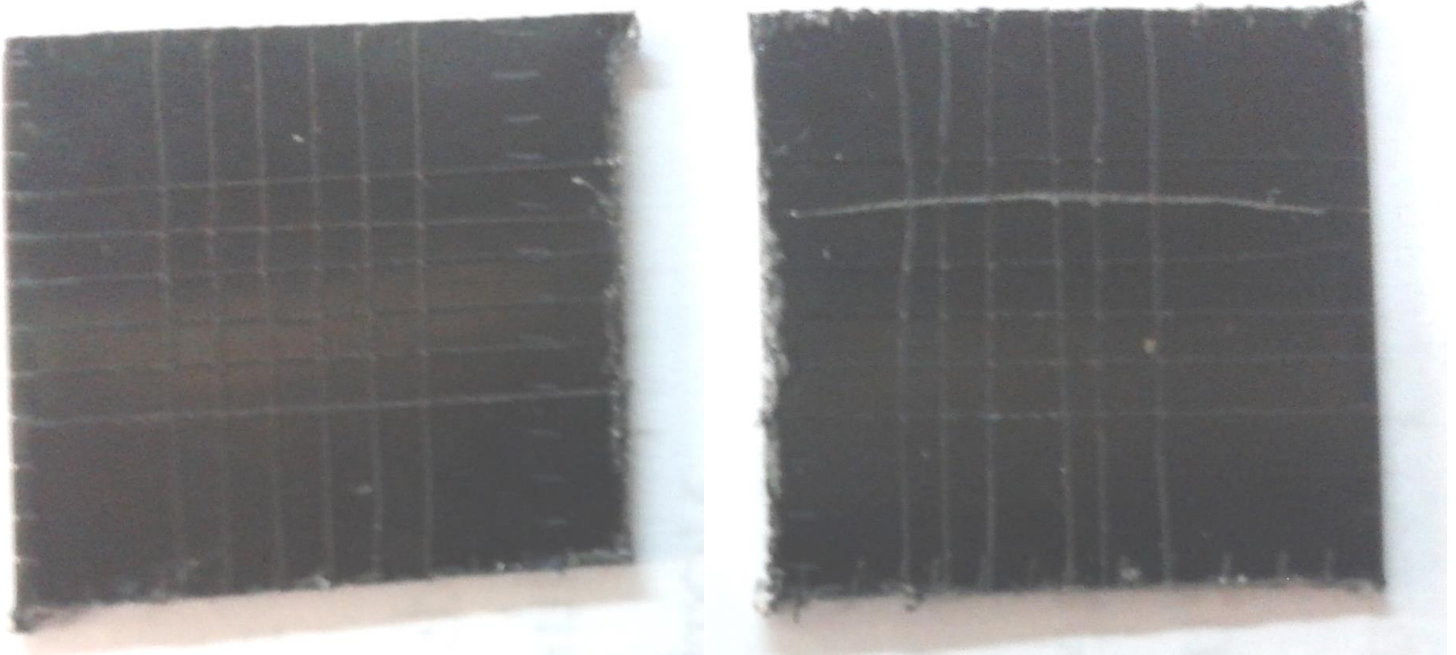


Figure 12: Results observed before the adhesion test for paint 1.

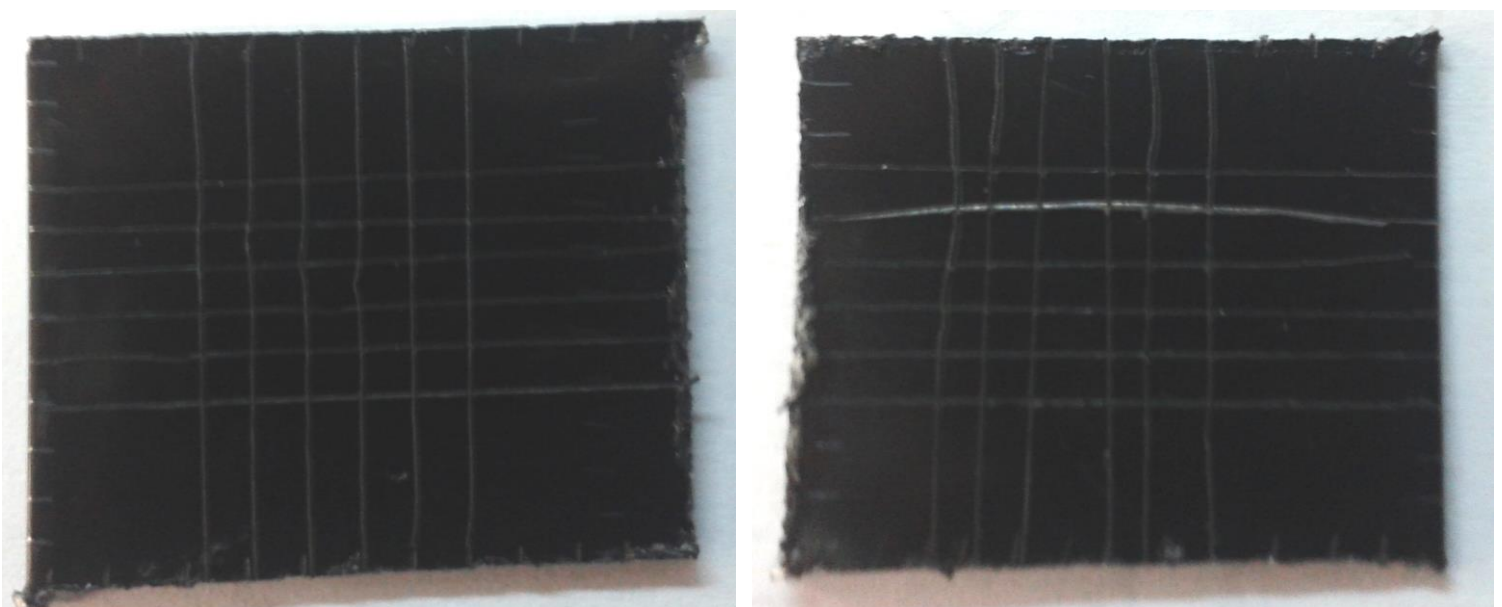


Figure 13: Results observed after the adhesion test for paint 1.

After the adhesion test, the 4 specimens for paint 1 were classified according to table 7 and the results are shown in table 8.

Table 8: Classification of the adhesion test results for paint 1.

Results from the adhesion test to paint 1			
Temperature: 23 °C			
Relative Humidity (%): 50			
Specimens:	Tape strength (N.mm⁻¹):	Classification	Observations
1	0.24	0	No observation of detachment of the squares in the surface.
2	0.24	0	No observation of detachment of the squares of the surface.
3	0.24	0	No observation of detachment of the squares of the surface.
4	0.24	0	No observation of detachment of the squares of the surface.

As we can see from the images 12 and 13, the adhesion of the first powder black coatings to all substrates was shown to be excellent - not a single square have been lifted- corresponding to Class 0 according to table 7. This means that the painting method was indicated for the aluminium substrate and for this kind of paint, not influencing the adhesion of paint.

The same procedure was made for the second paint and the results obtained before and after the adhesion test for two specimens are shown in figure 14 and 15, respectively. For other specimens the results are in annex. 3.

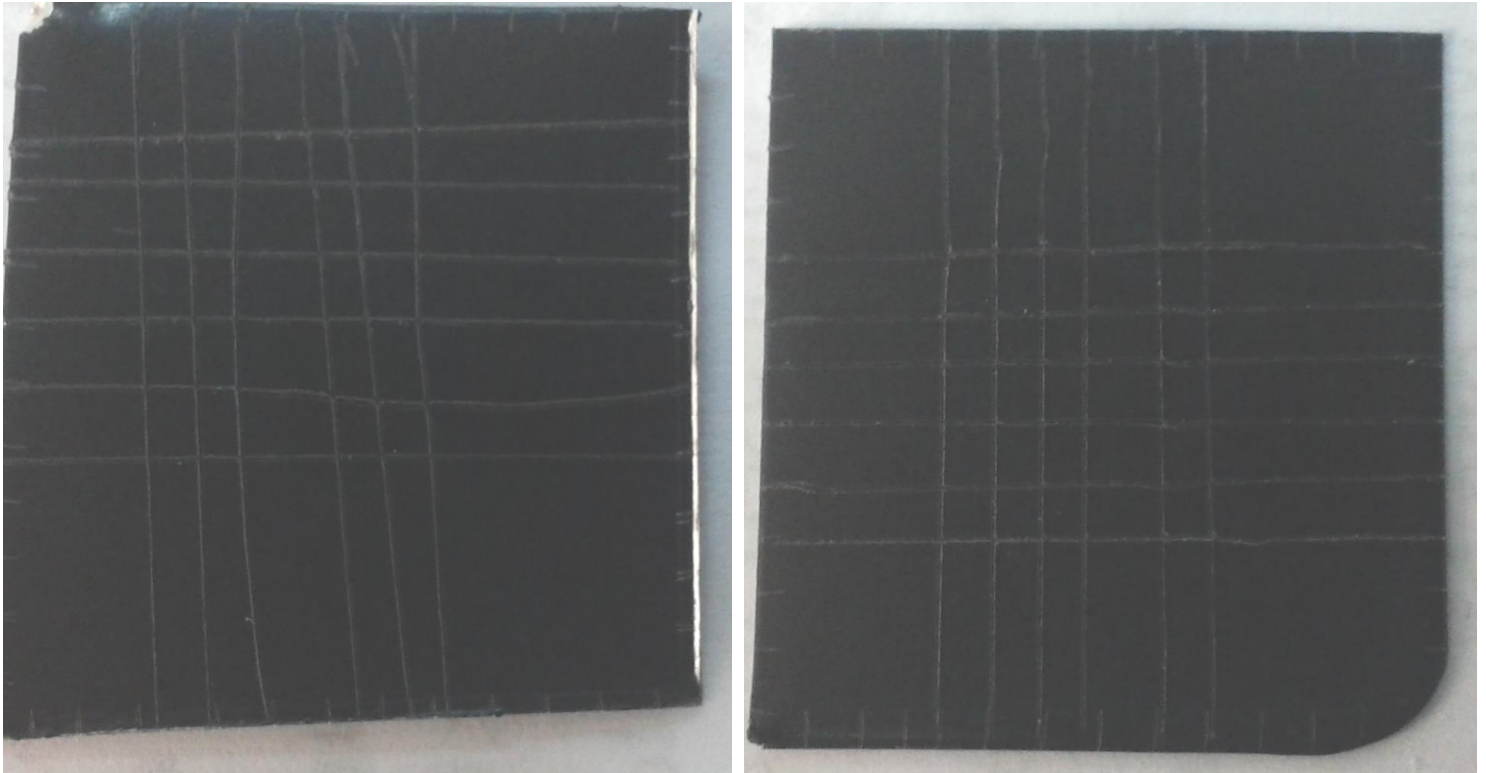


Figure 14: Results observed before the adhesion test for paint 2.

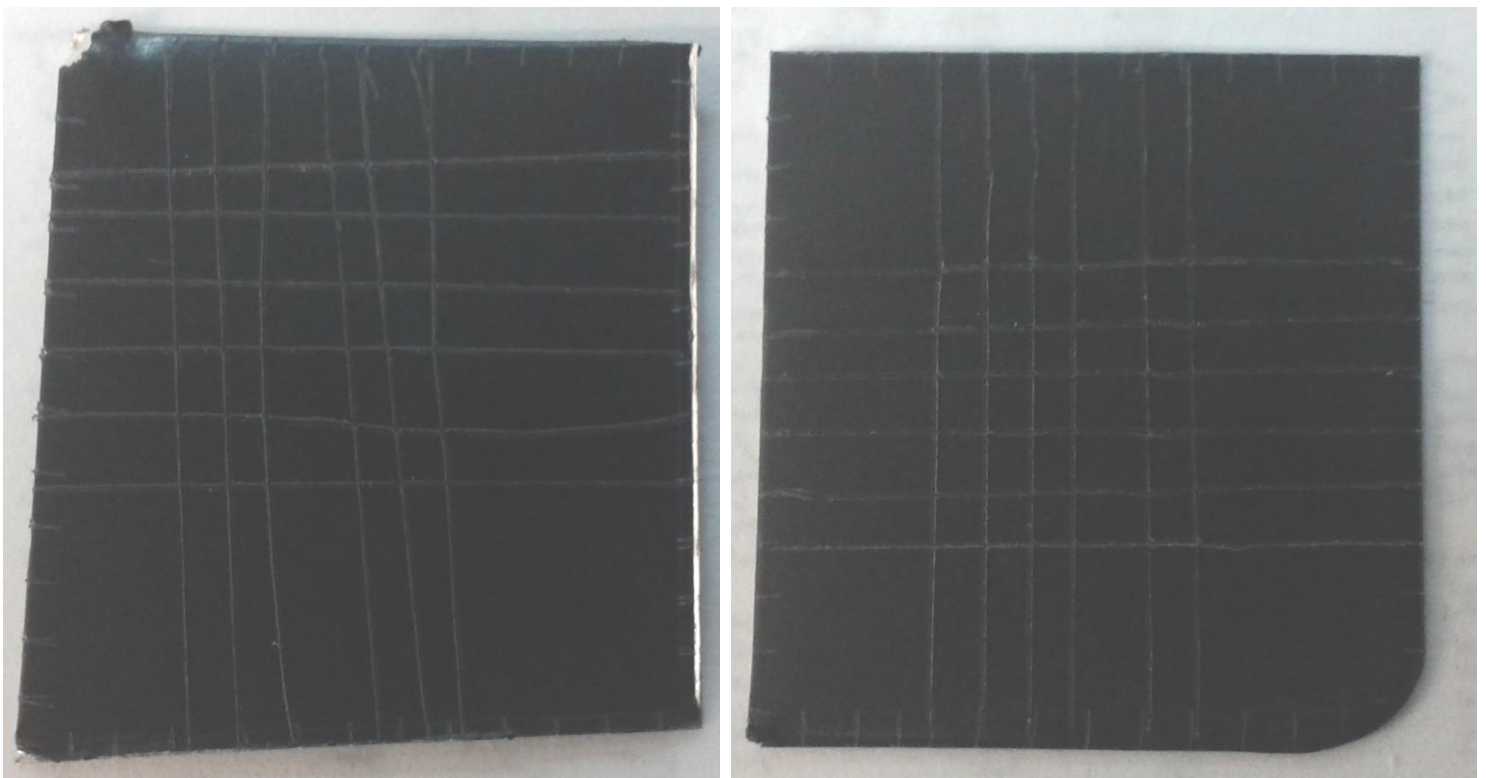


Figure 15: Results observed after the adhesion test for paint 2.

After the adhesion test, the 4 specimens for paint 2 were classified according to table 7 and the results are shown in table 9.

Table 9: Classification of the adhesion test results for paint 2.

Results from the adhesion test to paint 2			
Temperature: 23 °C			
Relative Humidity (%): 50			
Specimens:	Tape strength (N.mm ⁻¹):	Classification	Observations
1	0.24	0	No observation of detachment of the squares in the surface.
2	0.24	0	No observation of detachment of the squares of the surface.
3	0.24	0	No observation of detachment of the squares of the surface.
4	0.24	0	No observation of detachment of the squares of the surface.

This second powder black paint performed well under the cross-cut adhesion test and neither suffered any kind of separation from the aluminium substrate, or any change from their original appearances. No cracks or flaking were observed in the surface and after visualizing the tape after the test, not a single piece of paint was observed, there was no detaching from the surface, being classified as 0 according to table 7. This paint, as it happened to the previous paint can be used to perform the remaining standard tests demanded for the space industry.

3.3.3 Hygroscopic test

The main goal to this procedure was to test the resistance of the two powder black paints when subjected to the water contact, understanding this way if the coating can still have a good adhesion to the surface and if it can be protected, avoiding its corrosion. After the submersion test was made, the specimens were subjected to the adhesion test and where classified according to table 7. The results obtained for paint 1 before and after the adhesion test for the hygroscopic test for two specimens are shown in the figure 16 and figure 17, respectively. For other specimens the results are in annex. 3.

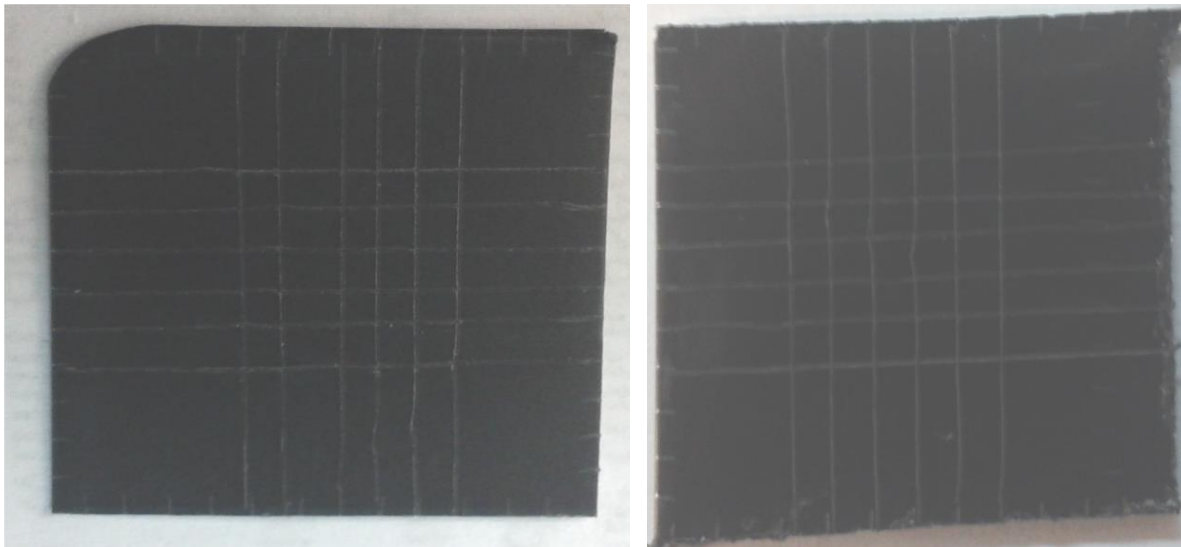


Figure 16: Results observed before the adhesion test for the hygroscopic test for paint 1.

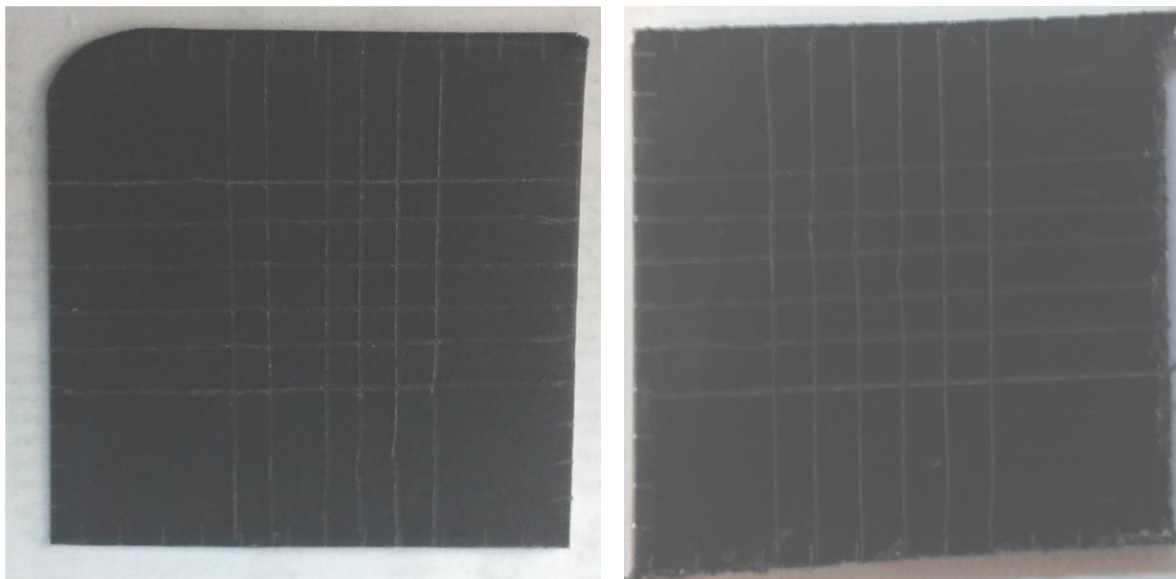


Figure 17: Results observed after the adhesion test for the hygroscopic test for paint 1.

After the adhesion test, the 4 specimens for paint 1 were classified according to table 7 and the results are shown in table 10.

Table 10: Results observed after the hygroscopic test and classification of the adhesion test for paint 1.

Results from adhesion test after the hygroscopic test for paint 1			
Temperature (°C): 23°C		Test duration time: 1 hour	
Specimens:	Water change	Adhesion test classification	Observations:
1	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
2	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
3	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
4	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.

Comparing both figure 16 and 17, after the hygroscopic test the four specimens for paint 1 shown no difference in the original appearance, specially no detachments or flaking was seen. According to table 7, the adhesion for this paint was classified as 0. This paint as no sign of water absorption and can be used to perform the remaining test in order to be classified to the space industry.

The same procedure was made for the second paint and the results obtained before and after the adhesion test after the hygroscopic test for two specimens are shown in figure 18 and 19, respectively. For other specimens the results are in annex. 3.

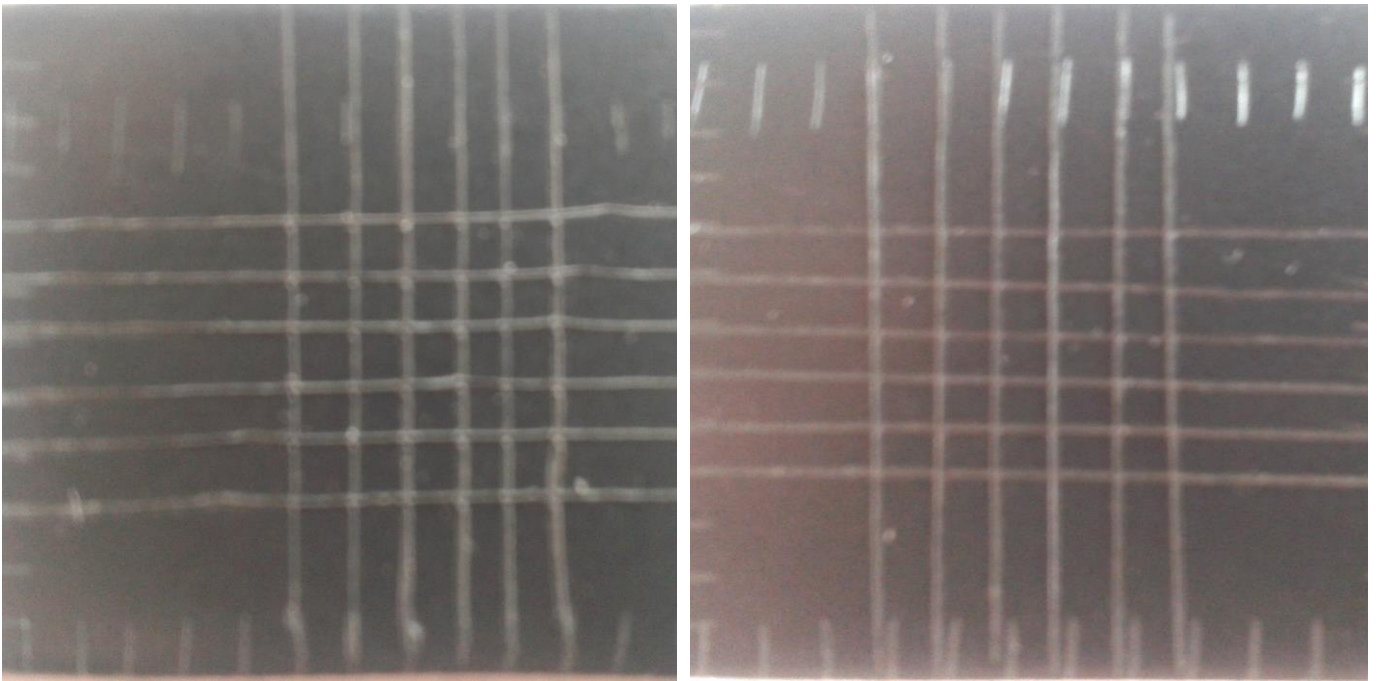


Figure 18: Results observed before the adhesion test for the hygroscopic test for paint 2.

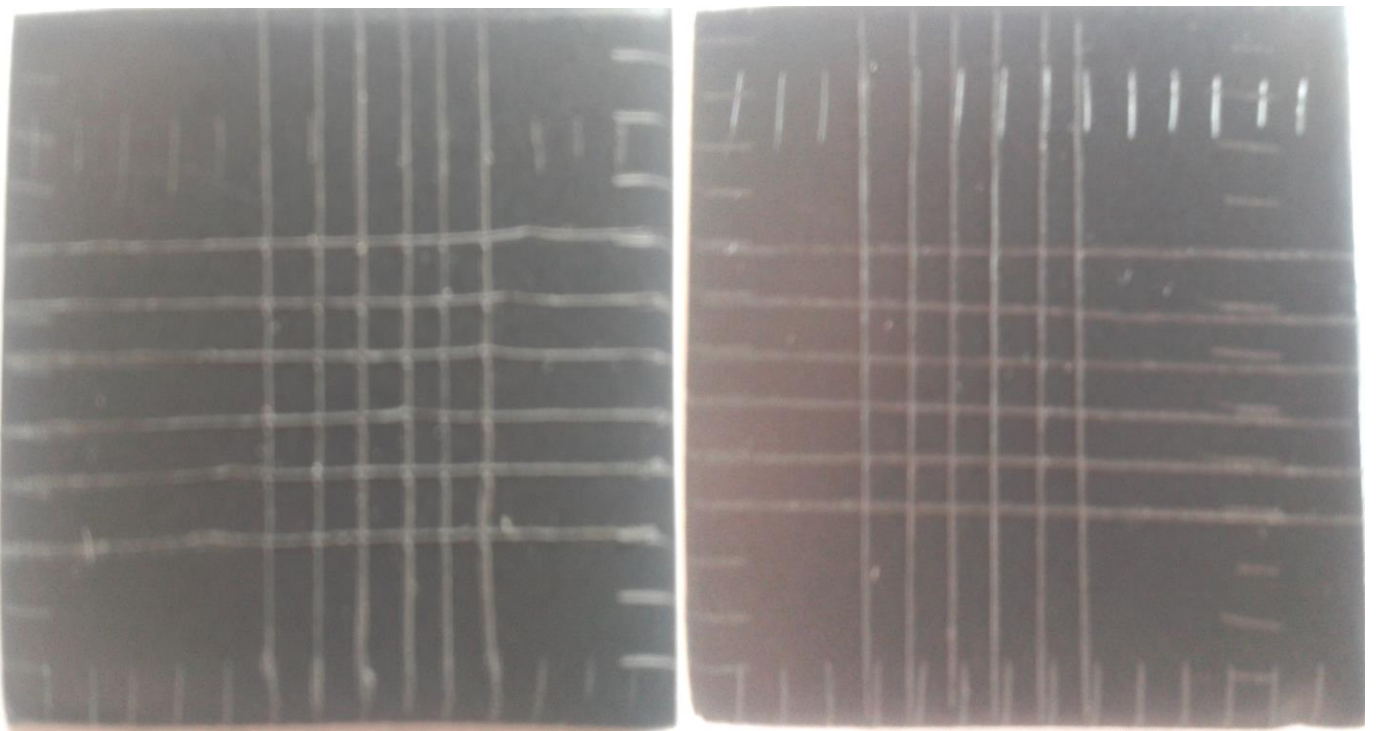


Figure 19: Results observed after the adhesion test for the hygroscopic test for paint 2.

Table 11: Results observed for the hygroscopic test and their adhesion classification.

Results from adhesion test after the hygroscopic test for paint 2			
Temperature (°C): 23°C		Test duration time: 1 hour	
Specimens:	Water change	Adhesion test classification	Observations:
1	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
2	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
3	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.
4	Was not necessary	0	No changes in water colour were observed and no observation of detachment of the squares in the surface.

The results observed from the hygroscopic for paint 2 test comparing figure 18 and 19 are equal to the paint 1, i.e. no difference was observed from the original appearance and no sign of water absorption. After the adhesion test, there were no detachments or any piece of paint in the tape, so this paint was classified as 0 according to table 7.

3.3.4 Thermal shock test

This test was intended to evaluate the resistance of the two powder black paints when subjected to extreme temperature between -195 °C and 150 °C and their adhesion to the aluminium substrate after the thermal shock performed. After 30 min of exposure to -195 °C and 150 °C, the adhesion test was done and their adhesion was classified according to the table 7. The results for two specimens obtained before and after the adhesion test after the thermal shock test for paint 1 are shown in the figure 20 and 21, respectively. For other specimens the results are in annex. 3.

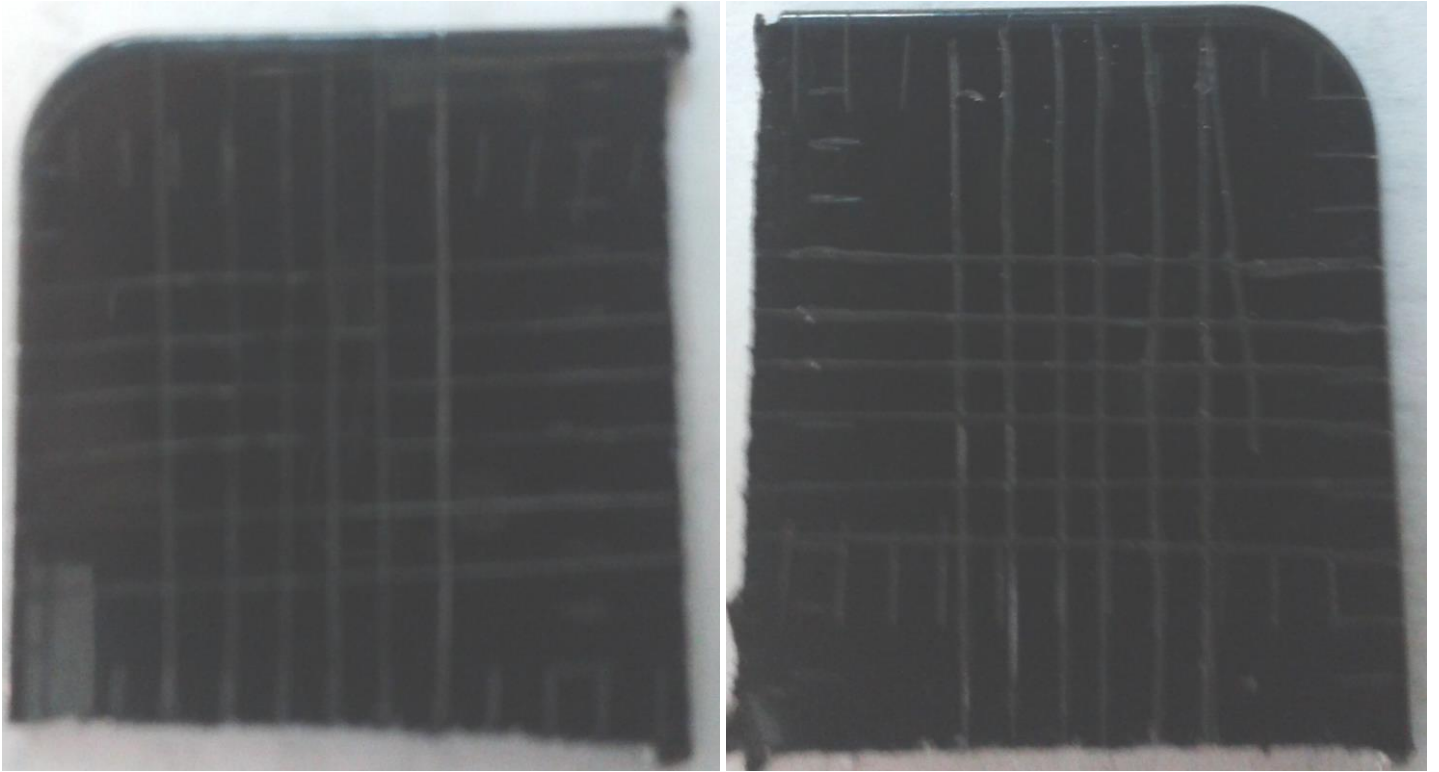


Figure 20: Results observed before the adhesion test after the thermal shock for paint 1.

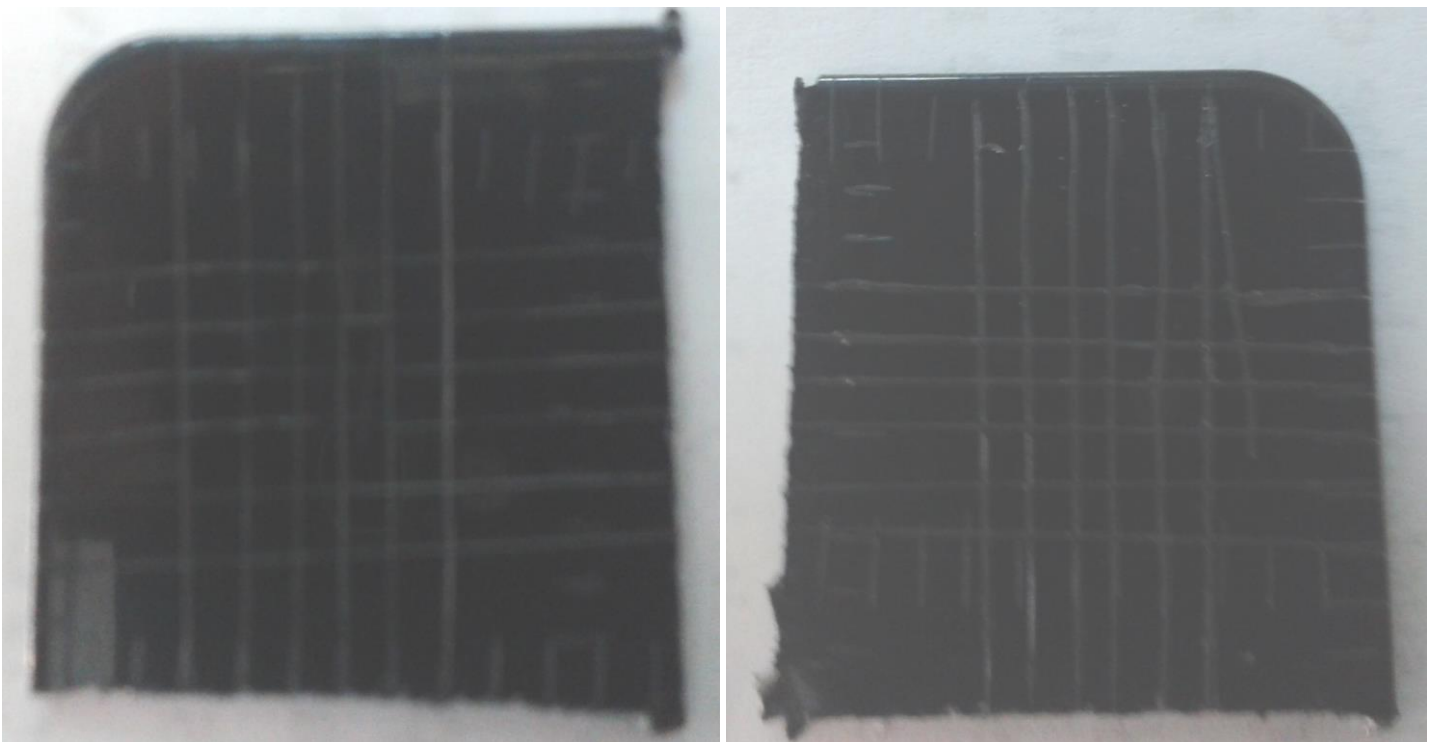


Figure 21: Results observed after the adhesion test after the thermal shock for paint 1.

After the adhesion test, the 4 specimens for paint 1 were classified according to table 7 and the results are shown in table 12.

Table 12: Results observed after the thermal test and classification of the adhesion test for paint 1.

Results from the adhesion test after the thermal stability test for paint 1		
Relative Humidity (%): 50%		
Specimens:	Classification of the adhesion test after the thermal shock:	Observations:
1	0	No observation of detachment of the squares in the surface.
2	0	No observation of detachment of the squares in the surface.
3	0	No observation of detachment of the squares in the surface.
4	0	No observation of detachment of the squares in the surface.

As we can see from the images before and after the adhesion of the first powder black coatings to all substrates was shown to be excellent - not a single square having been lifted - corresponding to Class 0 according to table 7. This means that the painting method used was indicated for the aluminium substrate and for this kind of paint, not influencing the adhesion of the paint.

The same procedure was made for the second paint and the results obtained before and after the adhesion test for two specimens are shown in figure 22 and 23. For other specimens the results are in annex. 3.

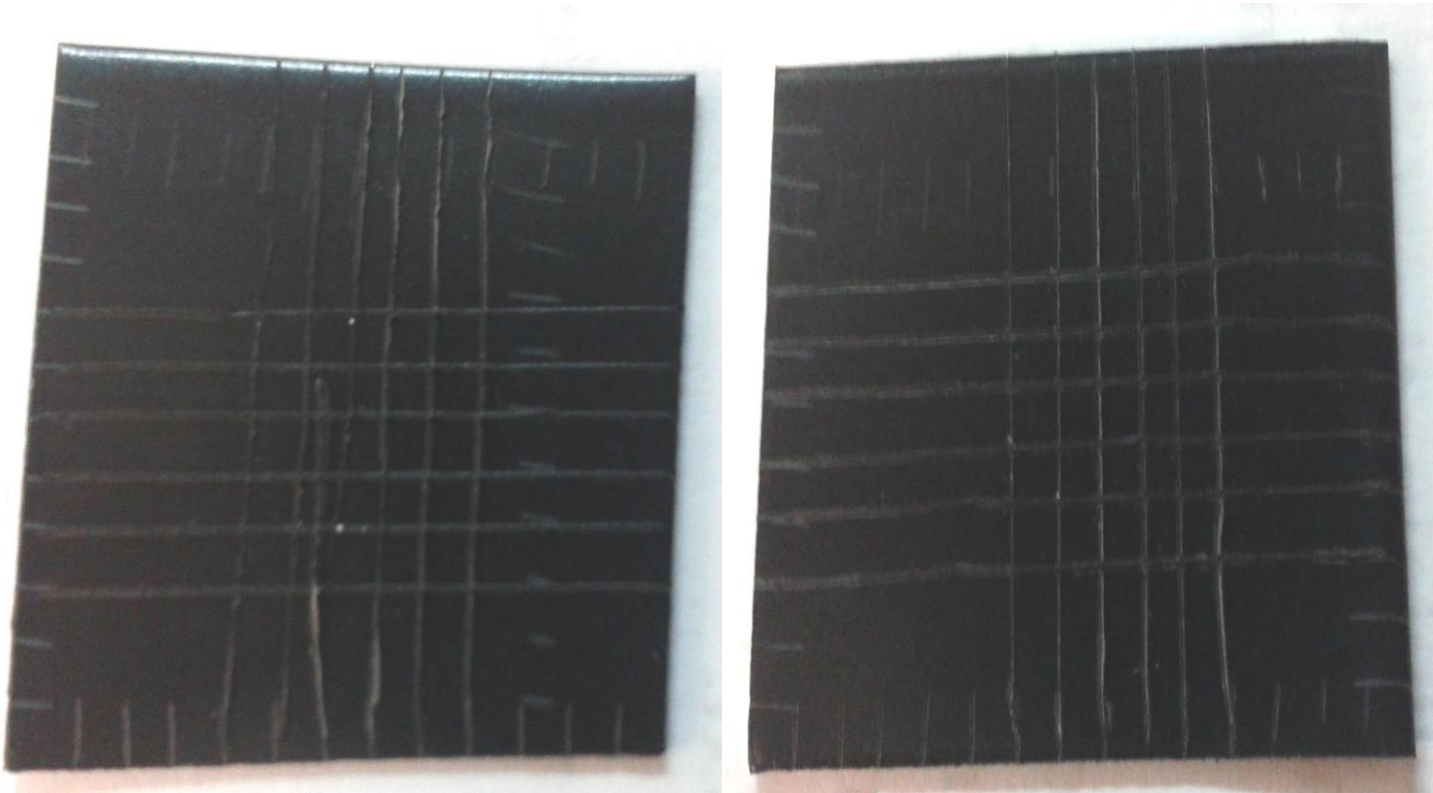


Figure 22: Results observed before the adhesion test after the thermal shock for paint 2.

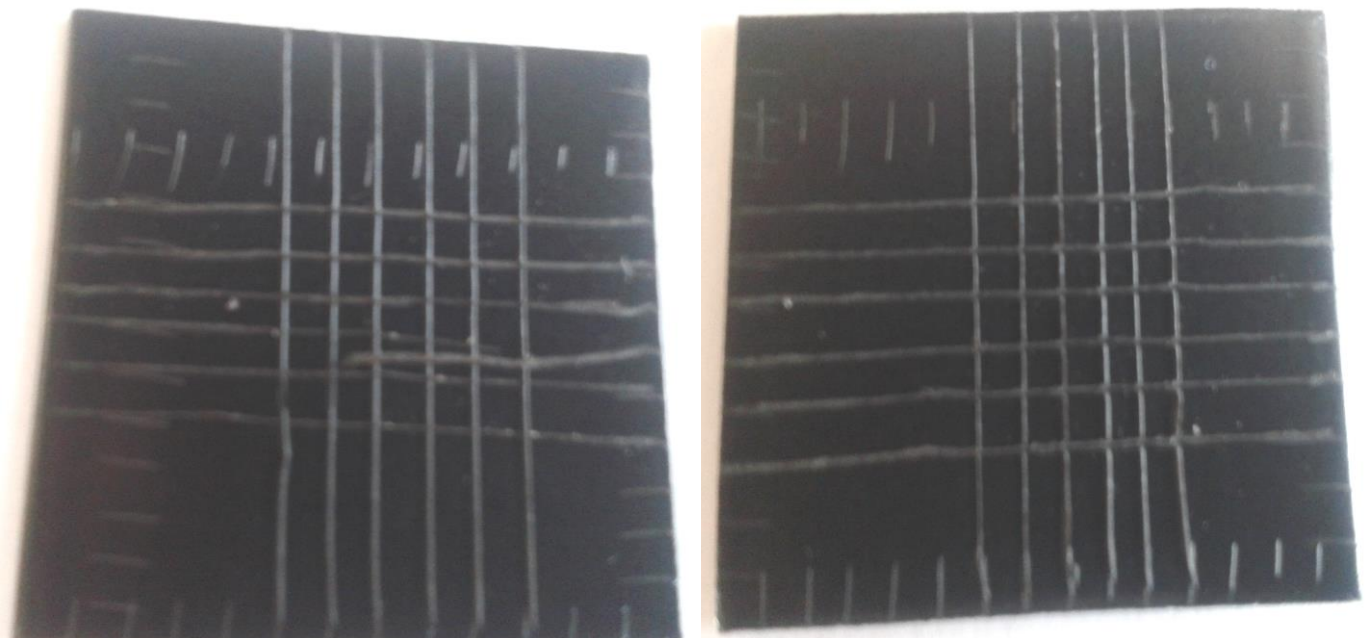


Figure 23: Results observed after the adhesion test after the thermal shock or paint 2.

After the adhesion test, the 4 specimens for paint 2 were classified according to table 7 and the results are shown in table 13.

Table 13: Results observed after the thermal test and classification of the adhesion test for paint 2.

Results from the adhesion test after the thermal stability test for paint 2		
Relative Humidity (%): 50 %		
Specimens:	Classification to the adhesion test after the thermal shock:	Observations:
1	0	No observation of detachment of the squares in the surface.
2	0	No observation of detachment of the squares in the surface.
3	0	No observation of detachment of the squares in the surface.
4	0	No observation of detachment of the squares in the surface.

For the second powder black paint, the adhesion test was performed after the thermal shock and comparing both images, the after and before the use of the tape, we can see no signal of any change on the colour or on the appearance of the paint. No cracks, no flaking and not a single square having been lifted, and classifying according to table 7, all specimens tested for this paint were classified with 0, meaning that no detachment of the squares in the surface were observed. This means that this paint can support extreme variations of temperature between -195 °C and 150 °C and its adhesion to the aluminium surface was not affected.

3.3.5 UV degradation test

This test had the goal to evaluate the performance of the two black powder coatings in terms of resistance when subjected to the effects of UV radiation for 336 hours in this environment. Also it was intended to classify the adhesion to the aluminium substrate for the two black paints after the UV degradation test to understand their negative effects.

After the UV degradation test was made, the specimens were subjected to the adhesion test and where classified according to table 7. The results obtained for paint 1 are shown in the figure 24 and figure 25, respectively. For other specimens the results are in annex. 3.

Figure 24: Results observed before the adhesion test for the UV degradation test for paint 1.

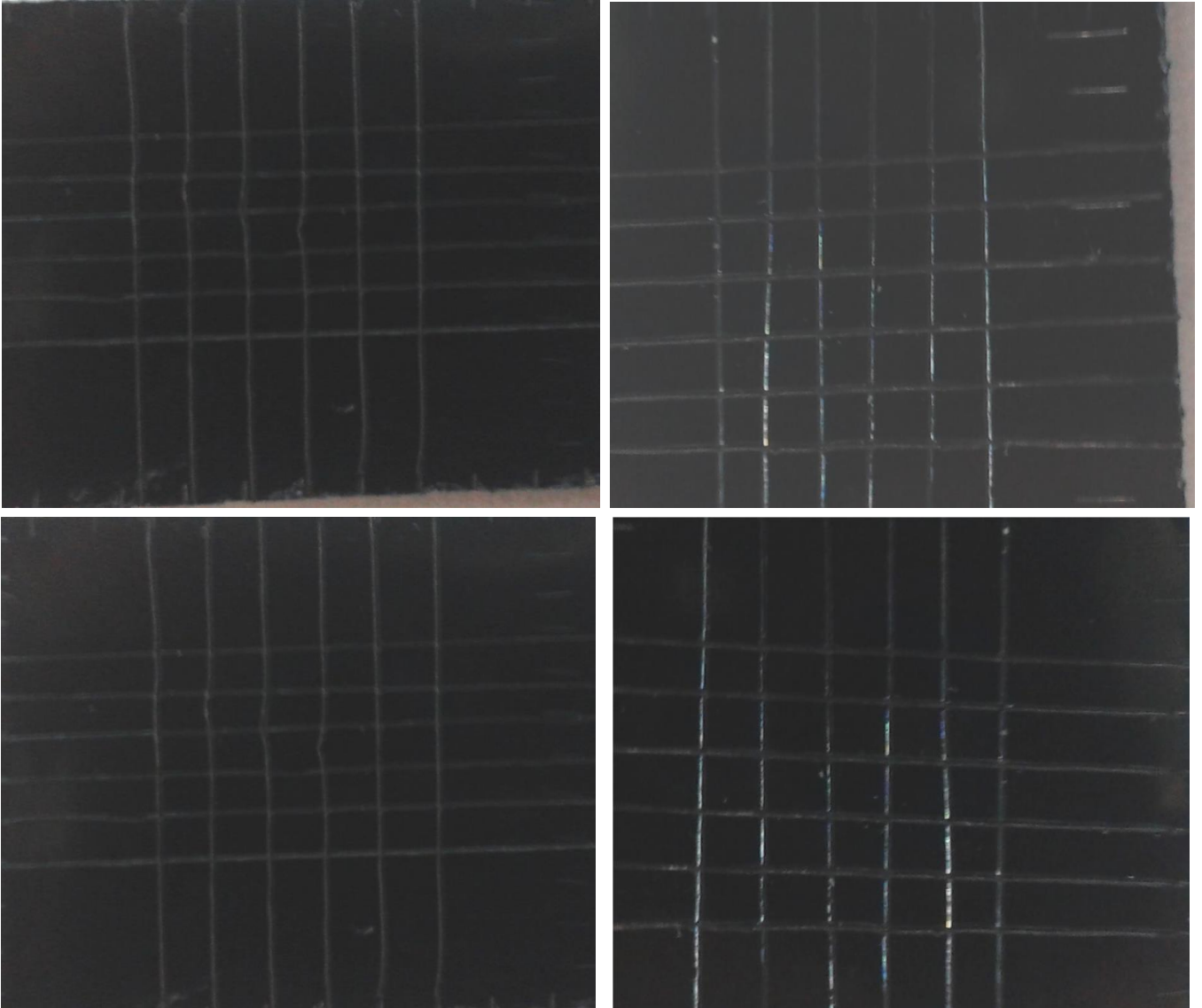


Figure 25: Results observed after the adhesion test for the UV degradation test for paint 1.

After the adhesion test, the 4 specimens for paint 1 were classified according to table 7 and the results are shown in table 17, represented in annex.3.

After performing the UV degradation test as we can see from figure 24 and 25 there was no visible changes in the original appearance of the surface for paint 1 and no flaking occurred. The adhesion of the paint to the aluminium ended to be excellent with no detachments of the squares being visible in the tape. Taking this into account this paint was classified as 0 according to table 7.

The same procedure was made for the second paint and the results obtained for two specimens are shown in figure 26 and 27. For other specimens the results are in annex. 3.

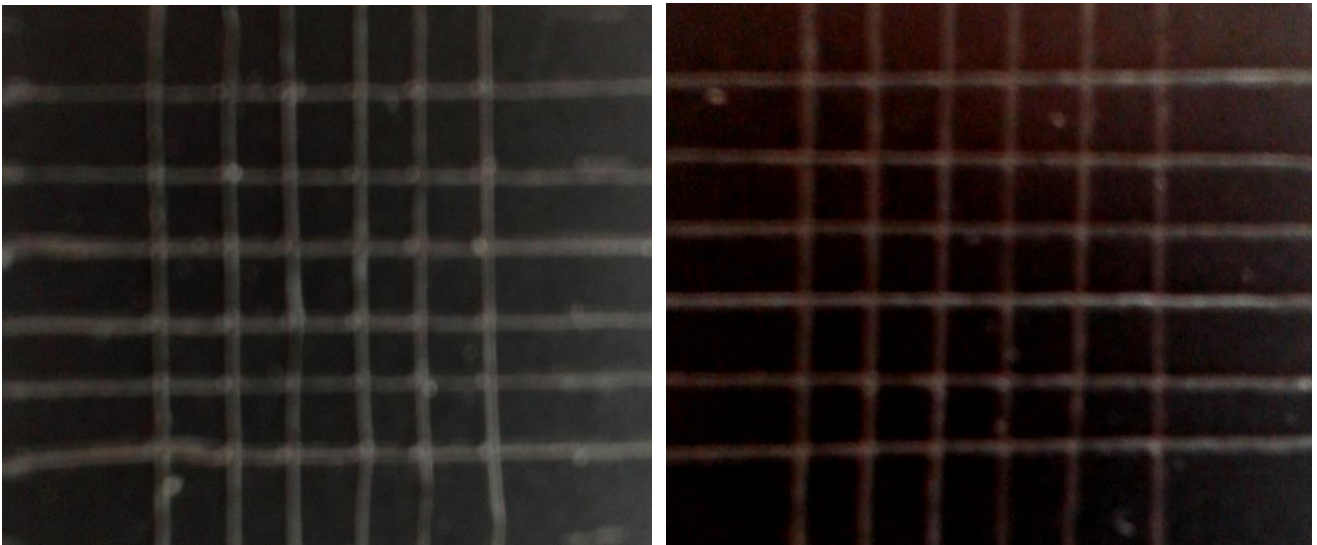


Figure 26: Results observed before the adhesion test for the UV degradation test for paint 2.

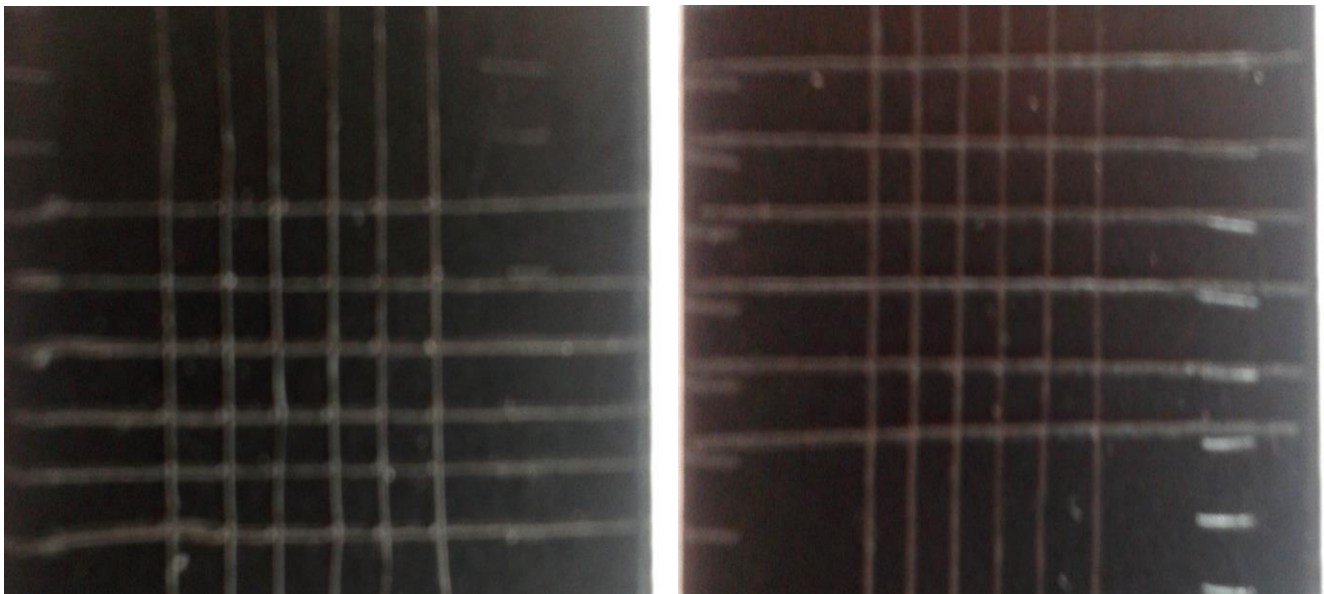


Figure 27: Results observed after the adhesion test for the UV degradation test for paint 2.

After the adhesion test, the 4 specimens for paint 1 were classified according to table 7 and the results are shown in table 18, represented in annex.3.

After the four specimens being subjected to UV degradation test for 336 hours in that environment, there was no evidence of changes on the colour or on the resistance of the paint 2. No flaking was observed or any kind of failure. Regarding the adhesion test for the paint 2, it showed excellent performance with no signs of detachments in any of the squares. This paint according to table 7 was classified as 0 and the observations are shown in table 18.

4 Conclusions

After the performance of this work the first conclusion we can take is related to the painting method applied to the aluminium surfaces. The painting method used allowed to have a well painted surface all around the aluminium, capable to form a uniform film with a constant thickness and with no signal of bubbles or detachments. This means that the painting method was done in ideal conditions and was appropriated to that kind of surface and paint.

In respect to the thermal stability test in order to understand which paint provided by CIN (Maia, Portugal) was able to withstand extreme temperatures between $-195\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$, we can conclude that the four paints tested can perform equally well under this conditions showing no signal of changes in the physical properties of the painted surface, showing no signs of any piece of paint degradation or detachment, maintaining their original appearance.

After the performance of the several standard test on both black powder paints chosen, we can conclude that these paints are stable functionally against adverse environment conditions such as humidity, thermal shock cyclings and UV radiation. These paints can be applied successfully well on aluminum substrates as a uniform layer and can find immense applications in various systems.

From both paints, there is no different in their performance under these extreme conditions. Both were capable to maintain their adhesion to the aluminum substrate after being subjected to a thermal cycling test, hygroscopic test and UV degradation test being classified with a 0 in the adhesion test according to the table 7, meaning no sign of detachment or flaking observed in the surface. Although, these paints had the best classification for the tests performed, they cannot be classified to be used in space applications because there were tests not performed and are normally required. These tests are the outgassing test, atomic oxygen testing, solar absorptance/reflectance measurement, normal and hemispherical emittance and electrostatic charging.

Note that this industry is very demanding in terms of safety and every paint to be used in this area should have an excellent performance when subjected to all these tests and every different aspect observed is crucial in their selection.

4.1 Goals Accomplished

The present work had as main objectives the performance of several standard tests in two available black powder paints applied in aluminium substrates in order to quantify them and its method of application for use in space applications.

In a first phase, after obtaining the paints, it was intended to practice the paint application, including the pre-treatment and the curing steps, with the application method indicated to that kind of paint in order to obtain a uniform thickness in the aluminium substrate. The objectives for this phase were not accomplished and the main reasons for this were the lack of means to apply the paint, because the paint were in powder and the means to apply it were not available, not easy to obtain and were expensive.

In a second phase the main objective was to test the performance of the two powder black paints provided by CIN (Maia, Portugal), realizing several standard tests required in order to see if these paints and its application method were the ideal for use in space applications, including the pre-treatment and the curing step. Most of the tests were successfully performed, including the adhesion test, the hygroscopic test, the thermal shock test and the UV degradation test but there was one of the tests that was in the main objectives and also very important that was not performed. The test was the outgassing test and the main reasons for this were once again the lack of all the means to perform it and the expensive costs that it takes.

4.2 Limitations and Future Work

One of the first limitations found during this work was the lack of means to apply the powder black paints in the substrate, as well as the pre-treatment and the curing step, being them provided by the CIN (Maia, Portugal) already applied in the aluminium substrate.

Other limitations from this work was found during the test phase, more precisely in the outgassing test, where due to the lack of all the equipment required and for being an expensive test was impossible to perform and measure all the variable needed like TML (Total Mass Loss), CVCM (Collected Volatile Condensable Materials) and WVR (Water Vapour Release).

One of the future works that can be associated to this is the measure of the black paints absorptance (α) and emittance (ϵ) in order to understand if they can be applied as thermal control systems or in optical instruments and how the tests performed can change these two variables. Other work that can be performed in the future is the outgassing test because there are limited values for the TML, CVCM and WVR that these paints cannot exceed in order to be used in space applications.

This intervention area has still much to investigate and test and will continue to arise in the attempt to find new paints and ways to apply them more efficiently and less expensive that can still fit and perform well under the space extreme environment.

4.1 Final Assessment

This type of study is quite interesting in addition to being valuable, especially in an area that takes a large investment with a large amount of paints already being tested and qualified to this industry but being most of them too expensive and not available in the market. If normal paints, used in daily bases and cheaper can perform well and pass the entire standard test required for the space industry this can lead to less economical investment, very important for small and growing companies like HPS, Portugal.

In terms of learning, we could learn a lot about a different area of study and not well known in Portugal. It is an area to invest, especially in companies that want to start to give the first steps in the painting for the Space area because despite being a small market it takes a lot of investment on the paints only available outside of Portugal that can be reduced by the use of cheaper paints used in daily bases.

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Annex 1 Available Black Surfaces

Table 14: Some available black anodized surfaces for optical instrumentation. [7]

Current name	Manufacturer or research source
Anodized surfaces, generic	
Infrablack	Martin Marletta Aerospace Denver, CO
Martin Black	Martin Marletta Aerospace Denver, CO
Martin Black, Enhanced	Martin Marletta Aerospace Denver, CO
Martin Black, Post-treated	Martin Marletta Aerospace Denver, CO

Table 15: Some available black paints for optical instrumentation. [7]

Current name (other names used)	Manufacturer or research source
Aeroglaze L300	Lord Corporation Erie, PA
Aeroglaze Z004	Lord Corporation Erie, PA
Aeroglaze Z302	Lord Corporation Erie, PA
Aeroglaze Z306	Lord Corporation Erie, PA
Aeroglaze Z306 with microspheres	Goddard Space Flight Center Greenbelt, MD
Aeroglaze Z307	Lord Corporation Erie, PA
Ames 24E	NASA Ames Research Center

(Ames 24E2)	Moffett Field, CA
Cardinal 6450	Cardinal Industrial Finishes South Elmonte, CA
Cornell Black	Cornell University Ithaca, NY
DeSoto Flat Black	DeSoto Inc., Chemical Coating Div.
Electrically conductive black optical paint	Jet Propulsion Laboratory Pasadena, CA
Floquil (ESA 110010)	Ftoquil Polly S Color Corporation Amsterdam, NY
IITRI Bone Black D-111 (IITRI D111)	Illinois Institute of Technology Chicago, IL
LMSC Black	Lockheed Missiles and Space Co Sunnyvale, CA
MH21-I	Illinois Institute of Technology Chicago, IL
MH55	Illinois Institute of Technology Chicago, IL
MH2200	Illinois Institute of Technology Chicago, IL
Solarchem	Eastern Chem Lac Corporation Malden, MA
463-3-8	AKZO coatings, Inc Orange, CA
443-3-8	AKZO coatings, Inc Orange, CA
443-3-17	AKZO coatings, Inc Orange, CA

Table 16: Some other types of available black materials and processes for optical instrumentation. [7]

Current name	Manufacturer or research source	Type of material or process
Black Chrome type surfaces	Martin Marietta Aerospace Denver, CO	Electrodeposition process
Black Cobalt type surfaces: Cobalt Black, Black Copper, Black Steel, etc.	Martin Marietta Aerospace Denver, CO	Electrodeposition processes that can be followed by chemical or thermal oxidation
Black Kapton film	Du Pont Willmington, DE	Film
Black Nickel, Ball Black, NBS Black	Ball Aerospace NIST, Gaithersberg, MD	Deposition and etching
Black optical thin film interference coatings	National Research Council of Canada, Thin Films Group, IMS Ottawa, Ontario, Canada	Vacuum deposition techniques: <ul style="list-style-type: none"> • Sputter deposition • Ion vapour deposition • Resistance heated source • Electron beam gun deposition
Black Tedlar film	Du Pont Willmington, DE	Film
Boron Black	Martin Marietta Aerospace Denver, CO	Plasma spray deposition
Boron Caarbide	Martin Marietta Aerospace Denver, CO	Proprietary process
Silicon Carbide	Martin Marietta Aerospace Denver, CO	Chemical vapour deposition
Texture Surfacces	<ul style="list-style-type: none"> • Optics MIDUL, Oak Ridge National Laboratory • SPIRE Corporation Bedford, MA • NASA AMES Research Center Moffat Field, CA 	Vacuum techniques: <ul style="list-style-type: none"> • sputter coated • ion beam etched • sputter coated then etched

Annex 2 Experimental Means

Adhesion test:



Figure 28: Single-blade cutting tool.



Figure 29: Pressure sensitive tape.

Hygroscopic test:

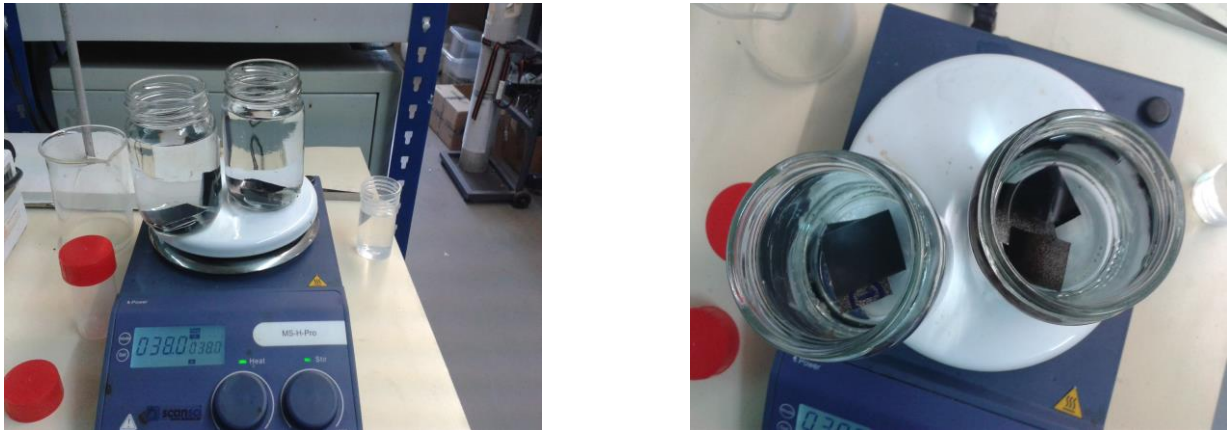


Figure 30: Experimental installation for the hygroscopic test.

Thermal shock test:



a)

b)

c)

Figure 31: Experimental installation for the thermal shock test.

a) Specimens in the nitrogen environment, b) Liquid nitrogen, c) Oven

Annex 3 Experimental Results

Adhesion test:

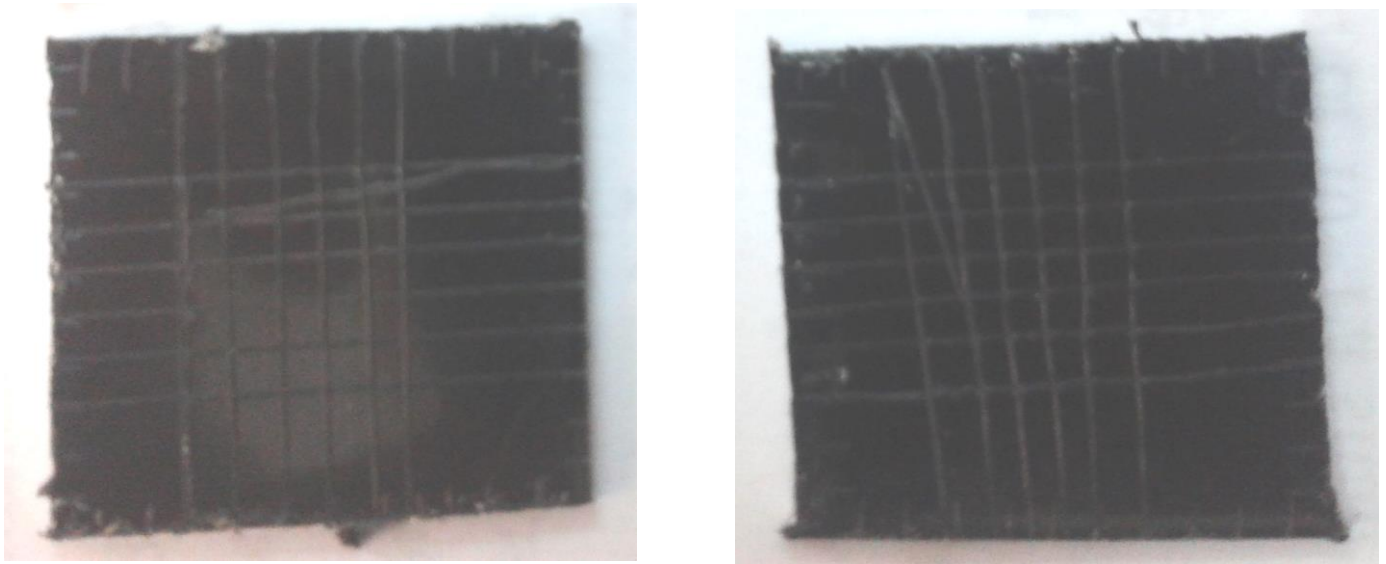


Figure 32: Results observed before the adhesion test for paint 1.

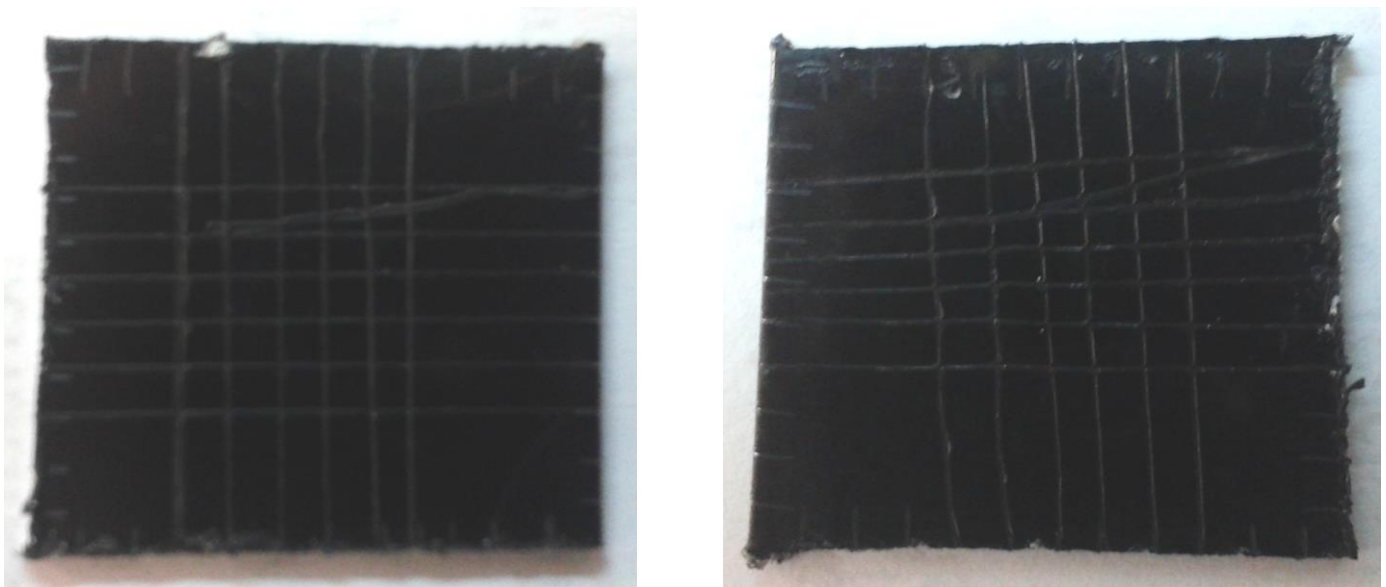


Figure 33: Results observed after the adhesion test for paint 1.

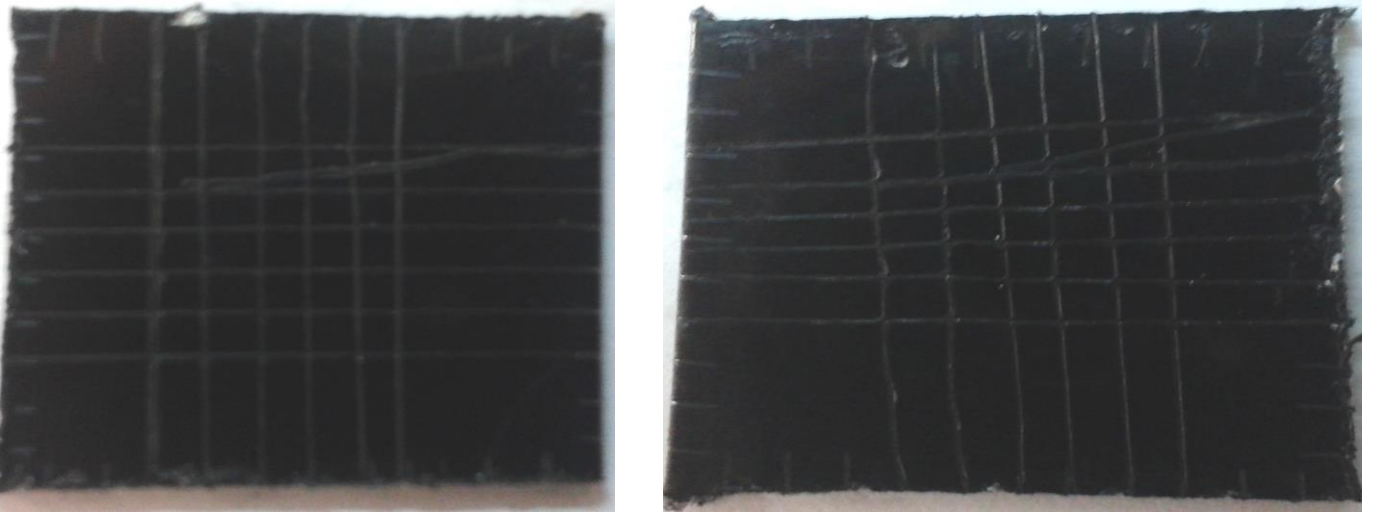


Figure 34: Results observed before the adhesion test for paint 2.

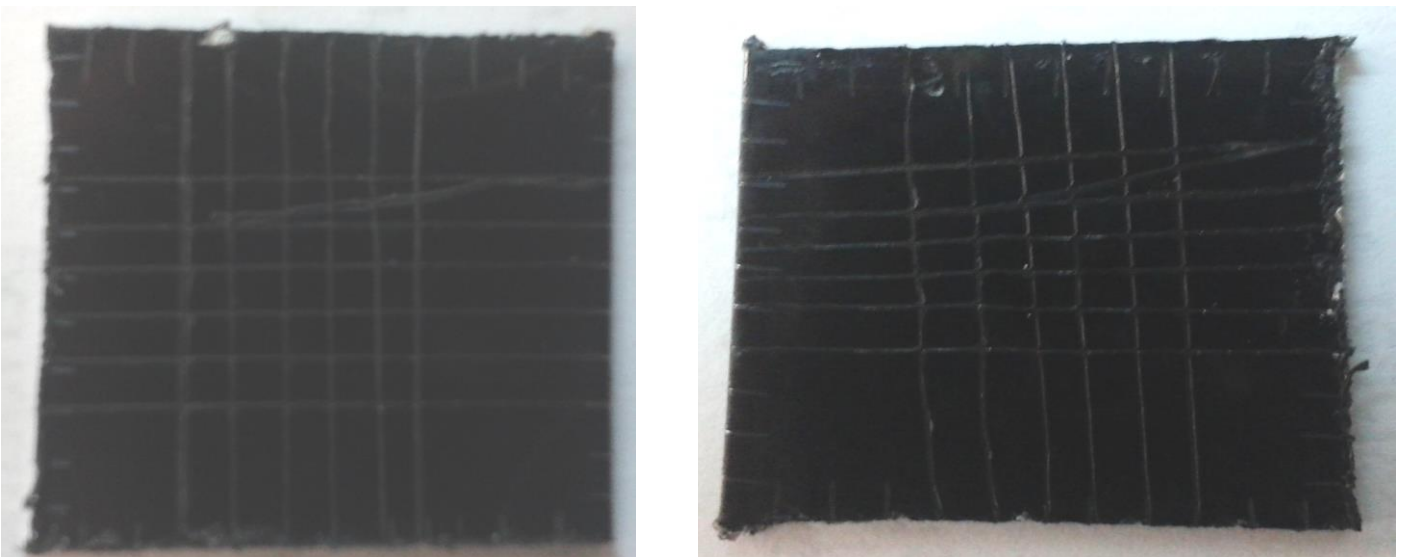


Figure 35: Results observed after the adhesion test for paint 2.

Hygroscopic test:

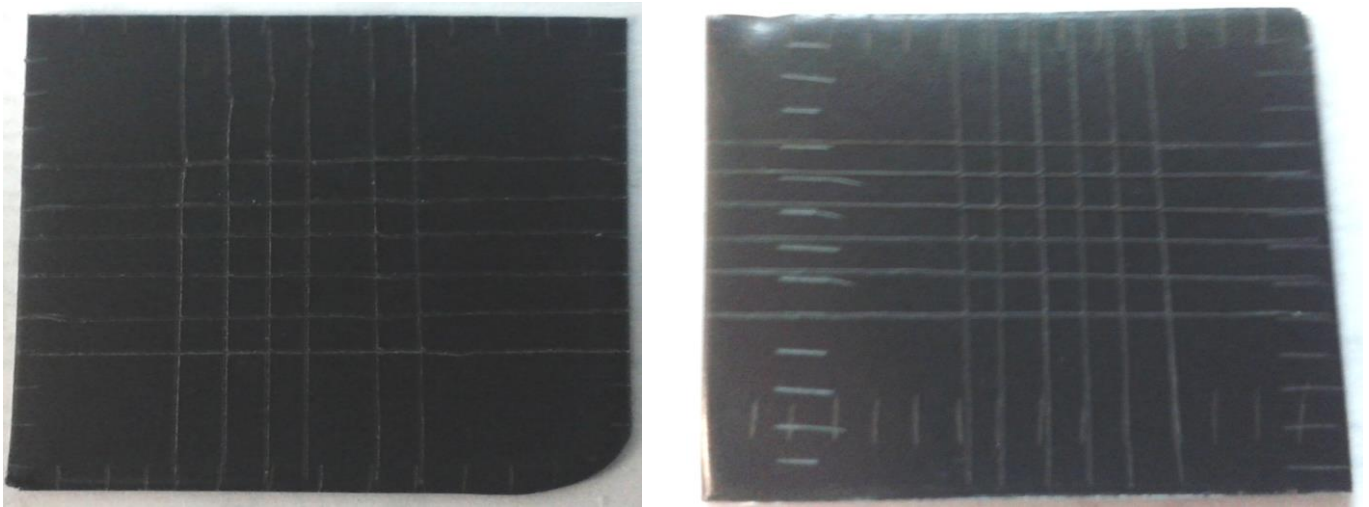


Figure 36: Results observed before the adhesion test after the hygroscopic test for paint 1.

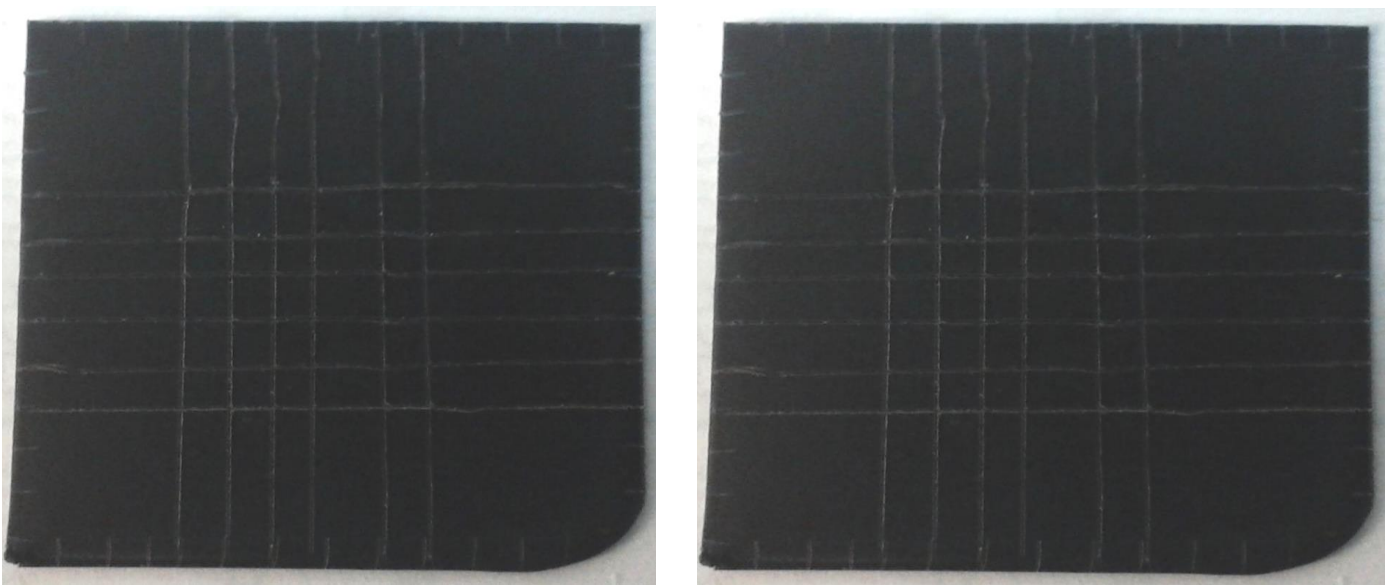


Figure 37: Results observed after the adhesion test after the hygroscopic test for paint 1.

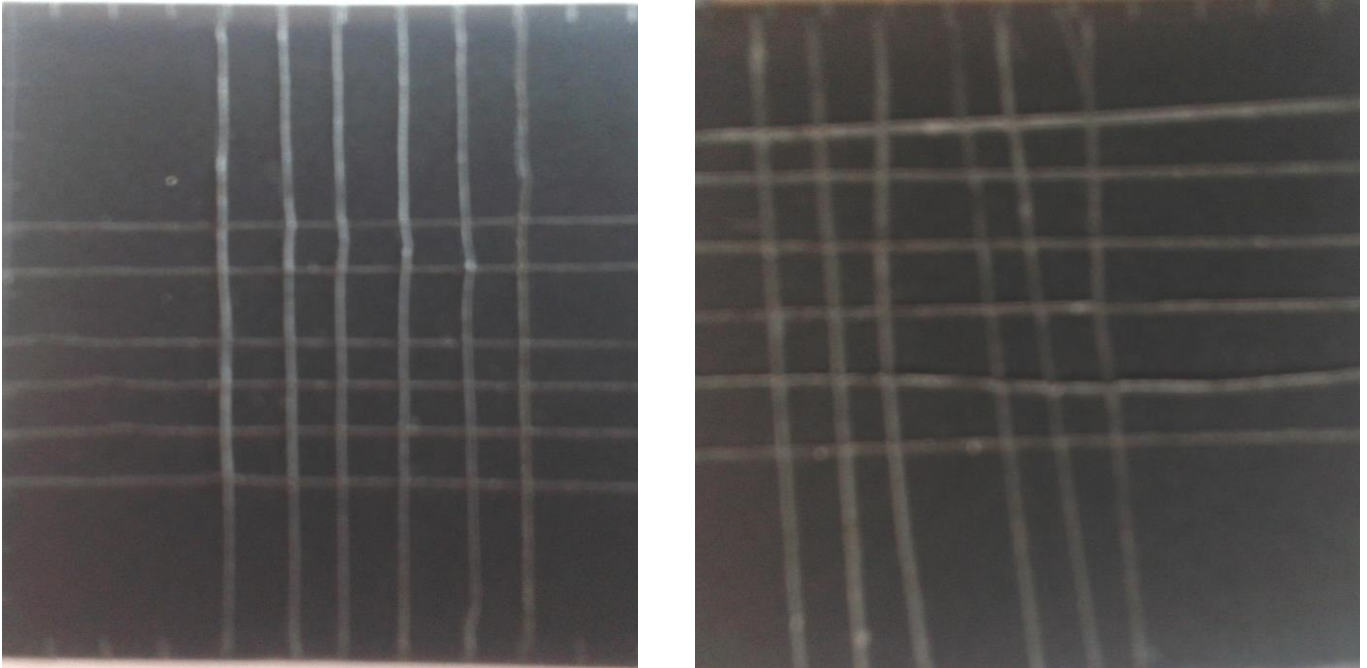


Figure 38: Results observed before the adhesion test after the hygroscopic test for paint 2.

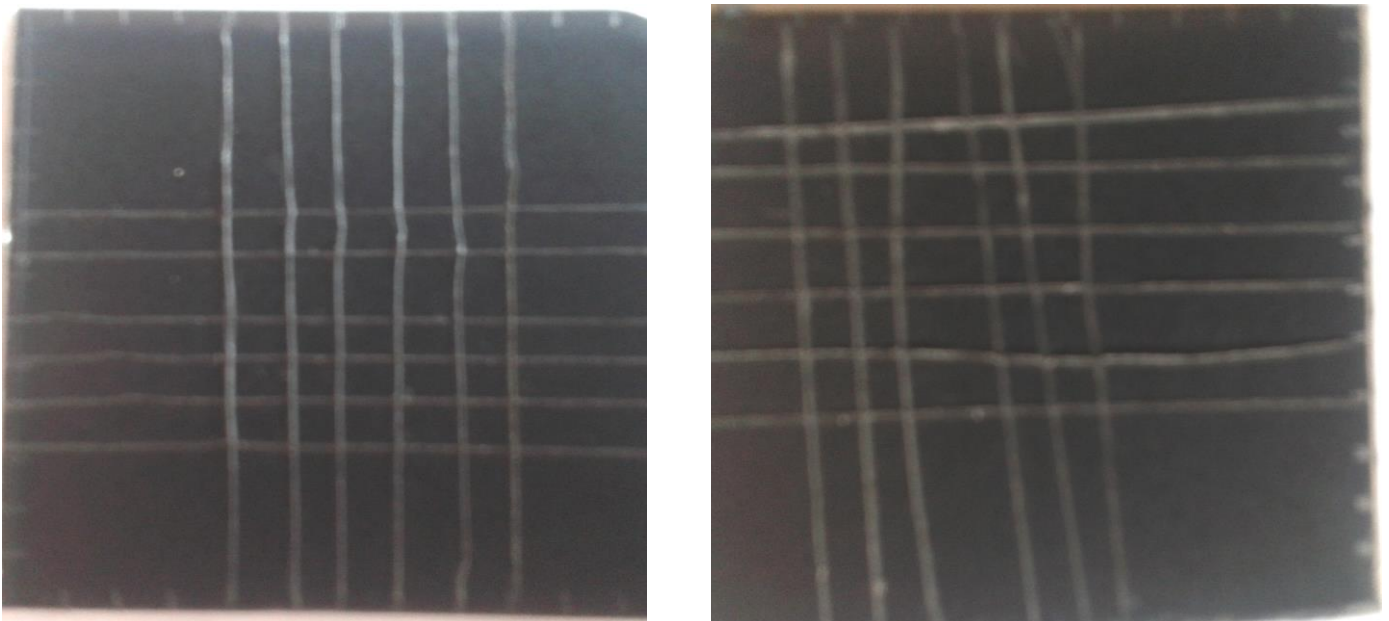


Figure 39: Results observed after the adhesion test after the hygroscopic test for paint 2.

Thermal shock test:

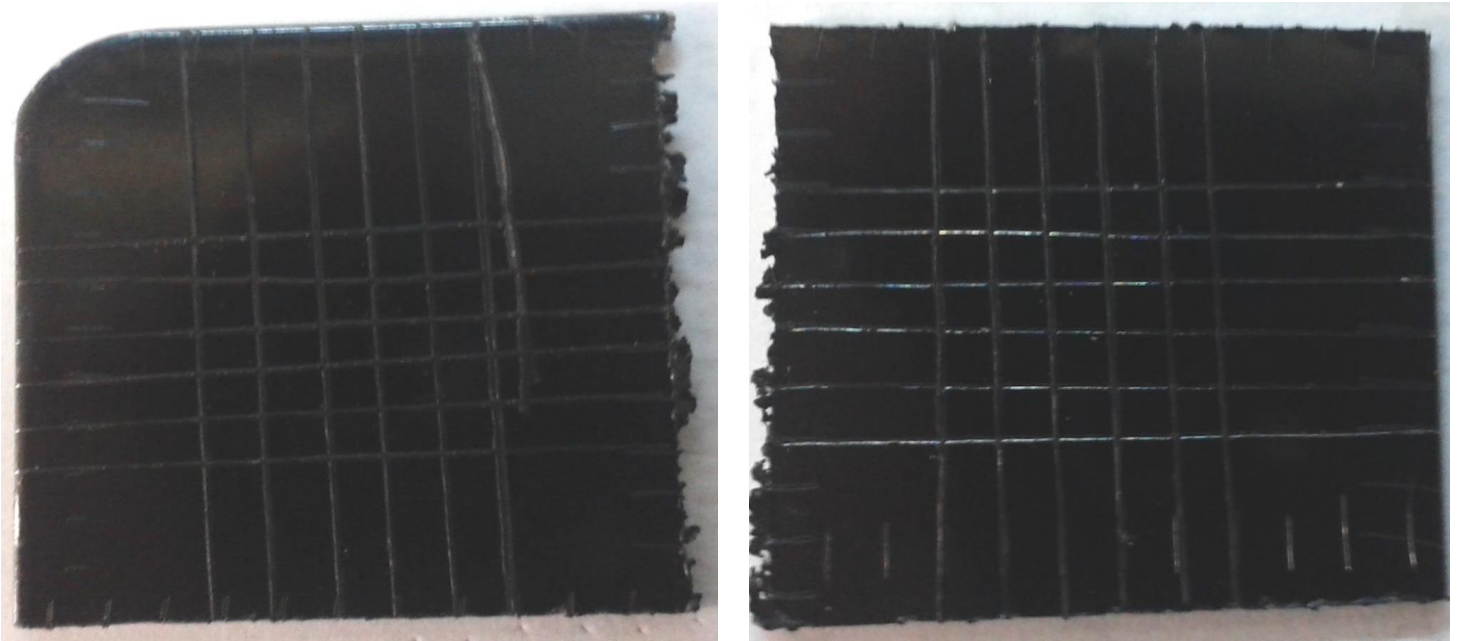


Figure 40: Results observed before the adhesion test for the thermal shock for paint 1.

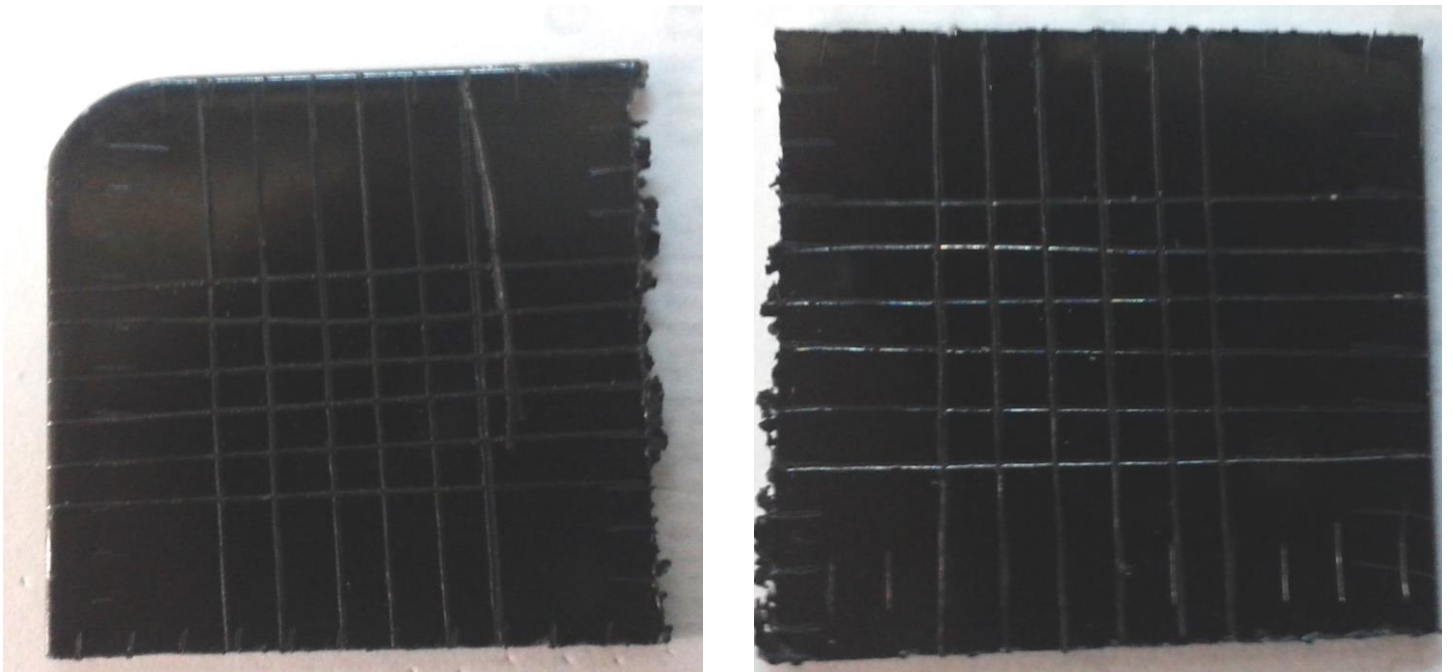


Figure 41: Results observed after the adhesion test for the thermal shock for paint 1.

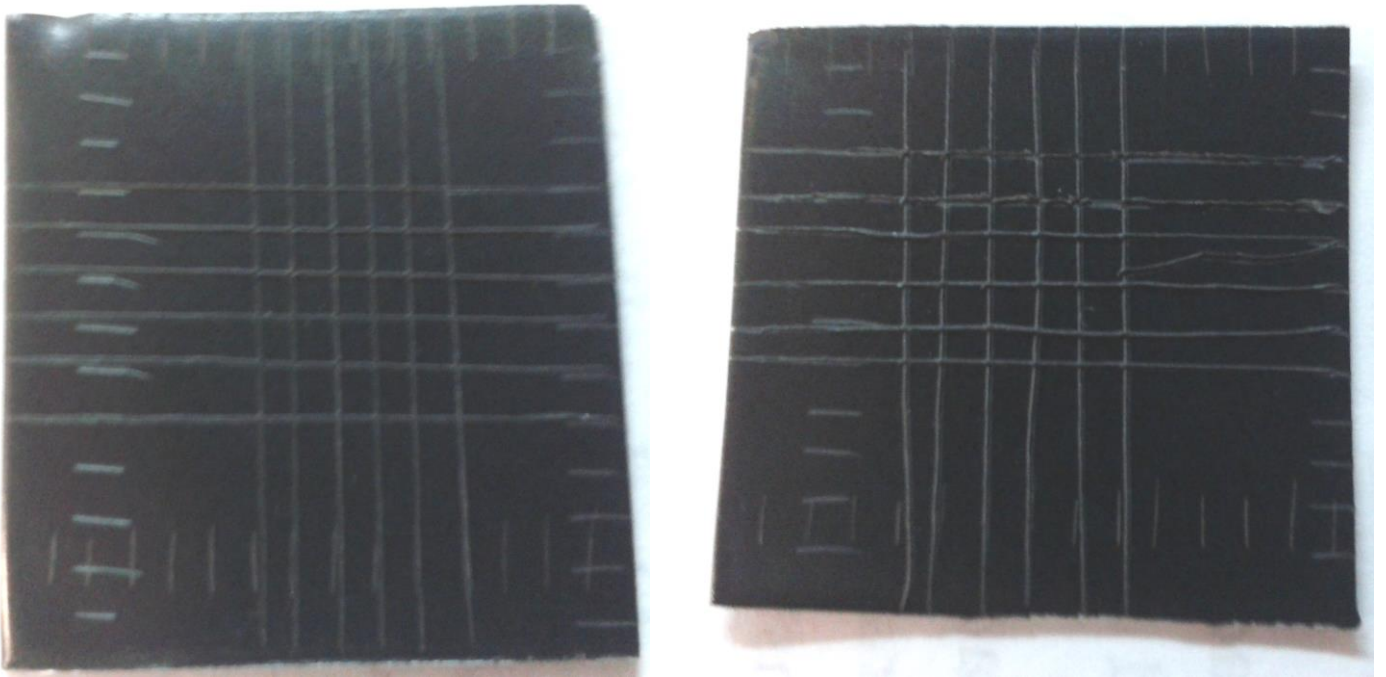


Figure 42: Results observed before the adhesion test for the thermal shock for paint 2.

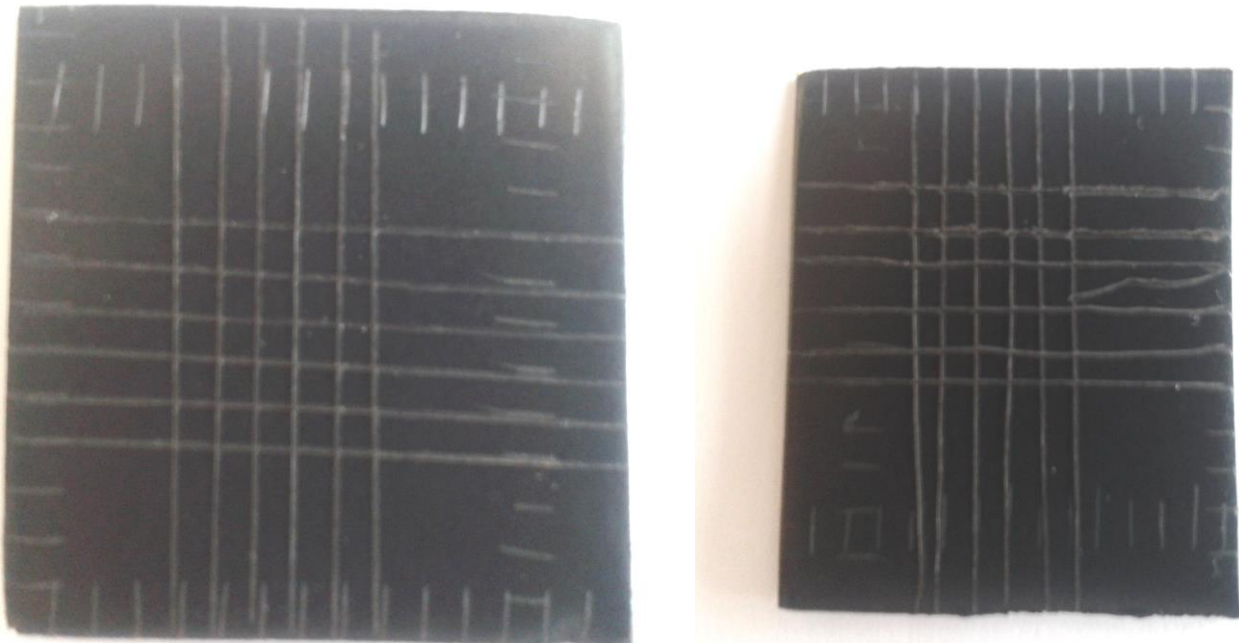


Figure 43: Results observed after the adhesion test for the thermal shock for paint 2.

UV degradation test:

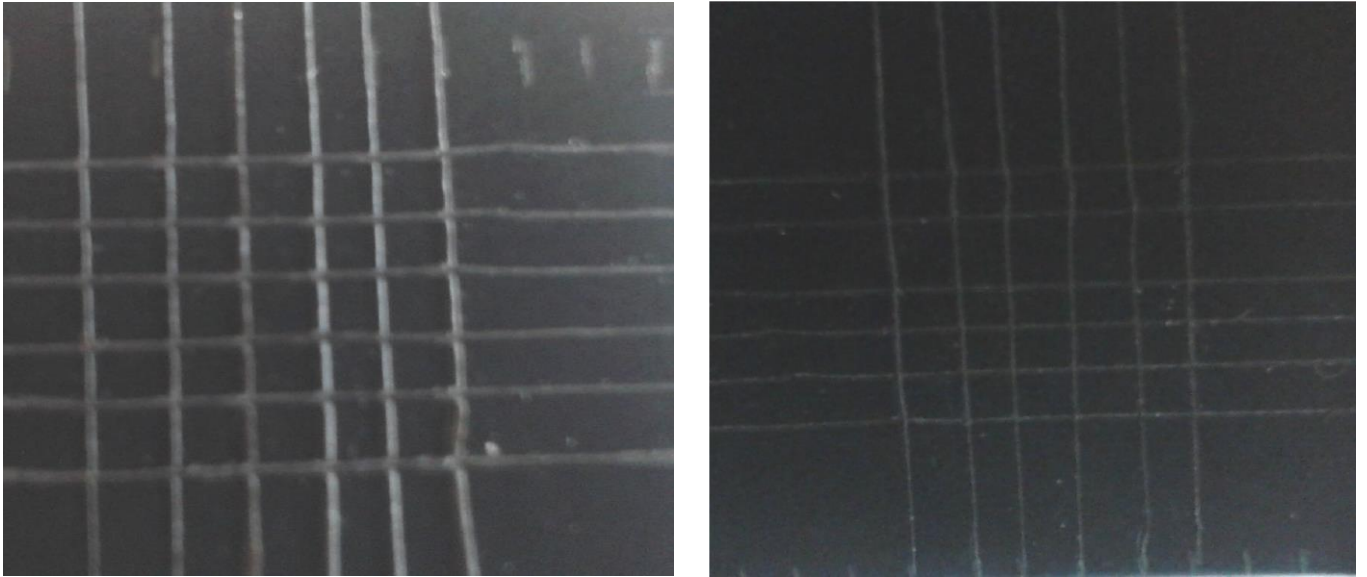


Figure 44: Results observed before the adhesion test for the UV degradation test for paint 1.

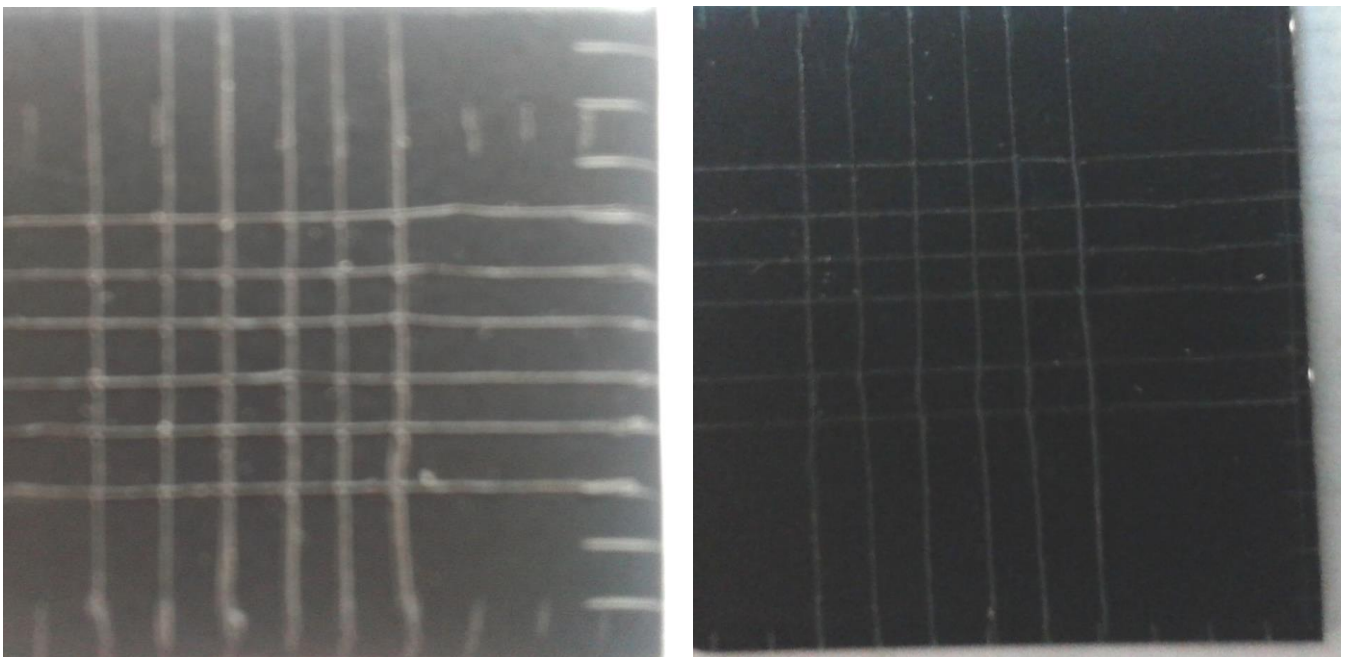


Figure 45: Results observed after the adhesion test for the UV degradation test for paint 1.

Table 17: Results observed after the UV degradation test and classification of the adhesion test for paint 1.

Results from the adhesion test after the UV degradation test for paint 1			
Specimens	Hours of exposure	Classification from the adhesion test after the UV degradation test	Observations
1	336	0	No observation of detachment of the squares in the surface.
2	336	0	No observation of detachment of the squares in the surface.
3	336	0	No observation of detachment of the squares in the surface.
4	336	0	No observation of detachment of the squares in the surface.

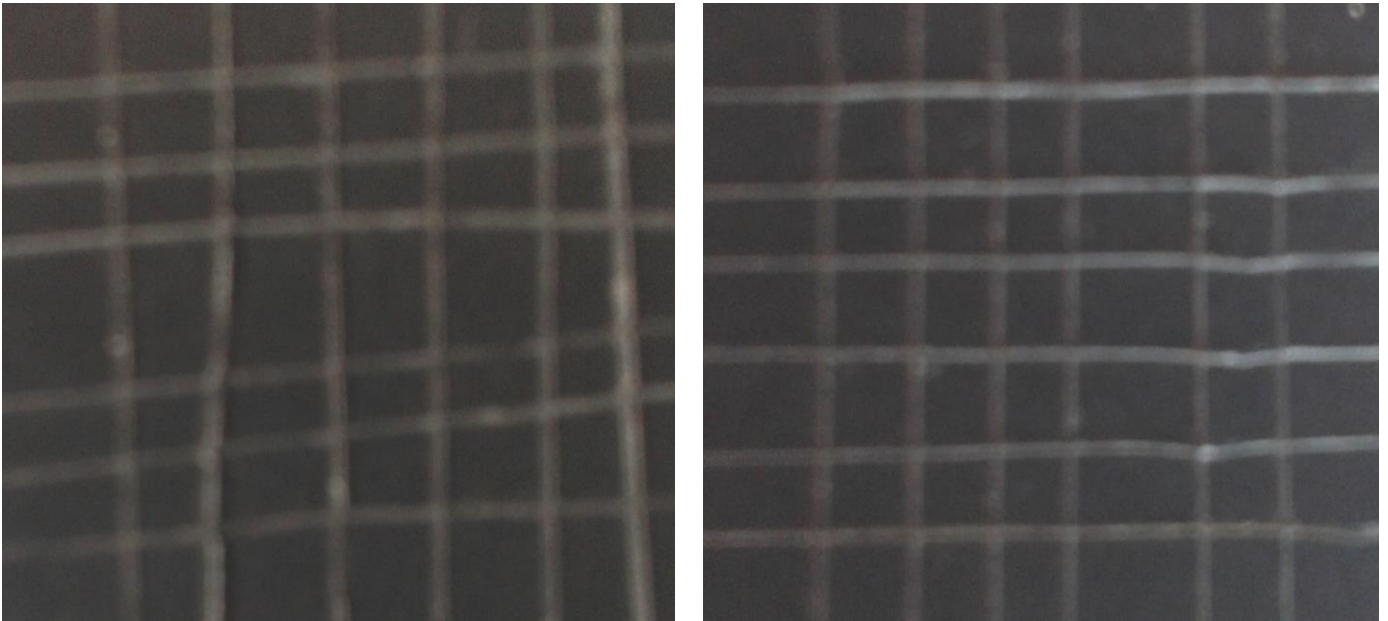


Figure 46: Results observed before the adhesion test for the UV degradation test for paint 2.

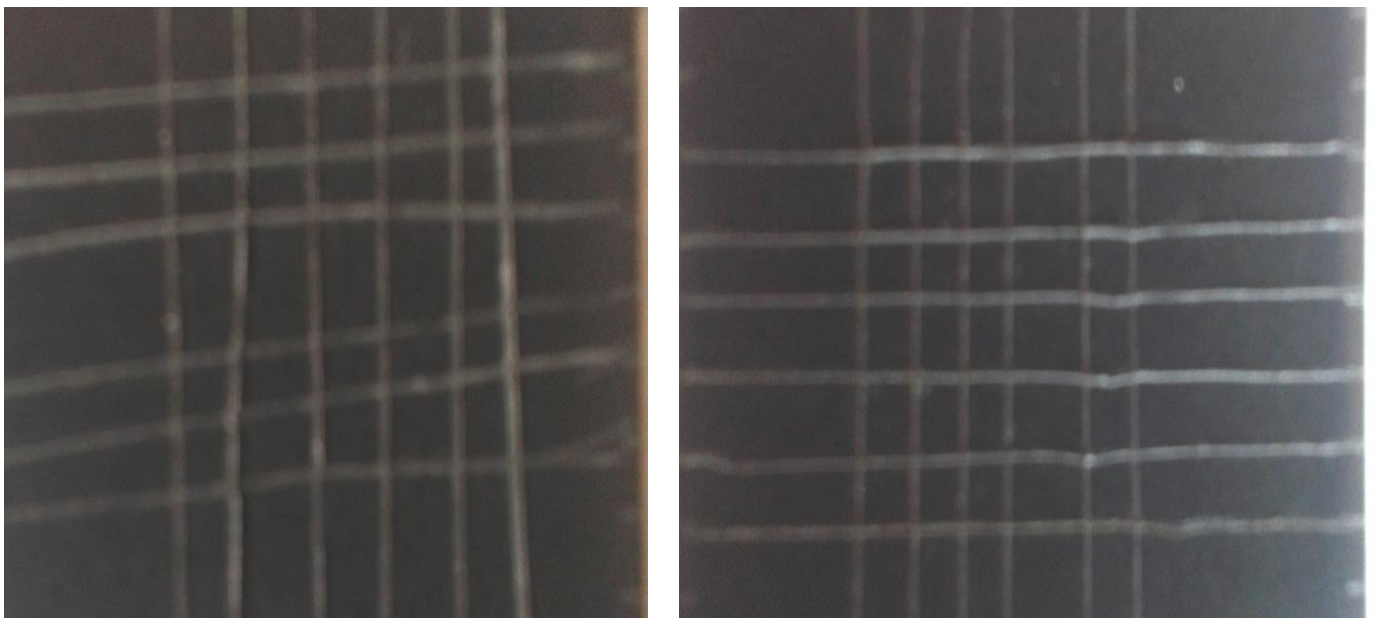


Figure 47: Results observed after the adhesion test for the UV degradation test for paint 2.

Table 18: Results observed after the UV degradation test and classification of the adhesion test for paint 2.

Results from the adhesion test after the UV degradation test for paint 2			
Specimens	Hours of exposure	Classification from the adhesion test after the UV degradation test	Observations
1	336	0	No observation of detachment of the squares in the surface.
2	336	0	No observation of detachment of the squares in the surface.
3	336	0	No observation of detachment of the squares in the surface.
4	336	0	No observation of detachment of the squares in the surface.