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Keywords: Waterborne paints, styrene-acrylic, natural ageing, accelerated ageing, color variation

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Abstract: Metals are mostly painted to improve corrosion protection of the coated item. Nevertheless, paints can be used to deliver visual aspects to them. Several investigations were conducted to comprehend color variation of paints as function of accelerated tests however, limited information is found concerning these variations versus field exposure. Thus, there is the interest to cover this lack of information and investigate color changes of waterborne paints versus field exposure. In this study colored styrene-acrylic painted steel panels were naturally aged in the alpine climate of Trento, northern of Italy. Color measurements were conducted according to the CIEL*a*b* system. Gloss measurements and FT-IR spectroscopy assessed variations on the surface topography and chemical structure of the coated panels. It was observed that the changes in color of the colored paints were commanded by the interaction of ultraviolet radiation and they were dependent on the chemical nature of the color pigments. In addition, in the months with attenuated solar irradiance and predominance of TOWISO conditions, gloss reduction rates and L* of the coated panels have their evolution trend shifted. Upon accelerated UV.B aging conducted in dry condition neither fluctuations on the L* nor attenuation on the gloss reduction rates were detected.

Cover Letter

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Trento, November 18th 2016

Dear Editor,

I am submitting to the journal Materials & Design a revised version of the research paper entitled "*Color variation of electrophoretic styrene-acrylic paints under field and accelerated ultraviolet exposure*" written by L.G Ecco, Michele Fedel, Stefano Rossi and Flavio Deflorian

The authors would like to thank the reviewers for the critical reading of the manuscript. The text has been revised according to the Reviewers comments in order to clarify the experimental approach, the aim of the study and the discussion of the experimental measurements. In the revised manuscript, all changes are highlighted with yellow background in order to facilitate the peer review moreover, the revised manuscript complied with all the points requested on re-submission checklist. In addition, a '*'Response to Reviewers*'' document has been prepared in which the authors answered back point-by-point each of the reviewers comments.

In particular:

- On the whole, the manuscript has been majorly re-written. As far as these changes are concerned, no different results were added. Conclusions of the work were totally re-written.
- Whenever mentioned, the correlation between gloss and roughness of the paints is now properly referenced in the text. New references were brought to the reference list in order to support the experimental outcomes with the assumptions proposed by the authors.
- A direct correlation between water uptake and changes on the coordinate L* and gloss are avoided. Since water uptake has not been measured, the discussion of these results is based on the period of predominance of time of wetness which, according to literature, induces water uptake.
- English grammar was carefully controlled.

With best regards,

Luiz G. Ecco

Reviewer #1:

1.1 - The comparison between exterior ageing and artificial indoor ageing, is especially interesting, as it is rarely seen in literature. Here are some minor points;

English needs revision.

Authors: English has been controlled. Reviewer can find that major changes were done in order to render the manuscript more readable.

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1.2 - I understand what the authors want to do. Still, for the sake of readers, the authors should point out that modern automotive coatings are protected by a very sturdy transparent varnish-like coating, over the colored coating. In the case here, both colored coatings and 'varnish' were studied separately.

Authors: Yes, the colored and the clear coat (varnish) were studied separately since the clear coat has been used as reference on the discussion of the results of colored paints. In the section *Introduction,* the paragraph concerning the cataphoretic deposition of paints has been re-written. It is highlighted that cathodic electrodeposition of paints in formulations containing color pigments enables a present-day growing variety of products which are beyond automotive industry. For instance, indoor furniture, household appliances, jewelry and glass frames industries.

Few other comments on this topic: in this study, cathodic electrodeposition technique has been used to produce a single layer which simultaneously delivers visual aspects with corrosion protection to the coated item. The focus remained on the visual modifications and to comprehend the changes it was essential to compare the colored paints with the clear styrene-acrylic (varnish) paint.

Reviewer is correct when says that automotive body-cars are protected by a primer which is deposited by means of cathodic electrodeposition and, nowadays, most of the paints currently used in electrophoretic corrosion protective automobile coatings are epoxy-based materials that are internally cross-linked through urethane chemistry. This primer layer has tens of µm and the purpose is corrosion protection of the metallic body-car structure. Over this primer layer several layers are further deposited to constitute the whole automotive paint system and the last layer is very sturdy transparent varnish-like coating. Since the primer is the very first layer, it is needless to coloring it and there is no paid attention on its visual aspects.

Although not reported in the manuscript, we have gone through the assessment of the corrosion protection properties of the studied coatings and impedance ranged near 10^{10} ohm.cm^2. It is a significant impedance values for 20 µm coatings.

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1.3 - It would have been nice to see roughness measurements, to correlate with gloss decrease.

Authors: We agree, roughness measurements could provide complementary information on the gloss evolution. In fact, an experimental approach to check the roughness of the paints was tried; roughness of coated panels was measured using a MAHR Marsuf PS1 profilometer, considering a measurement length of 5.6 mm and a cut-off length of 0.8 mm. However, no reliable results were obtained; the diamond probe of the profilometer was scratching the paint's surfaces while moving over the panels for the acquisition. Micro scratches were observed with optical microscopy. Thus, authors could not report such data. Perhaps, AFM analysis would have fulfilled this lack of information however authors decided not to go for it. AFM is time consuming and the outcomes from this analysis would be beyond the objectives of our investigation.

An additional clarification concerning the property roughness of the tested panels: in this paper, referring roughness to discuss the changes in gloss is mistaken. Indeed, the roughness of the paints was not measured and the proposed relation between gloss and roughness stands amongst the critical points to be revised/clarified by authors.

To the best of author's knowledge, there is a dependency of gloss on roughness aspects, this has been verified somewhere[1] by our group of research where a correlation between roughness and gloss of vitreous enamel coatings was demonstrated. Besides the findings of our group, there are enough literature which demonstrate the relationship between surface roughness with glossiness [2] and also with color [3].

Moreover, the standard practice itself (ASTM D523 14 - Standard Test Method for Specular Gloss) proposes a correlation between the specular gloss and surfaces aspects; e.g. texture or shininess.

Nevertheless, the present study deals with an organic paint instead a vitreous enamel coating and the since roughness as a property was not measured, the sentence which had been proposed in the text - *"the changes of gloss suggest modification of surfaces aspects, e.g. higher roughness".* – are now modified and referred accordingly.

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1.4 - In section 2.1 the authors should make an effort to identify precise chemical nature of red pigments. This is important as another coating with another red organic or inorganic pigment cannot be expected to behave in same way. Later in text it is shown that change in E is much stronger with red coating. Could it be discussed in terms of chemical nature of red pigment? Indeed it is well known that organic pigments are more light sensitive than inorganic ones. Such data would make paper more meaningful.

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[1] E. Scrinzi and S. Rossi, *The aesthetic and functional properties of enamel coatings on steel.* **Materials and Design** 31 (2010) 4138–4146.

[2] G.F. Tjandraatmadja et. al. *Evaluation of commercial polycarbonate optical properties after QUV-A radiation—the role of humidity in photodegradation,* **Polymer Degradation and Stability** 78 (2002) 435–448.

[3] M. Yonehara, et. al. *Experimental Relationships between Surface Roughness, Glossiness and Color of Chromatic Colored Metals,* **Materials Transactions** 45 (2004) 1027 – 1032.

Authors: Reviewer is correct, such data would render the paper more meaningful but also contribute to futures studies. The red pigment concentrated solution, likewise the white and black, used in this work are available commercial products and these new information are given in the revised section 2.1, *i.e.* trade mark names of these products.

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1.5. In section 2.3 state clearly in last lines that all coating were also, in a separate study, submitted to artificial ageing for 500 h.

Authors: As suggested, modification has been done.

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Reviewer #2:

It discusses mainly color variations of coated steel panels as function of field and accelerated exposure. Some aspects should be clarified and explained by the authors. Therefore, some revisions are recommended:

2.1. The title should refer ultraviolet "accelerated" exposure to distinguish it from field exposure;

Authors: *As suggested, modification has been done.*

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2.2. The authors refer in whole paper, including abstract and conclusions, that surface roughness influence the testing results. The authors should explain better this relation and the assessment of this property. Was the surface roughness measured in experimental program? Is this only a supposition, as mentioned in "paints evaluation section"?

Authors: Reviewer is correct. In this paper, referring roughness to discuss the results is mistaken. Indeed, the roughness of the paints was not measured and the proposed relation between gloss and roughness stands amongst the critical points to be revised/clarified by authors.

To the best of author's knowledge, there is a dependency of gloss on roughness aspects, this has been verified somewhere[4] by our group of research where a correlation between roughness and gloss of vitreous enamel coatings was demonstrated. Besides the findings of our group, there are enough literature which demonstrate the relationship between surface roughness with glossiness [5] and also with color [6].

Moreover, the standard practice itself (ASTM D523 14 - Standard Test Method for Specular Gloss) proposes a correlation between the specular gloss and surfaces aspects; e.g. texture or shininess.

Nevertheless, the present study deals with an organic paint instead a vitreous enamel coating and the since roughness as a property was not measured, the sentence which had been proposed in the text and questioned by Reviewer - *"the changes of gloss suggest modification of surfaces aspects, e.g. higher roughness".* – are now modified and referred accordingly.

Furthermore, Reviewer#1 also commented on roughness of the paints and the following response has been given: We agree. Roughness measurements could provide complementary information on the gloss evolution. In fact, an experimental approach to check the roughness of the paints was tried;

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[4] E. Scrinzi and S. Rossi, *The aesthetic and functional properties of enamel coatings on steel.* **Materials and Design** 31 (2010) 4138–4146.

[5] G.F. Tjandraatmadja et. al. *Evaluation of commercial polycarbonate optical properties after QUV-A radiation—the role of humidity in photodegradation,* **Polymer Degradation and Stability** 78 (2002) 435–448.

[6] M. Yonehara, et. al. *Experimental Relationships between Surface Roughness, Glossiness and Color of Chromatic Colored Metals,* **Materials Transactions** 45 (2004) 1027 – 1032.

roughness of coated panels was measured using a MAHR Marsuf PS1 profilometer, considering a measurement length of 5.6 mm and a cut-off length of 0.8 mm. However, no reliable results were obtained; the diamond probe of the profilometer was scratching the paint's surfaces while moving over the panels for the acquisition. Micro scratches were observed with optical microscopy. Thus, authors could not report such data. Perhaps, AFM analysis would have fulfilled this lack of information however authors decided not to go for it. AFM is time consuming and the outcomes from this analysis would be beyond the objectives of our investigation.

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2.3. At the abstract, the authors refer "a correlation between the lightness with the amount of water diffusion in the coatings is proposed". This issue should be at the conclusions sections and in more detail and quantification.

Authors: Agreed, the proposed correlation between water in the coatings with L* might be considered controversial since water uptake has not been directly measured and, up to the best of our knowledge, there are few investigations which propose the same thing. In the latest manuscript a revised abstract, discussion concerning this correlation and conclusion are proposed.

In addition, we would like to add few comments considering this point. In the present study, authors have come to this hypothesis after matching the changes on color, gloss with the meteorological data where it has been detected a fluctuation in the trend direction of lightness (L*) and an attenuation on gloss reduction rates in the period of predominance of TOW_{ISO}. It should be considered that, in equivalent period of time, solar irradiance was weakened due to the seasons of the year therefore any degradation which is due to the solar radiation was lessened enhancing the effect of TOW_{ISO} condition.

Nevertheless, authors came to be convinced on this correlation upon the results from the accelerated UV.B test wherein neither the fluctuation on the L* nor the attenuation on gloss reduction rates were seen.

Finally, such observation creates opportunities and the correlation between water uptake/ the lightness of the coatings could be the subject of another study.

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2.4. In the introduction, line 7, please separate the contribution of each study, references 2, 3 and 4.

Authors: *As suggested, modification has been done.*

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2.5. In the introduction, line 16, more references should be added, taking into account the comparison of accelerated laboratory and field exposure testing of materials

Authors: Perhaps, in the manuscript the objectives of the work were not clearly mentioned. Therefore, discrepancies in the results and discussion between natural and accelerated aging conditions emerged. The revised manuscript better clarifies the objectives which are also detailed in the discussion that follows:

Concerning organic coatings, several studies were focused on natural and accelerated weathering to comprehend the paints degradation and the results from these tests, most especially when a comparison between both approaches was attempted, have been debated for a long time. In general, a good correlation between natural and accelerated aging is critical to obtain. Some partial correlations can be found however, due to the huge number of parameters involved in the natural aging.

The objective of our work was the evaluation of color perception and their changes as function of natural aging in the alpine climate of Trento – (IT). In particular, the accelerated UV aging was conducted, in dry atmosphere, due to specific observations from the natural weathering test, i.e. fluctuations on L* and the attenuation on gloss reduction rates. Nevertheless, as suggested, new references were added and the whole paragraph concerning accelerate and field tests has been revised.

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2.6. In the second page of the introduction the following paragraphs (some parts) should be switch: first: Acrylic water borne…". and second: "Among the waterborne….". First the authors should refer materials, then application and finally the degradation mechanisms. Please revise it accordingly.

Authors: As suggested, modification has been done. Reviewer can notice that major changes have been done in the Introduction.

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2.7. In section 2, in general, the number of tested samples, their dimensions and the number of measurements in each testing technique, and the testing location within the sample, should be clarify.

Authors: As suggested, modification has been done.

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2.8. In section 2.1, the FTIR analysis should be mentioned to study chemical structure and composition.

Authors: Authors rebut this suggestion. According to us, it would be more adequate to keep the FT-IR description in section 2.4 – Paints evaluation. This technique has been used to assess the chemical structure and the changes of the paints, thus we keep in the section 2.4.

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2.9. In section 2.3 the field acquisition data equipment should be characterized. Why the wind action was not included in the field acquisition data?

Authors: As suggested, an improved description on the equipment is given. Authors understand the importance of wind action. It can be direct connected to the time of wetness, wind action can reduce TOW. In marine environment, it also can carry aggressive ions, e.g. Cl^-, from the sea side. Trento is known as an alpine environment, far from the sea side, and wind action in Trento can be excluded.

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2.10. In section 2.3 the UV-B chamber should also be characterized.

Authors: Mainly, the accelerated UVB aging test was conducted to simulate changes associated to the UV light during the outdoor aging; this test has been set-up with UV radiation as the only parameter promoting changes on the coatings. Authors decided to conducted this test upon the observed changes on the visual aspects of the coatings after natural exposure in which a correlation between the time of wetness (TOW_{ISO}) and the lightness (L*) were, at a certain extent, found. Thus, the UVB aging was designed in the dry condition under controlled temperature based on the practice description of ASTM G154-06. In this way, no cycles between wet/dry condition were used however, the standard practice ASTM G154-06 clearly states that the arrangements should be made according to the best conditions for the material to be tested. Information about irradiance is now provided.

Considering these points, a new description is now given in the revised manuscript. The UVB aging test has been conducted according to the ASTM G154-06 (Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials). The practice describes a number of exposure procedures however, this practice does not specify which exposure condition is best suited for the material to be tested.

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2.11. All the standards mentioned in the text should be included in the final references list

Authors: As suggested, modification has been done.

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2.12. The caption of Figure 1 should be completed in terms of solar radiation, temperature and combination of relative humidity and air temperature.

Authors: Modifications have been done, as suggested. In addition, readers can detailed find in the first paragraph of the section *Weathering data* a careful description of the stack plot displayed in Figure 1 and all the information which is delivered from it.

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2.13. Please complete the Figure 2 caption with cumulative solar radiation and also clarify it in the figure

Authors: Modifications have been done, as suggested. In addition, an improved discussion in given in the revised manuscript.

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2.14. Figures 3 (and also Figure 6) should be separate in two to illustrate better the minor changes in some color paints; one figure with the values for red paint and the other one with the remaining values;

Authors: Agreed, there was overlapped information, consequently not readable. New Figs. 3 and 6 are proposed however authors adopted a different approach; In order to have all in a single Fig. and maintaining the scale of the color space diagram, inserted pictures have been added into the new Figs. 3 and 6 wherein the color changes for the black, white and clear paints are zoomed allowing a better interpretation and comparison of the data.

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2.15. In results discussion the authors should quantify the results, when possible, as quantitative percentages or values. For example: please complete the following sentence with quantitative assessment: "..both coordinates…were reduce whereas the …..remained significantly constant".

Authors: In the revised manuscript, an improved discussion of results brings quantitative assessment.

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2.16. Figure 4 and 7 should be combined or a new figure should be added to illustrate better the tendency observed in field exposure and UV accelerated test. This illustration will support better the written text.

Authors: New Fig. is proposed merging the evolution of gloss after field and accelerated.

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2.17. The authors refer in "paints evaluation" section that 250 hours of exposition to UV can be related to one year of natural ageing. The same sentence is at the conclusions. The authors should discuss it better in the paper, referring other studies from other authors. Also the main degradation mechanism should be mentioned. This correlation is suitable for a specific type/color of paint r can be generalized? Please revise the conclusions taking into account this important contribution.

Authors: We agree. The objective of our work was the evaluation of color perception and their changes as function of natural aging in the alpine climate of Trento – (IT). In particular, the accelerated UV aging was conducted, in dry atmosphere, following the observations from the natural weathering test, i.e. fluctuations on L* and the attenuation on gloss reduction rates.

Authors did not intend to propose a direct correlation between accelerated and field. This has been done in past and a total connection between these two experimental approaches remains open to discussion.

In the present study, if one confronts the magnitudes of the changes on the total color perception and gloss after field and accelerated, the 250 hours of exposition to UV can be related to one year of natural aging. It is certainly a relation which fits for the colored styrene-acrylic paints aged in the exposure site of Trento, thus it cannot be generalized to other paints systems.

The manuscript has been revised and new conclusion is proposed.

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2.18. Table 2 is not mentioned in the text

Authors: *Table 2 has been removed from the manuscript.*

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2.19. Figure 9 only shows the UV exposure. Was FTIR analysis performed for pigmented coatings subject to field exposure?

Authors: FTIR spectra after field test has been added and an improved discussion is now given in the manuscript.

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2.20. Please explain better "water uptake phenomenon". Is water absorption or water retention of the paint layer? Also water diffusion should be better discussed. What is the water vapor permeability of the tested paints?

Authors: The water uptake phenomenon describes the ingress of water (e.g. moisture or humidity), either during the paint service life or while immersed for laboratory tests, into the paint volume. Once there was this ingress, the interactions between the organic coatings with water can occur in two ways: bounded and free water. The bound water is connected to polar group of polymer chains via hydrogen bonding and it is responsible for swelling of the coating layer. The free water, also called as retained water, is the water which is found in the free volume of the polymer network, it is un-bonded and it can evaporate from the coating depending on the environment conditions. Free water is responsible for internal stress due to the pressure formed by water clusters.

In the studied paints, the amount of water was not assessed. Therefore authors are not permitted to deepen the discussion concerning the quantities of water into the paints. However, based on previous experience and supported by literature, authors are convinced that TOW_{ISO} favors the water uptake.

Water permeability of the tested paints is not known.

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2.21. Please explain better, with quantitative results or with literature review the following sentence: "the changes of gloss suggest modification of surfaces aspects, e.g. higher roughness".

Authors: In fact, the proposed connection between gloss and roughness stands amongst the critical points to be revised/clarified by authors.

To the best of author’s knowledge, there is a dependency of gloss on roughness aspects, this has been verified somewhere[7] by our group of research where a correlation between roughness and gloss of vitreous enamel coatings was demonstrated. Besides the findings of our group, there are enough

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[7] E. Scrinzi and S. Rossi, *The aesthetic and functional properties of enamel coatings on steel.* **Materials and Design** 31 (2010) 4138–4146.

literature which demonstrate the relationship between surface roughness with glossiness [8] and also with color [9].

Moreover, the standard practice itself (ASTM D523 14 - Standard Test Method for Specular Gloss) proposes a correlation between the specular gloss and surfaces aspects; e.g. texture or shininess.

Nevertheless, the present study deals with an organic paint instead a vitreous enamel coating and the roughness as a property has not been measured.

Therefore, the sentence which has been proposed in the text and questioned by Reviewer - *"the changes of gloss suggest modification of surfaces aspects, e.g. higher roughness".* – are now modified and referred accordingly.

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2.22. "Lightness aspects" should be clarified at the conclusions.

Authors: *A revised conclusion is proposed.*

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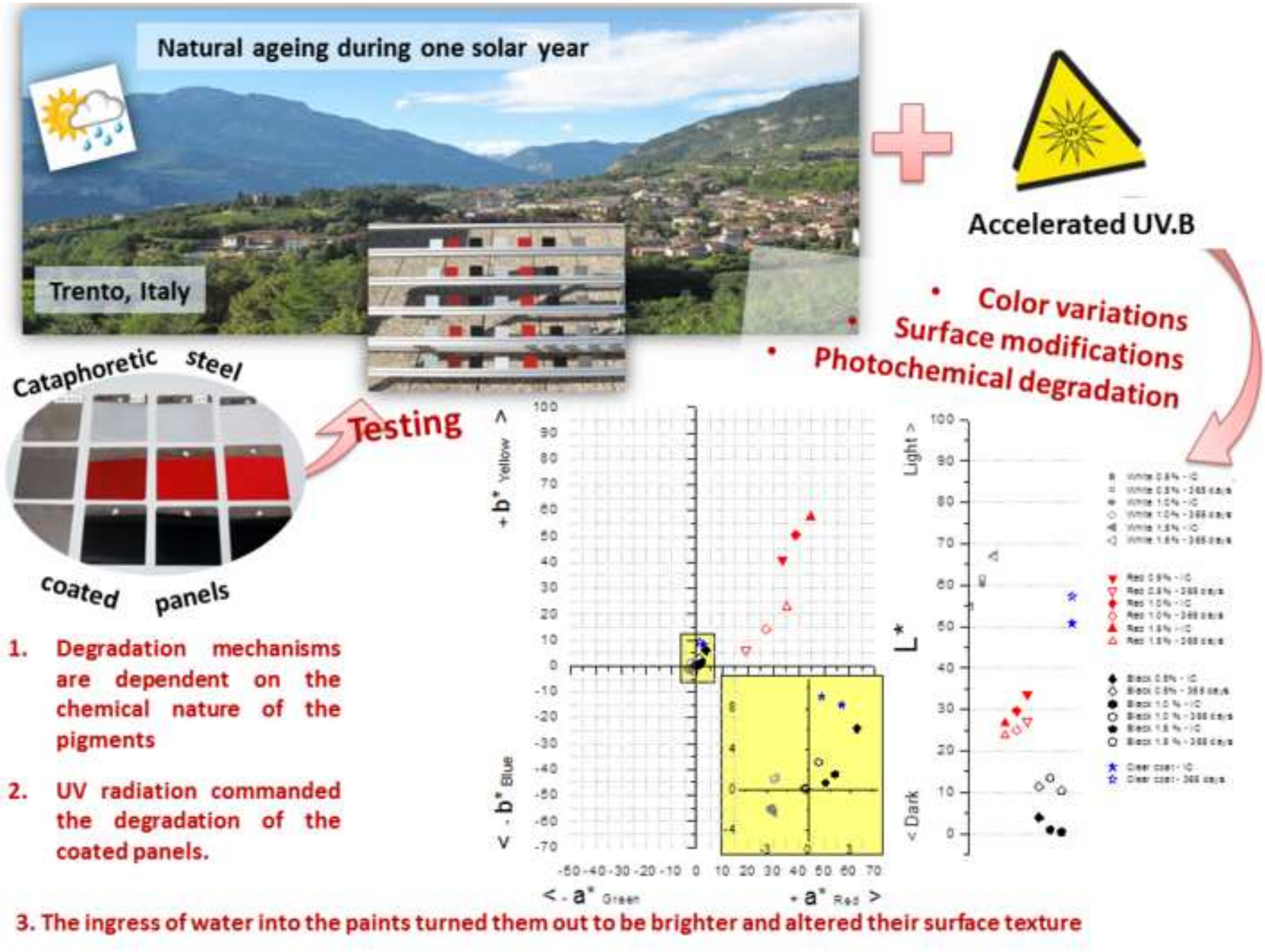
[8] G.F. Tjandraatmadja et. al. *Evaluation of commercial polycarbonate optical properties after QUV-A radiation—the role of humidity in photodegradation,* **Polymer Degradation and Stability** 78 (2002) 435–448.

[9] M. Yonehara, et. al. *Experimental Relationships between Surface Roughness, Glossiness and Color of Chromatic Colored Metals,* **Materials Transactions** 45 (2004) 1027 – 1032.

***Graphical Abstract**



- Color variations
- Surface modifications
- Photochemical degradation

1. Degradation mechanisms are dependent on the chemical nature of the pigments
2. UV radiation commanded the degradation of the coated panels.
3. The ingress of water into the paints turned them out to be brighter and altered their surface texture

***Highlights (for review)**

Color variation of pigmented coatings is sensible to RH and UV radiation

The time of wetness played a role on gloss and lightness

Different degradation mechanisms were observed in function of chemical nature of pigments

The accelerated UV ageing test discriminated the stability of the pigmented paints system

Color variation of electrophoretic styrene-acrylic paints under field and accelerated ultraviolet exposure

Luiz Gustavo Ecco[1], *Stefano Rossi, Michele Fedel and Flavio Deflorian*
Department of Industrial Engineering - University of Trento.
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Abstract

Metals are mostly painted to improve corrosion protection of the coated item. Nevertheless, paints can be used to deliver visual aspects to them. Several investigations were conducted to comprehend color variation of paints as function of accelerated tests however, limited information is found concerning these variations versus field exposure. Thus, there is the interest to cover this lack of information and investigate color changes of waterborne paints versus field exposure. In this study colored styrene-acrylic painted steel panels were naturally aged in the alpine climate of Trento, northern of Italy. Color measurements were conducted according to the CIEL*a*b* standard. Gloss measurements and FT-IR spectroscopy assessed variations on the surface topography and chemical structure of the coated panels. It was observed that the changes in color of the colored paints were commanded by the interaction of ultraviolet radiation and they were dependent on the chemical nature of the color pigments. In addition, in the months with attenuated solar irradiance and predominance of TOW_{ISO} conditions, gloss reduction rates and L* of the coated panels have their evolution trend shifted. Upon accelerated UV.B aging conducted in dry conditon neither fluctuations on the L* nor attenuation on the gloss reduction rates were detected.

Keywords: *Waterborne paints, styrene-acrylic, natural ageing, accelerated ageing, color variation*

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1. INTRODUCTION

Polymer coated metals are used in numerous fields of engineering applications such as construction buildings, bridges, in the automotive industry where the corrosion protection of the painted item is mainly desired. Nevertheless, the concept and usage of paints goes beyond the protection against corrosion. In the same way, paints deliver visual aspects to the coated item therefore organic coatings are also used in applications wherein the visual appearance is as important as the corrosion protection, for example, indoor furniture, cultural heritage [1,2], façades paintings [3], wood substrates paintings [4,5], etc.

In the last decades in Europe, the emissions of volatile organic compounds (VOC) to the atmosphere are a major concern. Late in the 90's, a strict environmental protection regulations controlled the use of organic solvents in certain activities and installation in order to reduce the emissions VOC to the atmosphere [6] and a following amendment limited the emissions of VOC due to the use of organic solvents in certain paints, varnishes and vehicle refinishing products [7]. In the search for viable alternatives to replace the traditional solvent based and to reduce the emissions of VOC, water based formulations appears as an environmentally friendly alternative. Initially, the drawbacks of waterborne coatings were associated to with the use of water as a dispersive medium. Due to the chemical reactivity of them with water, waterborne coatings were attributed lower chemical resistances and shorter lifetime. However, advances made on the chemistry of waterborne paints, turned them out to be technically and economically equivalent to the solvent based formulations [8,9].

Among the technologies used to paint metals, the cathodic electrodeposition can be considered an environmentally friendly method since the process is water based and heavy-metals free [10]. This method deposits a uniform layer over the substrate with a precise control of the film composition and thickness. Several metallic substrates can be coated via cathodic electrodeposition; hot/cold laminated and galvanized steel, copper and aluminum alloys. The chief example of successful application comes from the automotive industry wherein cathodic electrodeposition technology was implemented to coat automobile bodyworks in the 70's and is still widely used in present days [11–14]. Furthermore, the advantages of cathodic electrodeposition of paints associated with formulations containing color pigments enable a present-day growing variety of products which can be painted via cataphoretic coatings. Indoor furniture, household appliances, jewelry and glass frames industries are potential markets for colored cataphoretic paints since a single paint layer of tens of micrometers delivers visual aspects alongside corrosion protection to the coated item.

The durability of paints, i.e. paint's lifetime, can be denoted as the preservation of its properties, such as the visual aspects or the corrosion protection effectiveness, during the service life [15]. The lifetime of the paints is accurately and correctly estimated by field exposure wherein the testing and application conditions are equally reproduced [16]. Nevertheless, field exposure tests may last for several years before a reasonable conclusion could be drawn and for research and development purposes there is the need to obtain the outcomes in shorter period of time. With this purpose, accelerated laboratory tests were developed however, accelerated tests consider a limited number of parameters with respect to field test. Thus, it not often suitable to find a correlation between field and accelerated tests [17]. In corrosion science for instance, several studies were dedicated to comprehend the degradation mechanisms of polymer coated metals either as function of accelerated laboratory or field exposure tests focusing on the loss of anticorrosive protection efficiency of the paint [18,19]. Similarly, in paints technology there is a growing interest to assess the visual aspects durability of coated materials as function of accelerated tests [1,20–22]. On the other hand, up to the best of our knowledge, there is the need to investigate the visual aspects stability and applicability of waterborne paints as function of field exposure.

The color itself is the factor that predominates on the visual aspects delivered by a colored object or surfaces. Many fields of science are concerned to the color theory and to visual aspects of colored objects thus, research is conducted in order to advance knowledge on this subject. In this context, color measurements appear as a powerful tool to quantify the color perception of a random object and the CIE (*Commission Internationale de l'Eclairage*, 1976) adopted a set of color-matching functions as an international system. As an example, for architecture and interior design purposes color measurements were used to explore the influence of color and surface finishing on the perceived warmth delivered by an indoor wall [23]. Likewise, in forensic science color measures were used in a proposed methodology to shorter the time of identification of vehicles involved in a car accident [24].

Acrylic waterborne coatings are commonly used in the retail decorative market, industrial and building coatings [25]. Generally, in the case of styrene-acrylic co-polymers, the monomer styrene substitutes the metyl-meta-acrylate (MMA) in the copolymer in order to increase the glass transition temperature (Tg) as well as to reduce the costs of the formulation. On the other side, the presence of styrene renders the film more susceptible UV radiation, consequently, yellowing effect of this polymer is usually observed. Therefore, styrene-acrylic painted items for outdoor applications are prone to photo-oxidation induced by the solar radiation. The photo-oxidation process can be described as a series of reactions taking place in the polymer chain from the rupture of double bonds leading to the embrittlement, discoloring and eventually crack formation on the film surface [20,26].

In this context, this work assessed the visual aspects stability of colored styrene-acrylic painted steel panels and their changes as function of field exposure in the alpine climate of Trento, northern of Italy. Accelerated UV.B test was likewise conducted on extremely low humidity in the chamber in order to simulate the effects of ultraviolet radiation. The color pigments selected were based on $TiO_{2,}$ carbon black and organic compounds to deliver respectively white, black and red visual aspects to the steel coated panels. Attention was given to the effect of the pigment concentration on the color perception of each pigmented steel panel and their stability as function of field and accelerated exposure. The surface aspects and photochemical changes of the steel painted panels were likewise considered to understand the stability, applicability and degradation mechanisms of the paints. Up to the best of our knowledge, there is limited the information available in the literature concerning the color perception changes of paints as function of field exposure. Therefore, there is the need to better investigate the changes on the color perception, i.e. focusing on the color coordinates modifications, of polymer coated metals exposed to the outdoor environment. The objectives to be covered by this work were motivated by this lack of information.

2. Experimental

2.1 Materials

The materials used in this work are commercial products and have been supplied by Berkem S.r.l. (Padova - Italy); water based styrene-acrylic binder (CATAFOR 400 H), glass transition temperature (T_g) near 95 °C. The concentrated pigments solutions were: red (CATAFOR 502XC), white (CATAFOR 511XC) and black pigments (CATAFOR 506XC). The red pigmented solution was based on organic compounds whereas the white and the black contained TiO_2 and carbon black, respectively.

2.2 Paint application

Application of the paints onto steel panels was done by means cataphoresis (cathodic electrodeposition). The cataphoresis bath consisted in the dissolution of the binder into distilled water and the final volume of the bath has been set to 1.5 L. The ratio between the working and anode areas was 1:1. The bath solid content was 10.0 %, the pH was found near 4 and the ionic conductivity near 0.40 mS/cm. During coatings preparation, these parameters were continuously monitored and kept constant for all the depositions. Cold rolled steel from Q-Panel with dimensions of 70 x 70 x 15 mm and AISI 316 stainless steel were used as cathode and anode electrodes, respectively.

Before coatings deposition the steel panels were degreased with ultra-sonication in presence of acetone, later chemical etching with 1.8 M of H_2SO_4 solution during 1 minute for impurities and contaminants removal, rinsed in distilled water and dried by air flow. The cathodic electrodeposition parameters were 50 Volts and 120 seconds. After the deposition, the coated panels were given a thermal treatment at 140° C for the duration of 30 minutes.

The specimens produced and studied in this work involved the styrene-acrylic binder containing three different color pigments at three levels of concentration: red, white and black; 0.5, 1.0 and 1.5 wt. %. From this point forward, the term *clear coat* denotes the unpigmented styrene-acrylic coated steel panels. The clear coat was used as a reference.

2.3 Testing

Field exposure was conducted in the alpine climate of Trento, northern of Italy (46.0681429 N, 11.1499069 E), from 01/Jul/2015 to 30/Jun/2016. The coated panels were exposed with 45 ° of inclination facing the south direction at an elevation of 400 meters over the sea level. During field exposure, meteorological data were continuously monitored. Temperature and relatively humidity (RH) were monitored with a data logger from Delta Ohm model HD227. Solar radiation was monitored with photo-radiometer and thermometer data logger from Delta Ohm model DO9721. The acquisitions and storing of these data occurred every 10 minutes.

The coated panels were also submitted to artificial ageing for 500 h. The samples were exposed to fluorescent UV light under controlled humidity and temperature in the chamber. The light source was UV.B fluorescent lamps with peak intensity near 313 nm and the total energy in the chamber was near 600 W/m^2. The relatively humidity (RH) in the chamber was extremely low and the test was arranged following the ASTM-G154-06 standard [27].

2.4 Paints evaluation

The coating thickness was measured by PHYNIX equipment, model Surfix® FN following the ASTM D6132−13 standard [28].

The measurements of color perception were carried out using the spectrophotometer CM-2600d from Konica Minolta. The measurements were collected using a D65 illuminant with observer at 10° and aperture diameter of 3 mm. These are in accordance to the CIEL*a*b* color space system and in agreement to the ASTM E805 standard [29]. This method comprises three coordinates that constitute the color space system: *L**, *a** and *b** and precise information on the color perception, such as hue, lightness and saturation can be obtained. Precisely, L^* specifies lightness whereas the chromaticity is given by the coordinates a^* and b^*. For instance, changes from –L* to +L* values mean modifications from darker to a brighter aspects. In the same way, a^* and b^* coordinates indicate color directions: $+a^*$ goes to the red and $-a^*$ goes to the green direction. The $+b^*$ goes to the yellow and $-b^*$ goes to the blue direction. Additionally, the total color variation ($\Delta E^*_{a^*b^*}$) can be estimated using the equation:

$$\Delta \mathrm{E}^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad \text{Eq. (1)}$$

For the acquisitions of the color coordinates the SCE (Specular Component Excluded) instrument's measurement mode has been selected. Thus, during the course of the field and accelerated tests any possible modifications of the paints surface, such as roughness or texture, would be a factor of influence on the color coordinates and the ''true'' appearance of the coated panels is measured.

Changes the surface aspects of painted panels were estimated by monitoring the gloss. Gloss measurements were conducted with a Picogloss 20°-60°-85° model 503 Erichsen Glossmeter according to the ASTM D523 standard [30]. The gloss at 60° angle was considered. The measuring area of the glossmeter was: 10 x 15 mm. In this work both gloss and color data reported are representative of an average of 10 acquisitions on each sample.

The chemical information and modifications of the paints have been assessed by FT-IR (Fourier Transformed Infrared) spectroscopy. Measurements were carried out using Varian 4100 FTIR (Excalibur series) in reflectance mode with a resolution of 4 cm^{-1} and spectra wavenumber range between 4000 – 500 cm^{-1}.

3. RESULTS AND DISCUSSION

The dry film thickness (d.f.t.) values of the steel coated panels are given in Table 1. The clear coat and all the pigmented paints obtained significantly similar d.f.t values; average was found near 22 µm independent on the type or concentration of pigment.

Table 1 - Dry film thickness for the electrophoretic paints.

		Dry film thickness [µm]		
Clear coat	Colored paints	0.5 wt. %	1.0 wt. %	1.5 wt. %
21.2 ± 1.2	White	22.0 ± 0.8	21.9 ± 1.6	22.0 ± 2.0
	Red	22.8 ± 1.2	22.8 ± 1.6	22.7 ± 2.2
	Black	21.7 ± 1.5	22.2 ± 1.1	21.9 ± 1.6

Weathering data

The stack plot showed in Fig. 1 displays the meteorological data acquired during the tested period and the information can be interpreted as follows: the columns on the upper graph show the monthly solar radiation (left axis) in the UV frequency range alongside the cumulative irradiance (right axis); in the middle graph, the maximum, the minimum and the mean temperatures for each month are reported. Lastly, the columns in the lower graph bring the monthly (left axis) and the cumulative (right axis) amount of hours in which the coated panels were found at two specific combinations of temperature and relativity humidity: i) RH ≥ 80 % and T > 0 °C or else ii) RH < 30 % and T > 20 °C. The first condition denotes the time of wetness (TOW_{ISO}) according to the standard ISO 9223, where vapor condensation onto the surface of the panels is favored leading to ingress of water into the coatings, i.e. water uptake phenomenon. Condition ii) describes a combination of low humidity and high temperature that induces the diffused water into the coatings to evaporate [19,31].

In Fig. 1, the incident monthly solar radiation and the temperatures were expected according the seasons of the solar year; higher in the initial and final periods, lower in the intermediate months. After one year of testing, the cumulative irradiance was 4700 MJ/m^2 whereas the temperature difference between maximum and minimum, which provides basis on the thermal expansion and shrinkage of the coated panels, was found close to 20 °C all over the field exposure. In the period comprised between August 2015 and February 2016 there was a considerable majority number of hours of TOW_{ISO} with respect to evaporation conditions. After one year of testing, the total numbers of TOW_{ISO} was approximately 4 times higher than the number of hours of evaporation condition.

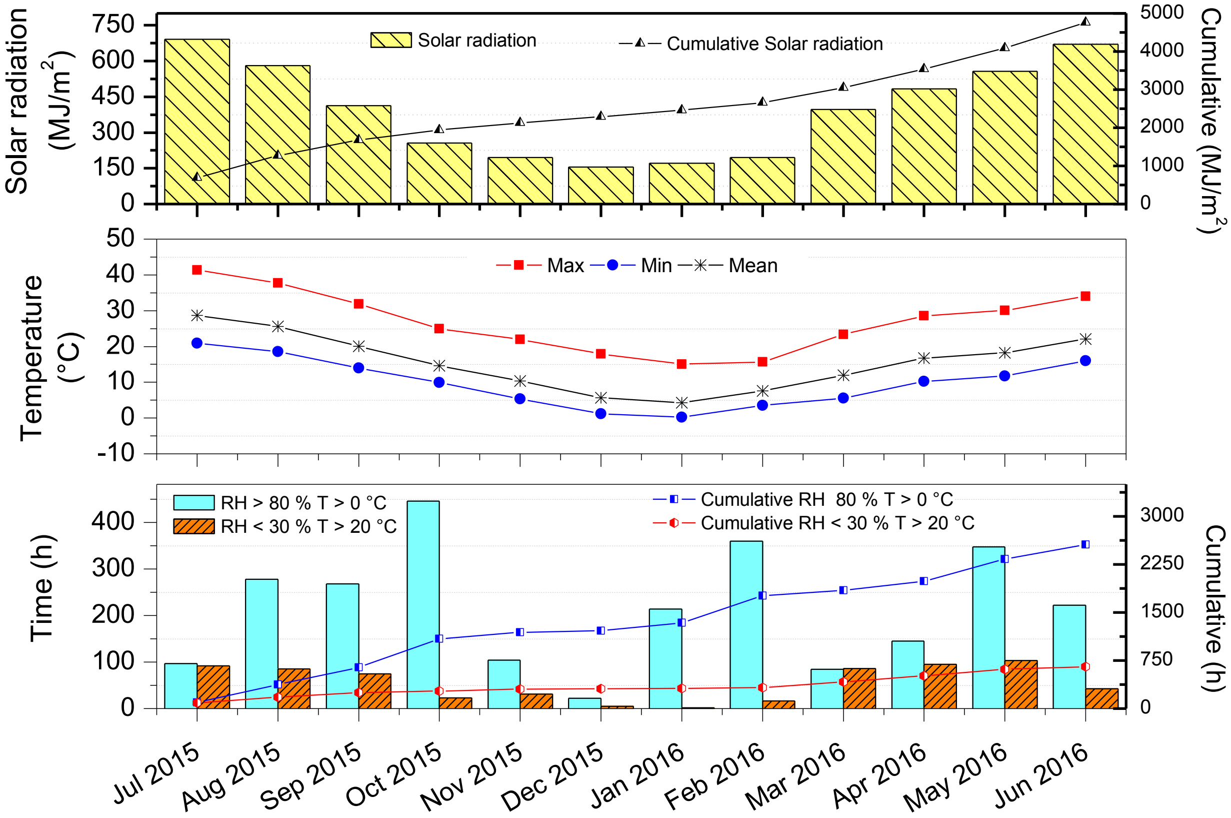

Figure 1 – Weathering data of Trento from 01/Jul/2015 to 30/Jun/2016. Upper plot: monthly solar irradiation (left axis) and cumulative solar irradiation (right axis); Middle plot: maximum, minimum and mean temperatures; in the lower plot: the total number of hours of each combination of RH and temperature: monthly hours (left axis) and cumulative (right axis).

Paints evaluation

The evolution of the total color variation ($\Delta E^*_{a^*b^*}$) as function of field exposure for all the coated panels is shown in Fig. 2. In terms of total color variation, a general trend for all the coated panels is seen; there was an increase on the $\Delta E^*_{a^*b^*}$ in the first 45-90 days. Afterwards, in the period comprised between the 90th and he 270th day of field exposure there was a deceleration on the increasing rates of $\Delta E^*_{a^*b^*}$, in some cases the values were even reduced, followed by another increase from the 270th day up to the end of the test. After one year of field exposure, the major color variations were observed for the red colored coated panels where total color was found near 35. For the black and white paints, the final $\Delta E^*_{a^*b^*}$ was 13 and 3, respectively. Next, the cumulative solar radiation (right axis in Fig. 2) throughout field exposure is recalled and superimposed to the evolution of $\Delta E^*_{a^*b^*}$. In the first 45-90 days, the cumulative solar radiation is quickly increased due to the summer season in the northern hemisphere.

In the same period of time, it is noticed major modifications on the total color evolution where the values of were $\Delta E^*_{a^*b^*}$ were moved towards higher values.

To better comprehend the color aspects changes, $\Delta E^*_{a^*b^*}$ has been split into the three coordinates of CIE system. Fig. 3 gives the CIEL*a*b* color space diagram where the color coordinates at initial condition and after one year field exposure are compared.

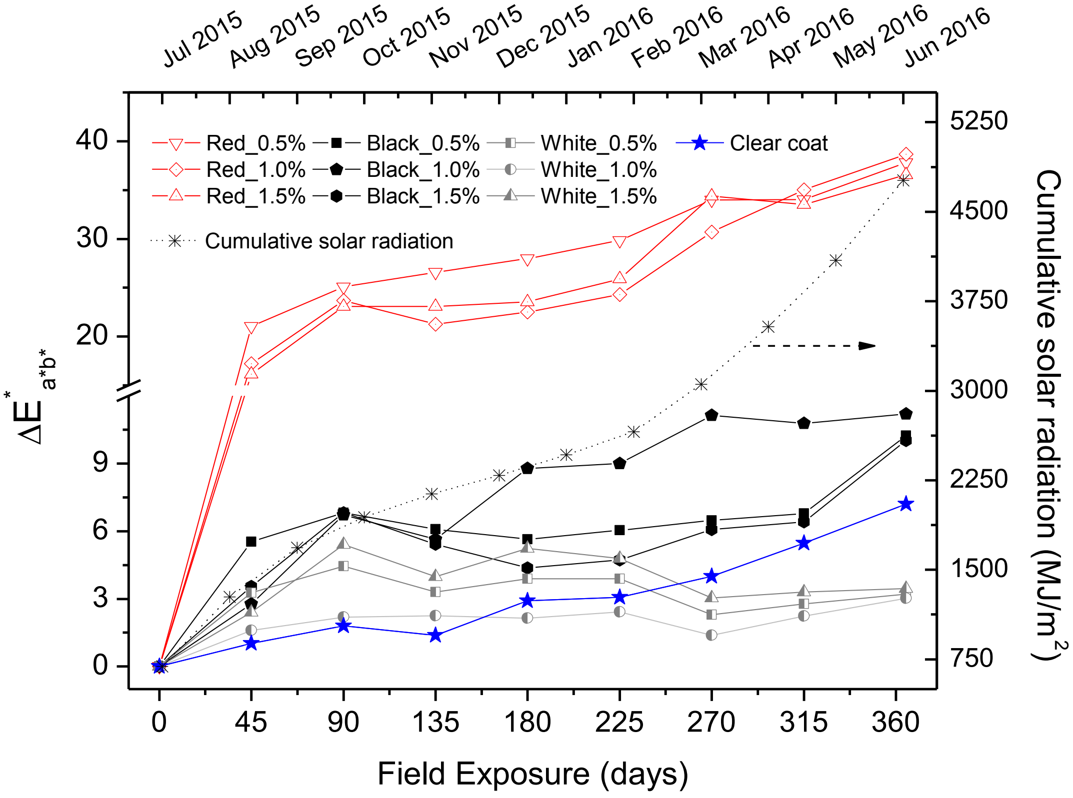

Figure 2 – Evolution of ΔE for all the paint systems in function of field exposure (left axis). Cumulative solar radiation during field exposure (right axis).

Before field exposure, the incorporation red color pigment modified both lightness and chromaticity aspects of the red colored paints; higher the red pigment concentration, higher the values of L*, a* and b*. In the case of the white pigmented coated panels, the incorporation of pigment provided brighter aspects for the paints, higher L* values were detected for higher quantities of white pigment whereas the a* and b* coordinates were not significantly altered. For the black pigmented paints, the incorporation of different quantities of pigment promoted slight modifications on chromaticity and lightness; the color aspects saturation of these panels were reached with 1.0 wt. % of black pigment solution.

After one year of field exposure, changes in the colored panels can be described as follows: the red pigmented panels became slightly darker, the L* was moved towards lower values, while chromaticity was greatly modified; there was reduction of the red perception since a* coordinate was shifted towards green and b* coordinate was moved in the direction of blue. The black pigmented paints lost their blackness aspects, all the black pigmented paints turned out to be brighter while minor changes were detected for a* and b* coordinates. Slight changes occurred for the white pigmented paints; the coordinate b* was moved towards higher values, a yellowing effect was observed.

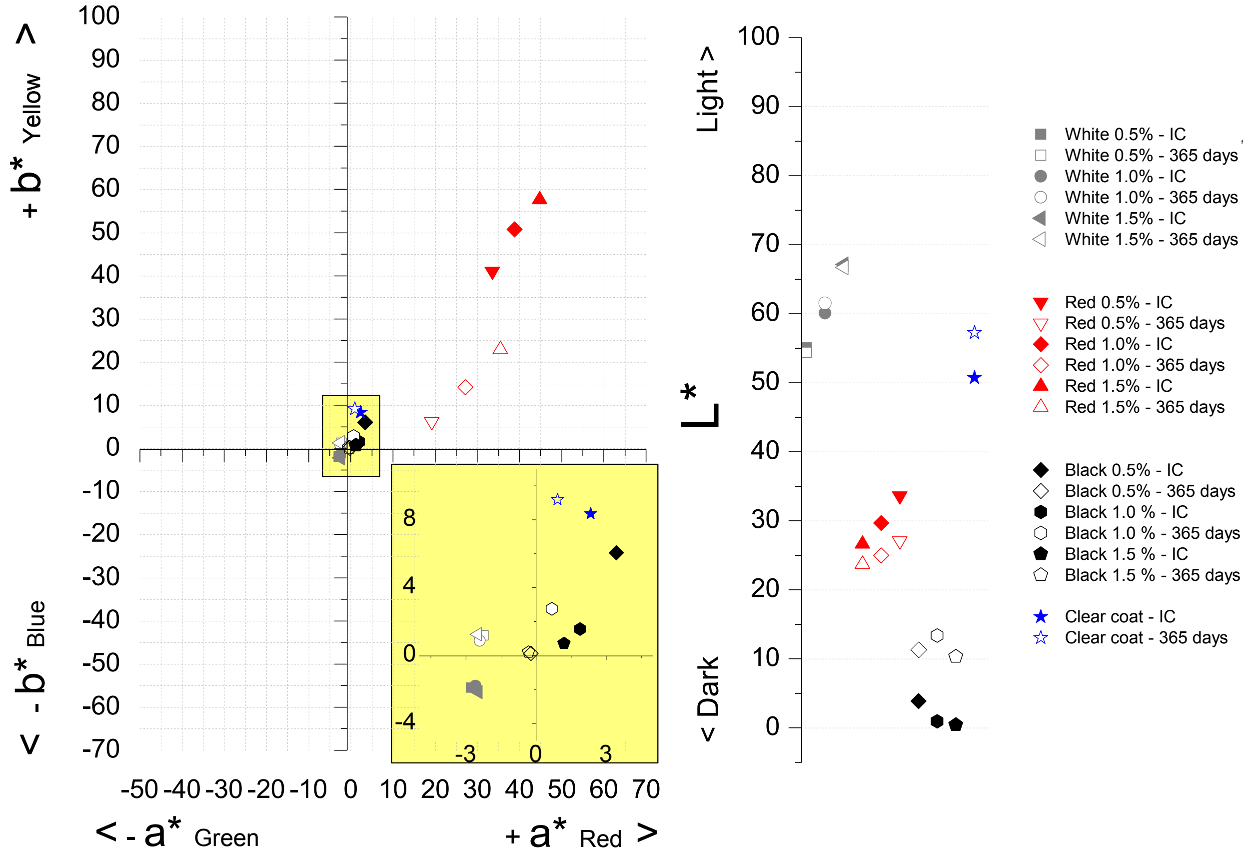

Figure 3 – CIEL*a*b* color space diagram of pigmented coated panels: initial condition (solid symbols) and after one year of field exposure (open symbols).

In addition to Fig. 3, the Tables A.1 - A.4 in the Appendix show the evolution of each the coordinates for all the coated panels as function of field exposure. Accordingly, over one year of field exposure the L* for the white and red pigmented paints fluctuated as follows: the values of L* were reduced in the first 45 days. Between the 45th and the 225th days there was a fluctuation the values of L*, independent on the loading content of these pigments. Later, there was a shift in the direction of L* and they were moved towards higher values. In the case of the black pigmented paints, the L* was increased in the first 90 days, reduced between the 90th and 225th and then increased again up to the end of the test.

With the purpose of investigating the color variation of the coated panels, the samples were likewise aged in the UV.B chamber. It is important to remember that humidity in the chamber remained extremely low in this experiment, therefore the modifications on the coated panels were exclusively a contribution of ultraviolet radiation. The $\Delta E^*_{a^*b^*}$ of the coated panels versus exposure to the UV.B radiation is shown in Fig. 4. There was a gradual increase of $\Delta E^*_{a^*b^*}$ for the white pigmented paints, independent on the pigment concentration, at the end the values of $\Delta E^*_{a^*b^*}$ were found near 7. Considerable $\Delta E^*_{a^*b^*}$ modifications were observed for the red and black pigmented paints. For these two sets of coated panels a common trend is seen; the lower the concentration of pigment in the paint system the lower was the color perception variation. For example, the final $\Delta E^*_{a^*b^*}$ observed for the paints containing 0.5, 1.0 and 1.5 wt. % of black pigment was 14, 19 and 22, respectively whereas for red pigmented paints the $\Delta E^*_{a^*b^*}$ was found near 29, 34 and 38 for the respective loading content. Besides that, the trends of the $\Delta E^*_{a^*b^*}$ as function of UV ageing did not show fluctuations during accelerated test, the total color variation were continuously moved towards to higher values. These evolutions differ from those of field exposure (Fig. 2) where $\Delta E^*_{a^*b^*}$ fluctuated in the intermediates months.

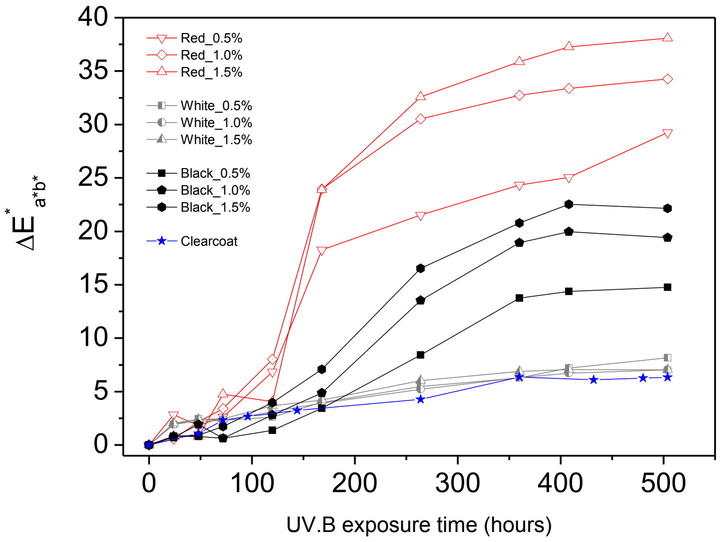

Figure 4 - Evolution of ΔE for all the paint systems in function of exposure time to UV.B radiation.

Fig. 5 brings the CIEL$^*_{a^*b^*}$ color space diagram where the color coordinates of the coated panels at initial condition and after 500 h of ultraviolet ageing are compared. The Tables A.1 – A.4 in the Appendix show the evolution of each color coordinate as function of ultraviolet exposure. During exposure to the ultraviolet radiation, the lightness of the clear coat as well as the white and red pigmented paints was not significantly modified. Therefore, the color changes of these panels were verified accordingly: for the red pigmented paints both coordinates a* and b* were reduced. For the white pigmented paints b* was continuously moved towards the yellow direction independent on the loading content of pigment while a* remained constant. In general, for these paints the modifications on chromaticity as function of UV ageing was as similar as those observed during field exposure however the L* coordinate evolved differently. For the black pigmented coatings during exposure to the ultraviolet radiation the major changes occurred on the lightness aspects; the L* coordinate was moved in the direction of brighter aspects and this was correspondingly observed in the field exposure. The decay on the darkness can be interpreted as loss of efficacy of the black pigments themselves to deliver the black color perception to the coated panels.

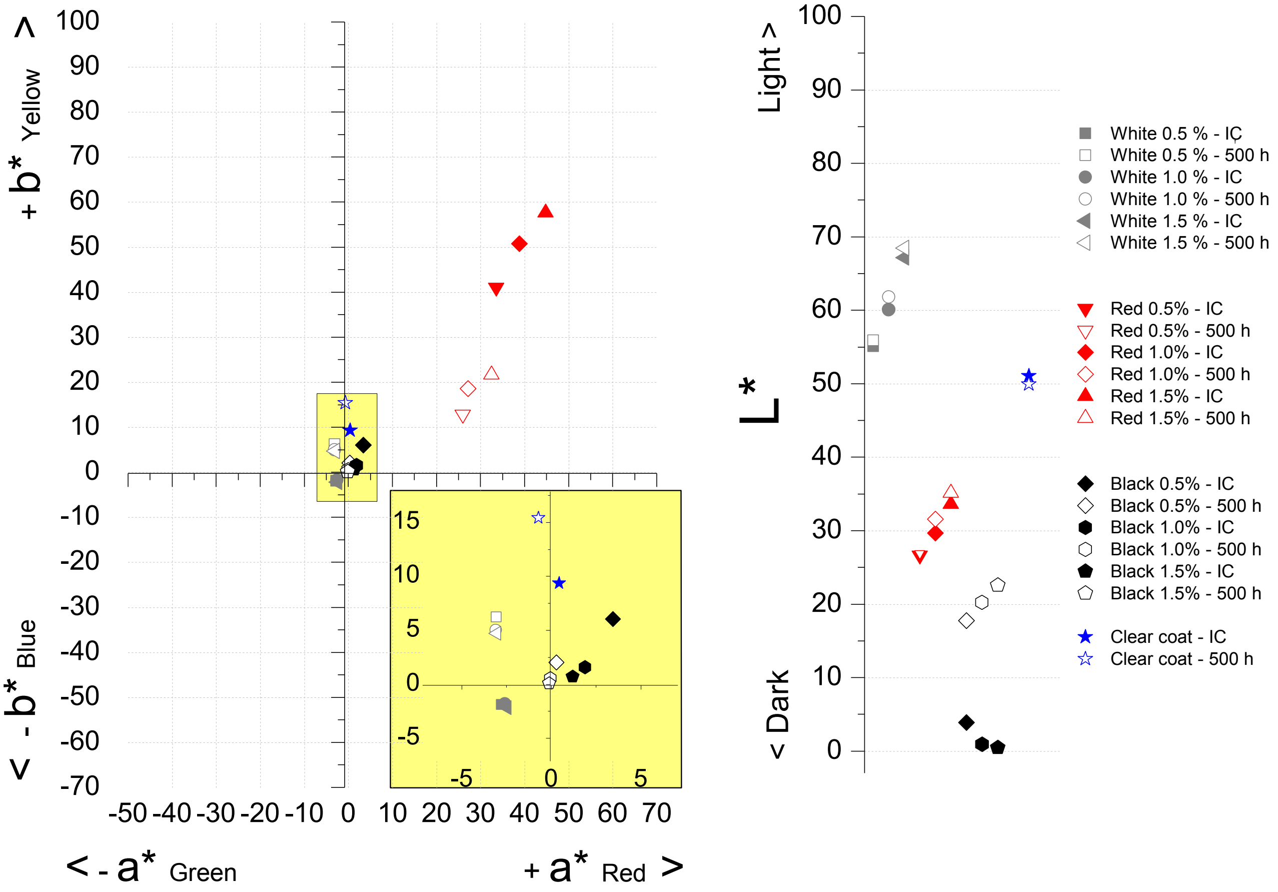

Figure 5 - CIEL*a*b* color space diagram of pigmented coated panels: initial condition (solid symbols) and after 500 hours of UV.B (open symbols).

Next, the two stack plots given in Fig. 6 show the evolution of gloss at 60° of specular reflection for the pigmented paints as function of field exposure (left stack plot) and accelerated UV.B (right stack plot). Initial gloss values were observed near 95 for all the paints systems. During field exposure, there was loss in gloss wherein the faster gloss decay is seen in two well-defined periods of the year; from the beginning until the 90th day and from the 225th day onwards. In a different way, in the period comprised between Sep/Oct 2015 to Feb/Mar 2016 the gloss reduction rates were attenuated. On the right stack plot, the variations on gloss as function of UV.B exposure can be described as follows: during the first 72 h the values have not been significantly modified. Afterwards, there was a reduction wherein the higher the pigment concentration the faster was the gloss decay. From the 400th hour up to the end of the test the values of gloss were slightly modified.

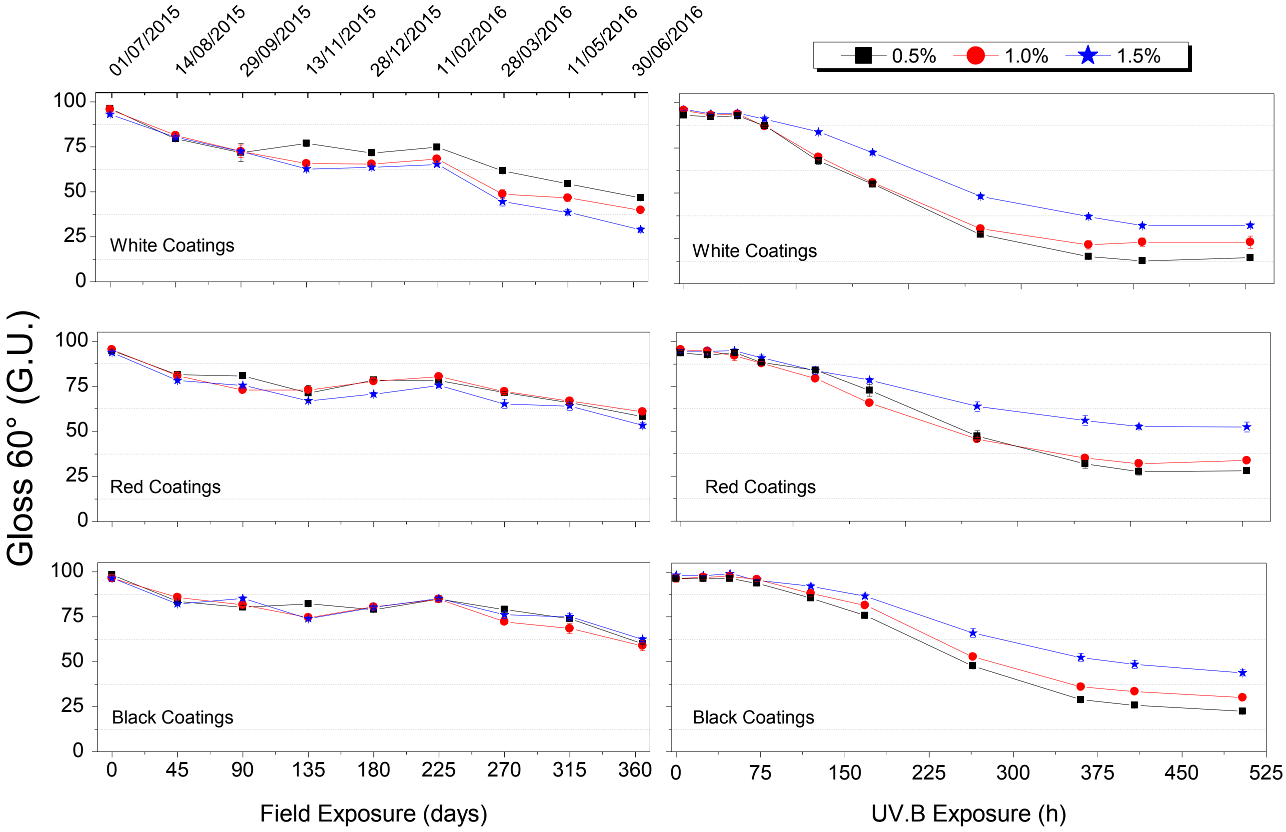

Figure 6 – Evolution of specular gloss at 60° in the course of field exposure (left stack plot) and accelerated UV.B (right stack plot).

The gloss can be attributed to surface aspects of the painted panels, such as the roughness [32]. Changes on surfaces aspects of paints, e.g. rougher surfaces or higher surfaces texture, increase the scattering of the reflected light and lower gloss ratings are expected to be measured [33,34]. In this way, the equivalent initial gloss 60° for all the pigmented paints indicates that the cathodic electrodeposition produced colored coated panels with significant homogeneous surface finishing; a relatively good incorporation and dispersion of these pigments into the styrene-acrylic binder were obtained, independent on the type and loading content of each pigment. The later reduction on the gloss ratings suggested that surface aspects of the paints were altered.

Matching the evolutions of $\Delta E^*_{a^*b^*}$ and gloss with the weathering data depicted in Fig.1, on the whole, during one solar year of field exposure the greater changes on color perception and gloss were appreciated in two well-defined periods of the year, from the beginning up to the 90th day and from the 225th day onwards, which are the months with higher solar irradiance. In the intermediate months, from Sep-Oct/15 to Feb-Mar/16, there was an oscillation on the values of total color variation mainly caused by a fluctuation of L* and the gloss reduction rates were attenuated. During concurrent period of time, despite the reduction of the solar irradiance due to the seasons of the year in the northern hemisphere, there was a predominance of TOW_{ISO} condition and, in particular, these meteorological conditions favored the water condensation over the paints leading to water uptake. In other words, in the period comprised between Sep-Oct/15 to Feb-Mar/16 the amount of water into the paints was probably increased. Therefore, the changes in total color perception, i.e. lighter aspects, as well as the variations on the surface aspects, i.e. lowering of gloss reduction rates, can be related with an eventual increase on the amount water into the paints. This correlation is supported by the outcomes of accelerated ultraviolet test; upon accelerated UV.B aging conducted in dry condition neither fluctuations on the L* nor attenuation on the gloss reduction rates were detected.

Confronting the outcomes of field and accelerated exposure, on the whole, the accelerated ageing test evidenced the effect of the color pigment concentration on the stability of the painted panels. With respect to the field exposure test equivalent information was obtained in much shorter period of time, the magnitudes of the variations observed after one year of natural ageing can be linked to approximately 250 hours of exposition to UV.B lamps. It is certainly a relation which fits for the colored styrene-acrylic paints produced in this study and aged in the exposure site of Trento.

In Fig. 7 the FT-IR spectra for the clear styrene-acrylic paint at initial condition as well as after field and UV.B radiation ageing are shown. The lower graph in Fig. 7 highlights the fingerprint zone where the main absorption peaks certified the co-polymer styrene-acrylic coating and are described as follows: in the higher wavenumbers C-H aliphatic stretching around 2958, 2920, 2866 cm^{-1}. The strong peaks around 1490 and 1445 cm^{-1} and that near 910 cm^{-1} are attributed to the aromatic C-C skeletal ring and 4 adjacent H out-of-plane absorptions of the benzene ring, respectively. The absorption peaks detected near 1726, 1689, are assigned to C=O bond. The peaks detected near 1601 and 1152 cm^{-1} are respectively attributed to the stretching vibration mode C=C, and C-O-C bonds [3].

The spectra recorded after field and UV.B exposure revealed changes on the chemical structure of the polymer coating. The previous peaks detected around 1726 and 1689 cm^{-1} were fused and broadened and there was a broadening of C=O and C-O-C absorption peaks. These changes indicate the decomposition of the carbonyl group, the formation of oxidation products such as ketones, aldehydes or esters with the sub-sequent formation of new compounds [35]. The absorptions peaks near 1490, 1445 and 910 cm^{-1} were vanished suggesting the development of phenyl ring opening reactions. Such reactions were observed elsewhere and are linked to a yellowing effect of the unpigmented styrene-acrylic paint [1].

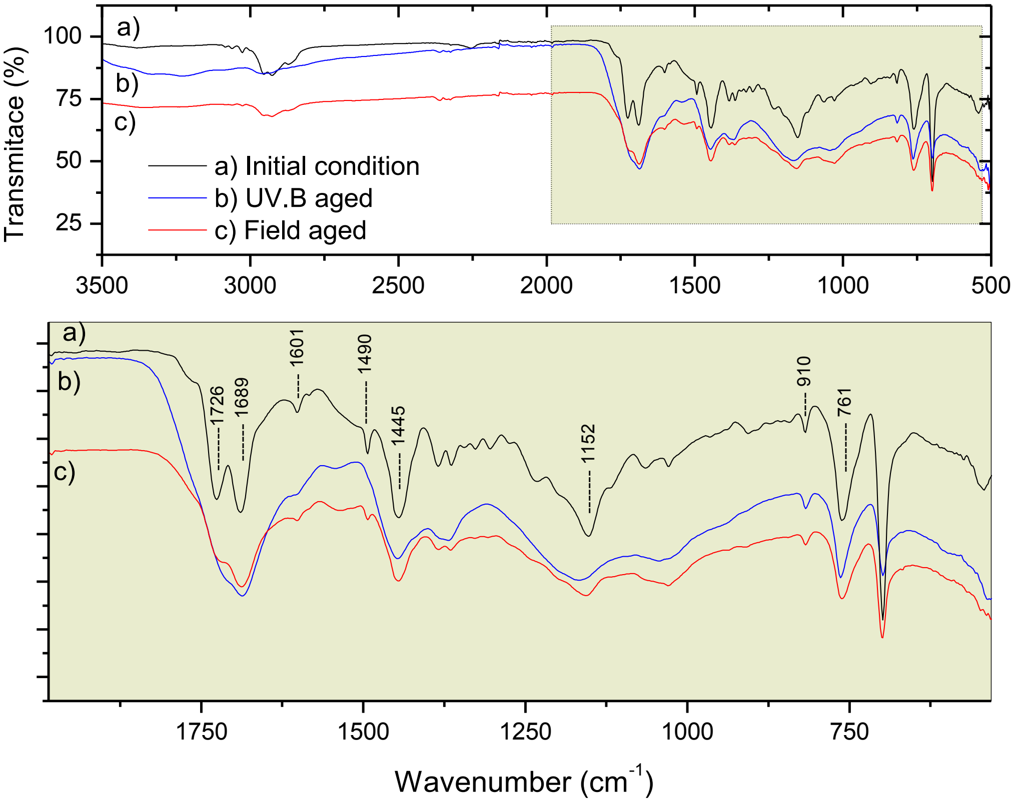

Figure 7 – FT-IR spectra with highlighted fingerprint zone for the clear acrylic coating before testing (a), UV.B aged (b) and natural aged (c).

Next, the reflectance FT-IR spectra of the pigmented coatings before testing and after accelerated and field exposure is shown on the stack plot displayed in Fig. 8. The spectra depicted in Fig. 8 were recorded for the pigmented coatings with 1.5 wt. % of each color pigment. The aged reflectance spectra for the black and the white pigmented coating was found equivalent to the clear styrene-acrylic after exposure to UV.B. Therefore, the photo degradation reactions developed described for the unpigmented coating are equivalent proposed to the white pigmented coating. In the case of the red pigmented paint, after 500 h there were the new absorption peaks near 1545 cm^{-1} alongside a slight absorption shoulder around 1712 cm^{-1}. These can be attributed to the degradation of the red pigment and subsequent formation of new compounds. The outcomes from FT-IR analysis identified the photochemical degradation reactions of the clear styrene-acrylic paint, such as the opening of benzene ring and decomposition of the carbonyl group and subsequent formation of new compounds. These effects were more pronounced after UV.B radiation test and comparable reactions were seen for the pigmented coatings which suggest that the matrix of the colored paints developed similar degradation processes.

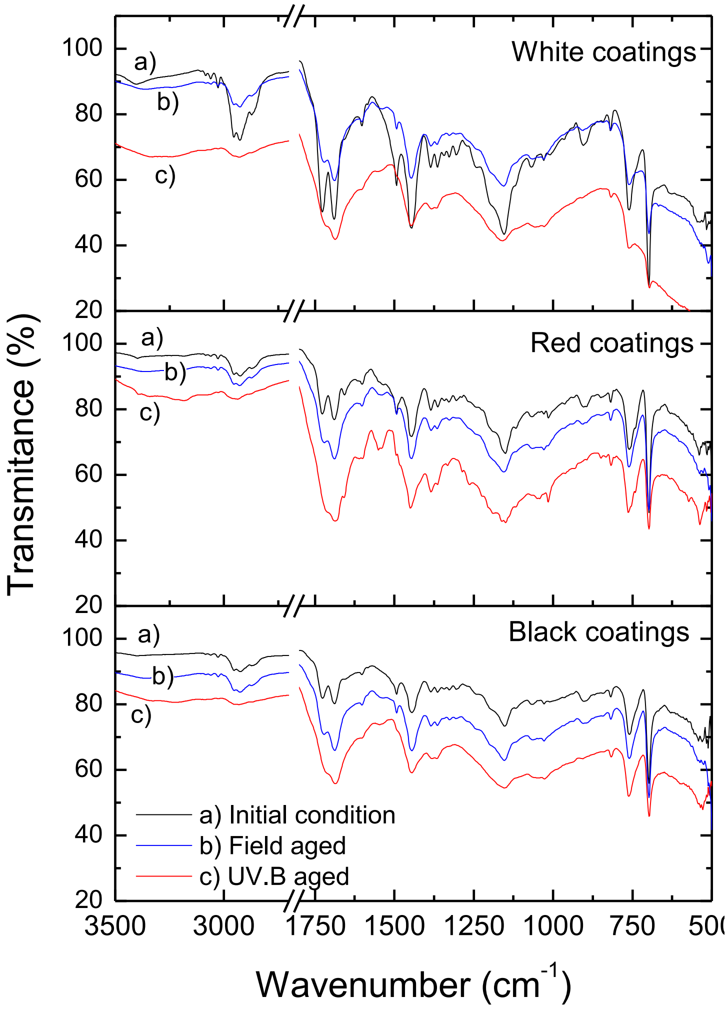

Figure 8 - FT-IR spectra of the 1.5 % pigmented acrylic coatings before testing (a), after field exposure (b) and after UV.B exposure (c).

The above observations provided basis in the degradation mechanisms of the investigated cataphoretic colored styrene-acrylic paints. For the white pigmented paints, it is suggested a degradation of the styrene-acrylic matrix rather than the color pigment itself; before testing, the incorporation of higher amounts of white pigment concentration affected the values of L* however, after testing the modifications of these paints were detected on the coordinate b*, i.e. color perception was moved towards yellow. These changes can be attributed to the high refractive index of TiO_2 to the ultraviolet radiation. Indeed due to the inertness upon UV radiation, TiO_2 is one of the most used additives for outdoor applications [36].

For the black pigmented paints; the blackness perception for these coatings was found dependent on the addition of black pigment solution, *i.e.* values of L* close to zero, whereas chromaticity has not been given similar dependency. After testing, there was an increase on the coordinate L* indicating a loss of the black color aspects and these observations suggested degradation of the black pigment. In another study, the reactivity of carbon black as additive to epoxy coatings towards ultraviolet radiation has been investigated and its incorporation into epoxy binder improved the UV resistance [37] and corrosion protection efficiency [38] of the composite coatings. These improvements have been attributed to the ability of carbon black to absorb ultraviolet radiation and preserve the polymer matrix.

Similarly, in the cases of the red pigmented paints the changes in the color coordinates and those on the gloss ratings suggested a major degradation of the color pigment; before testing, the chromaticity aspects, *i.e*. the coordinates a* and b*, initially increased by the incorporation red pigment were significantly reduced after field exposure demonstrating the susceptibility of these pigments to the environmental atmosphere. Moreover, the gloss ratings reductions after field exposure were less intense with respect the white pigmented paints suggesting that the styrene-acrylic matrix, up to a certain extent, has been preserved. Mainly, organic pigments are attributed faster photochemical degradation rates when compared to inorganic due to the carbon-based chemical structures [39].

4- Conclusion

The color stability of waterborne styrene-acrylic paints, produced by means of cathodic electrodeposition, has been investigated as function of field exposure. The panels were naturally aged in the alpine climate of Trento, northern of Italy in the period comprised between July/2015 and June/2016. In addition, the panels were exposed to UV.B lamps in dry condition for accelerated ageing. Glossiness and chemical structure were assessed to provide complementary information.

- The initial values of gloss 60° of specular reflection were found significantly similar for all the paints independent on the type and loading of color pigment. These observations indicated that both chemical nature and weight concentration did not play a role on the initial surface finishing of the cathodic electrodeposited paints.

- In the months with predominance of time of wetness, there were a shift on the trend evolution of the total color variation and a deceleration on the gloss reduction rates. These observations are attributed to the ingress of water from the atmosphere into the paints which turned them out to be brighter and modified the surface texture of the paints. Such observations were not detected throughout the accelerated test.

- With regard to the color stability; for the white pigmented paints the changes on the color coordinates were due to degradation of the styrene-acrylic matrix rather than the white color pigment itself. Only for the white paints the changes were less intense when compared to the clear styrene-acrylic coat. In a different way, the changes in the color coordinates for the red and black pigmented paints indicated higher degradation of the color pigments rather than the polymer matrix.

- By means of accelerated UV.B test it was possible to rank the different pigments used in this work. This experimental approach, appropriately evidenced the influence of the pigment concentration on total color variation and gloss reduction ratings of the paints whereas, through the field exposure the paints stability is similar appreciated but remained limited only to type of pigment. In these cases, the higher the pigment loading concentration in the paints, the higher was the total color variation as well as the gloss retention.

- Considering the paints produced in this work as well as the environmental and accelerated ageing conditions, the variations on gloss suggested that one year of field exposure in Trento corresponds to approximately 250 hours of exposition to UV.B lamps in dry condition.

Acknowledgements

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APPENDIX

Table A.1 – Evolution of the color coordinates as function of field and accelerated exposure for the white pigmented paints.

White pigmented coatings

Field Exposure (days)	0.5 %			1.0 %			1.5 %		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	55.1 ± 0.4	-2.7 ± 0.1	-1.9 ± 0.2	60.1 ± 0.4	-2.6 ± 0.1	-1.8 ± 0.4	67.1 ± 0.4	-2.5 ± 0.1	-2.2 ± 0.4
45	51.8 ± 0.5	-2.6 ± 0.0	-2.4 ± 0.2	58.6 ± 0.3	-2.7 ± 0.1	-1.1 ± 0.3	65.1 ± 0.5	-2.7 ± 0.5	-0.9 ± 0.3
90	50.6 ± 0.3	-2.5 ± 0.0	-1.7 ± 0.4	58.2 ± 0.3	-2.6 ± 0.1	-0.6 ± 0.4	65.0 ± 0.5	-0.1 ± 0.1	2.2 ± 0.4
135	52.5 ± 0.2	-2.4 ± 0.1	0.1 ± 0.1	57.5 ± 0.9	-2.3 ± 0.1	0.4 ± 0.3	64.5 ± 0.3	-2.5 ± 0.0	0.9 ± 0.3
180	51.9 ± 0.2	-2.4 ± 0.0	0.3 ± 0.2	57.2 ± 0.7	-2.3 ± 0.1	0.2 ± 0.3	62.9 ± 0.2	-2.5 ± 0.0	0.8 ± 0.3
225	51.9 ± 0.2	-2.4 ± 0.1	0.4 ± 0.2	56.1 ± 0.5	-2.3 ± 0.0	0.4 ± 0.3	63.7 ± 0.4	-2.5 ± 0.0	1.1 ± 0.3
270	54.1 ± 0.3	-2.5 ± 0.0	0.1 ± 0.6	60.4 ± 1.5	-2.4 ± 0.4	-0.5 ± 0.4	66.3 ± 0.1	-2.5 ± 0.1	0.7 ± 0.5
315	53.7 ± 0.2	-2.4 ± 0.1	0.4 ± 0.7	60.9 ± 0.1	-2.4 ± 0.1	0.3 ± 0.4	66.4 ± 0.1	-2.6 ± 0.1	1.0 ± 0.2
365	54.4 ± 0.0	-2.2 ± 0.0	1.2 ± 0.1	61.5 ± 0.7	-2.4 ± 0.0	0.8 ± 0.1	66.7 ± 0.4	-2.5 ± 0.0	1.2 ± 0.0

UV.B Exposure (h)	0.5 %			1.0 %			1.5 %		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	55.0 ± 0.4	-2.7 ± 0.0	-1.9 ± 0.2	60.1 ± 0.4	-2.6 ± 0.1	-1.8 ± 0.4	67.1 ± 0.3	-2.4 ± 0.1	-2.1 ± 0.4
24	54.5 ± 0.4	-2.0 ± 0.1	-0.2 ± 0.3	59.4 ± 0.2	-2.1 ± 0.14	0.3 ± 0.6	66.9 ± 0.7	-2.0 ± 0.2	-0.2 ± 0.7
48	54.0 ± 0.4	-1.9 ± 0.1	0.2 ± 0.3	59.3 ± 0.6	-2.1 ± 0.15	0.3 ± 0.6	66.7 ± 0.6	-2.0 ± 0.12	0.2 ± 0.8
72	54.1 ± 0.6	-2.1 ± 0.1	0.1 ± 0.3	59.5 ± 0.1	-2.2 ± 0.13	0.3 ± 0.4	66.6 ± 0.1	-2.1 ± 0.1	0.2 ± 0.6
120	54.2 ± 0.3	-2.1 ± 0.1	0.5 ± 0.3	59.9 ± 0.3	-2.1 ± 0.16	1.3 ± 0.5	67.3 ± 0.8	-1.9 ± 0.2	1.4 ± 0.7
168	55.0 ± 0.2	-2.8 ± 0.0	2.8 ± 0.1	60.9 ± 0.4	-2.9 ± 0.02	2.03 ± 0.2	67.6 ± 0.4	-2.8 ± 0.0	2.0 ± 0.5
264	55.9 ± 0.5	-2.9 ± 0.0	3.5 ± 0.5	62.1 ± 0.3	-3.1 ± 0.1	3.0 ± 0.1	68.5 ± 0.6	-2.9 ± 0.2	3.6 ± 0.3
360	56.6 ± 0.6	-3.0 ± 0.1	4.1 ± 0.5	61.7 ± 0.7	-3.2 ± 0.1	4.3 ± 0.2	69.3 ± 0.3	-3.2 ± 0.1	4.3 ± 0.7
408	56.5 ± 0.2	-3.1 ± 0.1	5.1 ± 0.5	62.2 ± 0.6	-3.1 ± 0.1	4.5 ± 0.2	69.3 ± 0.6	-3.0 ± 0.1	4.5 ± 0.5
504	55.9 ± 0.6	-3.0 ± 0.0	6.2 ± 0.4	61.8 ± 0.9	-3.1 ± 0.1	5.0 ± 0.5	68.4 ± 0.5	-3.0 ± 0.0	4.7 ± 0.2

Table A.2 - Evolution of the color coordinates as function of field and accelerated exposure for the red pigmented paints.

	Red pigmented coatings								
Field Exposure (days)	0.5 %			1.0 %			1.5 %		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	26.6 ± 0.2	33.6 ± 0.5	41.0 ± 1.1	29.6 ± 0.2	38.8 ± 0.5	50.7 ± 0.4	33.6 ± 0.1	44.7 ± 0.2	57.6 ± 0.2
45	19.3 ± 0.3	28.7 ± 0.3	21.9 ± 0.9	23.3 ± 0.1	37.8 ± 0.1	34.7 ± 0.1	26.2 ± 0.4	44.4 ± 0.7	43.3 ± 0.7
90	19.7 ± 0.1	26.2 ± 0.1	18.0 ± 0.6	23.4 ± 0.3	34.9 ± 0.3	28. ± 0.8	26.0 ± 0.4	41.1 ± 1.2	36.0 ± 1.6
135	21.1 ± 0.5	28.1 ± 0.5	15.6 ± 1.1	23.3 ± 0.2	36.0 ± 0.4	30.6 ± 0.8	26.2 ± 0.3	41.5 ± 0.8	36.0 ± 1.5
180	20.9 ± 0.2	27.4 ± 0.2	14.3 ± 0.9	22.9 ± 0.1	35.4 ± 0.4	29.5 ± 0.6	25.7 ± 0.2	41.3 ± 0.6	35.7 ± 1.5
225	20.8 ± 0.2	26.5 ± 0.8	12.6 ± 1.8	22.4 ± 0.2	34.9 ± 0.5	27.8 ± 0.9	25.4 ± 0.1	40.4 ± 0.7	33.4 ± 1.1
270	22.7 ± 0.5	23.2 ± 0.7	8.9 ± 0.9	24.5 ± 0.4	31.7 ± 1.0	21.2 ± 1.0	25.3 ± 0.6	36.8 ± 0.6	24.5 ± 1.1
315	22.7 ± 0.1	22.3 ± 0.2	8.1 ± 0.2	24.7 ± 0.4	29.9 ± 0.6	29.9 ± 0.6	26.8 ± 0.1	37.5 ± 0.3	25.6 ± 0.2
365	23.7 ± 0.0	19.2 ± 0.3	6.2 ± 0.1	24.9 ± 0.4	27.2 ± 0.9	14.1 ± 1.0	27.1 ± 0.1	35.5 ± 0.6	22.9 ± 0.6
UV.B Exposure (h)	0.5%			1.0%			1.5%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	26.6 ± 0.2	33.6 ± 0.5	41.1 ± 1.1	29.6 ± 0.2	38.8 ± 0.5	50.7 ± 0.4	33.6 ± 0.1	44.7 ± 0.2	57.6 ± 0.2
24	25.2 ± 0.3	32.2 ± 0.4	39.1 ± 1.2	29.5 ± 0.3	38.4 ± 0.5	50.3 ± 0.6	33.5 ± 0.1	44.1 ± 0.4	57.1 ± 0.5
48	26.2 ± 0.3	32.9 ± 0.6	39.4 ± 1.1	30.0 ± 0.5	37.6 ± 0.5	48.9 ± 1.5	33.7 ± 0.4	44.0 ± 0.5	57.2 ± 0.5
72	26.6 ± 0.1	32.9 ± 0.5	38.5 ± 1.6	30.2 ± 0.3	37.5 ± 0.1	47.6 ± 1.0	33.6 ± 0.1	43.3 ± 0.3	53.1 ± 0.8
120	27.2 ± 0.3	31.8 ± 0.8	34.5 ± 2.5	30.7 ± 0.2	36.2 ± 0.3	43.2 ± 0.0	33.8 ± 0.1	42.9 ± 0.3	54.0 ± 0.8
168	23.1 ± 0.3	31.6 ± 0.5	23.3 ± 0.3	28.6 ± 0.1	34.9 ± 0.4	27.2 ± 0.5	28.7 ± 0.2	41.9 ± 0.3	34.4 ± 0.8
264	24.7 ± 0.5	29.4 ± 1.0	20.0 ± 1.1	29.8 ± 0.2	31.0 ± 0.4	21.2 ± 0.3	31.6 ± 0.3	37.7 ± 0.2	25.9 ± 0.4
360	26.3 ± 0.5	27.4 ± 1.2	17.5 ± 1.2	30.9 ± 0.1	29.4 ± 0.4	19.3 ± 0.3	33.3 ± 1.1	35.4 ± 1.9	23.0 ± 2.2
408	26.7 ± 0.5	26.7 ± 1.1	16.9 ± 1.0	31.2 ± 0.3	28.3 ± 0.5	19.0 ± 0.1	34.0 ± 0.1	34.5 ± 0.4	21.8 ± 0.2
504	26.9 ± 0.8	25.9 ± 0.8	12.8 ± 1.4	31.5 ± 0.2	27.2 ± 0.4	18.5 ± 0.1	35.1 ± 0.2	32.4 ± 0.6	21.6 ± 0.2

Table A.3 - Evolution of the color coordinates as function of field and accelerated exposure for the black pigmented paints.

Black pigmented coatings

Field Exposure (days)	0.5 %			1.0 %			1.5 %		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	3.8 ± 0.4	3.4 ± 0.1	6.0 ± 0.5	0.9 ± 0.2	1.8 ± 0.0	1.8 ± 0.1	0.4 ± 0.1	1.2 ± 0.1	0.6 ± 0.1
45	9.0 ± 0.6	1.5 ± 0.1	6.6 ± 0.4	2.6 ± 0.6	0.3 ± 0.8	3.0 ± 0.3	3.2 ± 0.3	0.0 ± 0.1	2.5 ± 0.0
90	11.4 ± 0.1	1.1 ± 0.0	5.4 ± 0.1	7.3 ± 0.2	0.1 ± 0.0	2.8 ± 0.1	7.2 ± 0.3	-0.1 ± 0.1	2.3 ± 0.2
135	9.4 ± 0.1	1.2 ± 0.1	4.8 ± 0.1	6.2 ± 0.2	0.1 ± 0.0	1.9 ± 0.1	5.6 ± 0.3	-0.0 ± 0.0	1.7 ± 0.2
180	5.6 ± 0.2	-0.0 ± 0.0	1.9 ± 0.2	8.9 ± 0.3	1.1 ± 0.1	5.1 ± 0.2	4.4 ± 0.2	-0.1 ± 0.0	2.1 ± 0.1
225	5.2 ± 0.8	-0.1 ± 0.1	1.3 ± 0.4	9.3 ± 0.4	1.0 ± 0.1	4.5 ± 0.3	4.9 ± 0.8	-0.1 ± 0.1	1.4 ± 0.3
270	7.0 ± 0.5	-0.4 ± 0.0	1.9 ± 0.3	11.8 ± 0.6	0.6 ± 0.0	3.6 ± 0.2	5.9 ± 0.9	-0. 4± 0.1	2.6 ± 0.6
315	7.6 ± 0.1	-0.1 ± 0.4	1.6 ± 0.19	11.4 ± 0.9	0.9 ± 0.1	3.8 ± 0.7	6.6 ± 0.7	-0.3 ± 0.0	1.4 ± 0.2
365	11.3 ± 0.5	-0.2 ± 0.0	0.1 ± 0.1	13.4 ± 0.4	0.7 ± 0.1	2.7 ± 0.7	10.4 ± 1.3	-0.3 ± 0.0	0.2 ± 0.2

UV.B Exposure (h)	0.5%			1.0%			1.5%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Initial condition	3.8 ± 0.1	3.4 ± 0.1	6.0 ± 0.5	0.9 ± 0.2	1.8 ± 0.0	1.5 ± 0.5	0.4 ± 0.1	1.2 ± 0.1	0.6 ± 0.1
24	4.5 ± 0.1	3.1 ± 0.1	6.5 ± 0.3	1.3 ± 0.4	1.8 ± 0.0	2.1 ± 0.4	0.9 ± 0.1	1.3 ± 0.0	1.3 ± 0.2
48	4.5 ± 0.1	3.1 ± 0.1	6.3 ± 0.2	2.4 ± 0.4	1.7 ± 0.1	2.7 ± 0.6	0.9 ± 0.0	1.4 ± 0.1	1.4 ± 0.3
72	4.3 ± 0.1	3.1 ± 0.1	6.2 ± 0.2	1.3 ± 0.4	1.8 ± 0.1	2.0 ± 0.6	1.4 ± 0.0	1.3 ± 0.1	2.1 ± 0.3
120	5.0 ± 0.1	2.6 ± 0.2	6.0 ± 0.4	2.8 ± 0.6	1.2 ± 0.0	3.5 ± 0.1	3.8 ± 0.3	0.8 ± 0.0	2.8 ± 0.1
168	6.4 ± 0.0	1.1 ± 0.1	6.3 ± 0.5	5.1 ± 0.6	0.3 ± 0.0	3.5 ± 0.1	7.2 ± 0.6	-0.0 ± 0.0	2.3 ± 0.1
264	11.6 ± 0.1	0.4 ± 0.0	4.2 ± 0.4	14.3 ± 2.0	0.0 ± 0.2	1.2 ± 0.4	16.9 ± 1.0	0.0 ± 0.3	0.5 ± 0.3
360	16.6 ± 0.1	0.2 ± 0.0	2.0 ± 0.3	19.7 ± 0.7	-0.1 ± 0.0	0.0 ± 0.0	21.2 ± 0.7	-0.2 ± 0.0	-0.1 ± 0.0
408	17.3 ± 0.0	0.2 ± 0.0	2.0 ± 0.1	20.7 ± 0.4	-0.1 ± 0.0	0.1 ± 0.0	22.9 ± 0.4	-0.2 ± 0.0	-0.2 ± 0.0
504	17.7 ± 0.1	0.9 ± 0.0	2.0 ± 0.3	20.2 ± 0.8	-0.0 ± 0.0	0.5 ± 0.1	22.5 ± 0.4	-0.1 ± 0.0	0.0 ± 0.0

Table A.4 - Evolution of the color coordinates as function of field and accelerated exposure for the styrene-acrylic paint.

Field Exposure (days)	Clear coat		
	L*	a*	b*
Initial condition	50.7 ± 0.3	2.3 ± 0.1	8.3 ± 0.5
45	51.4 ± 0.5	2.5 ± 0.1	9.1 ± 0.4
90	52.4 ± 0.1	2.0 ± 0.0	9.0 ± 0.1
135	51.2 ± 0.1	1.2 ± 0.2	9.0 ± 0.1
180	53.2 ± 0.2	1.3 ± 0.1	9.4 ± 0.2
225	53.2 ± 0.6	0.9 ± 0.2	9.6 ± 0.4
270	53.9 ± 0.4	1.2 ± 0.1	10.5 ± 0.3
315	55.4 ± 0.2	0.8 ± 0.5	10.6 ± 0.2
365	57.3 ± 0.4	0.8 ± 0.1	11.2 ± 0.2

UV.B Exposure (h)	Clear coat		
	L*	a*	b*
Initial condition	50.3 ± 0.4	0.3 ± 0.1	8.4 ± 0.2
24	49.4 ± 0.4	0.2 ± 0.1	8.4 ± 0.1
48	47.4 ± 0.4	0.1 ± 0.1	8.9 ± 0.2
72	47.4 ± 0.2	0.0 ± 0.1	9.2 ± 0.2
120	47.3 ± 0.3	-0.1 ± 0.2	9.9 ± 0.4
168	47.5 ± 0.3	-0.5 ± 0.1	11.8 ± 0.2
264	46.9 ± 0.3	-0.7 ± 0.0	13.5 ± 0.4
360	46.9 ± 0.3	-0.8 ± 0.0	14.1 ± 0.3
408	49.3 ± 0.3	-0.8 ± 0.1	14.4 ± 0.1
504	49.4 ± 0.4	-0.9 ± 0.1	14.5 ± 0.1

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