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Efficacy of Colour Protectors in Urban Art Paintings under Different Conditions: From a Real Mural to the Laboratory

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Abstract: Contemporary muralism is one of the most widespread manifestations of urban art in cities nowadays. Loss of colour (fading) due to degradation of the pictorial materials is one of the main manifestations of deterioration in this type of artwork. However, the application of protective coatings is considered to slow down fading. In this study, two acrylic-based protective coatings were applied to selected areas of a real mural painted with six different alkyd paints and one acrylic paint. The impact of the protective coatings on the original paint colour and the long-term efficacy were evaluated. For purposes of comparison, the same protective coatings were applied to paint mock-ups prepared under controlled conditions and exposed to an outdoor environment with marine influence and to an ultraviolet aging test. At the end of the exposure periods, physical and chemical changes were evaluated using a multi-analytical approach based on stereomicroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. Both protective coatings modified the original colour of the paints, with the impact being greater in the mural than in the mock-ups. The efficacy of the coatings as colour protectors is more appreciable in the most colour-stable paints. Thus, neither of the coatings provided good protection for the paints most sensitive to deterioration. The protective efficacy of the coatings was also influenced by their chemical composition and affinity for the painted surfaces.

Keywords: urban art; colour protectors; spray paints; alkyd paints; concrete; painting conservation; contemporary muralism

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1. Introduction

The art created in public spaces constitutes an important part of the cultural richness of modern society [1]. These artworks are considered part of contemporary heritage; however, there is much debate about their conservation and preservation [2–7]. The absence of clear conservation guidelines, the changing nature of the context where these works are created (the urban environment) and the scarce information about the mechanisms of deterioration of the materials used and about preventive conservation techniques hamper the conservation of these cultural heritage elements.

The scarce interest that citizens, public administrations and other authorities responsible for conserving cultural heritage often show in regard to the conservation of urban art may be partly due to the lack of an agreed definition of this type of artwork, from artistic, social and legal points of view [6,8]. This situation has led to a dearth of guidelines for the conservation of urban art [5,8,9]. On the other hand, the ephemeral nature of urban art may actually be part of the work and its significance [4,10,11], and conservation may therefore be contrary to the definition and meaning of the work. The scientific community accepts that the ephemeral nature of this type of art is mainly due to the constant changes that take place in urban spaces, sometimes condemning the pieces to disappear [10].

Contemporary muralism is one of the multiple artistic manifestations included within urban art and has become important in regard to the public image of cities. In recent years, studies involving this type of artistic expression have been promoted with the aim of defining the most important factors (social, economic, artistic and technical) in terms of conservation of the artworks. One of these funding initiatives (CAPuS Erasmus + KA2) yielded, among other tools, a digital repository on urban muralism in different European cities and a specific glossary of technological terms and alteration forms and supports [12,13]. Both tools, together with subsequent related findings [7,14–29], constitute the current basis of knowledge regarding diagnosis of the state of conservation of urban art that will enable a specific conservation protocol to be defined.

In the case of contemporary muralism, one of the main manifestations of deterioration that affects pictorial materials is the loss of colour, or fading [13,21,24,28]. Colour loss is associated with photodegradation of the organic components of the modern paints used in urban art. This is illustrated by the numerous scientific studies evaluating the physical–chemical stability of the materials used in this type of art, particularly those involving degradation of the organic polymers (alkyd, acrylic, vinyl, styrene, polyurethane etc.) used in modern paints [18,19,23,26,30–40]. In these studies, the paints were exposed to different conditions such as outdoor conditions and UV tests with the aim of determining which ones were most susceptible to degradation. The findings should enable artists to choose the most appropriate paints to use, thus notably reducing the risk of disappearance or loss of the pictorial register over time. Other studies have aimed to test the influence of the quality and state of conservation of the substrate on which the artwork is painted, finding that good quality, on-site application and prior preparation play a decisive role in the paint/substrate stability and therefore on the durability of the artwork [7,19,21,25,28,41]. On the other hand, many pieces of urban art are painted directly on top on others, so that the paint/substrate interface takes on a new complexity; this added factor may contribute to the deterioration by influencing the adhesion of the paint layer to the substrate [28]. In addition to the resistance of the paints and pigments to photodegradation and problems derived from interactions between the paint and substrate, the deterioration of urban artwork is also affected by the appearance of other deterioration forms, which may accelerate the ephemeral nature of the pieces. Other types of deterioration include biological colonization, surface deposits of different nature (precipitated salts, contamination crusts), loss of material due to abrasion or vandalism [21,22,26,28].

One type of direct intervention aimed at conservation of contemporary muralism that has been considered recently is the application of protective coatings to the pictorial layer. However, studies of the compatibility of these protective layers with the paints used in urban art are scarce. To date, some studies have focused on the use of "anti-graffiti" products that modify the properties of the exposed surface, preventing the adherence of dirt, dust and graffiti paint and also facilitating the cleaning and removal of subsequent layers of paint; depending on the durability on the treated surface, these layers may be sacrificial, semi-sacrificial or permanent [42,43]. Use of these products on architectural heritage [44–47] and contemporary murals [18,48–50] can reduce the deterioration associated with the deposition of atmospheric contaminants, biological colonization and graffiti vandalism. Another research line involves the application of colour protectors or anti-UV coatings [24,29,51]. Cimino et al. [24] evaluated the efficacy of two colour protectors (one alkyl-based and one acrylic-based) applied to paints used in urban art, by subjecting mock-ups to outdoor conditions and accelerated aging with xenon lamps; the findings suggested that the application of layers of colour protectors may conserve urban art for longer time periods, although at the expense of the original appearance of the paintwork. Pozo-Antonio et al. [29] applied an acrylic protector to acrylic paint mock-ups, which were then subjected to an accelerated aging test with ultraviolet (UV) light, concluding that the efficacy of the protector depended on the substrate and the composition of the paint.

The studies involving the efficacy of protectors conducted using mock-ups prepared in the laboratory and subjected to tests are an appropriate method for evaluating the efficacy of products developed with the aim of protecting the colour of modern paints. However, in order to determine whether protective coatings are worthwhile and effective in the context of preserving urban art, all of the variables involved and the complexity surrounding pictorial objects in urban spaces must be taken into account. In this respect, the efficacy of the selected products should ideally be evaluated by applying them to real murals and monitoring the effects in situ. Kerr-Allison [51], in a first approach, evaluated the efficacy of one acrylic-based colour protector applied to selected areas of two murals; however, the coating was applied when the murals had already been created for 4 and 15 years. Therefore, a study is necessary to evaluate the protective performance from the first moment (when the mural is created) by applying techniques that allow an objective evaluation.

This study evaluated and compared the efficacy of two colour protectors applied to seven different types of paint used in a real contemporary urban mural. Both the impact of the protective coatings on the original colour of the paints (a relevant aspect from an artistic point of view) and the long-term (2 years) efficacy of the colour protectors were evaluated. For purposes of comparison and with the aim of investigating the influence of the type and complexity of the substrate and the environmental and local conditions, concrete mock-ups painted with four of the seven paints used in the mural were subjected to two different aging tests: one in a natural environment with a marine influence, and the other in the laboratory, with UV radiation. The impact of the protective coatings on the original colour of the paints and the protective efficacy of the coatings were evaluated by spectrophotometry. The reasons for the observed differences regarding the paint tone and exposure conditions were investigated by microscopic and molecular analytical techniques.

As far as we are aware, this is the first study to apply and evaluate the efficacy of colour protectors in a real contemporary urban mural from the first moment of creation. The results may serve as a starting point for defining the parameters that most influence the durability of pictorial materials in urban art and the efficacy of protective coatings.

2. Materials and Methods

2.1. Urban Mural Selected

The urban mural selected for evaluation of the colour protectors, called *A Guarda Escrita Nas Estrelas*, was painted in August 2018 by the artists Nuvi and Éxfico on the northern harbour wall in the port of A Guarda (NW Spain) (Figure 1A,B). The harbour wall extends southwards (N220°) and is of length 220 m. It consists of three sections constructed from reinforced concrete slabs and is protected on both sides by a breakwater made of concrete blocks. The southernmost section, where the harbour traffic lights are located, is semicircular; the middle section is 170 m long and has three high steps (up to 12.5 m), while the northern section, of length 50 m, has two steps (up to 8 m high). The mural was painted on the inner harbour wall, which faces the port and is oriented ESE, and on the circular end, oriented NNE.

The harbour walls are constructed from reinforced concrete and have rough surfaces due to fissures and to defects caused by compaction of the concrete mass (Figure 1C), although the surface of concrete used in a reconstructed section of the wall is smoother. The wall was first spray gun-painted with blue base paint (BLB). The rest of the mural was painted using a stencilling technique, with Montana Colors MTN 94 spray paint in blue (BL), brown (BR), green (GR), pink (PI), orange (OR) and yellow (YE). The characteristics of these products, outlined in the manufacturer's specifications, are summarised in Table 1.

2.2. Colour Protectors

Two colour protectors, made by different manufacturers, were selected for testing: a water-based anti-UV varnish produced by Proa (PR) and another one produced by Ega (EG) (Table 1). These colour protectors were selected according to the recommendations of the manufacturers, who were interested in their application in urban art murals.

The impact of the products on the original colour of the 7 paints used in the mural (blue base paint and the other 6 spray paints) and also the long-term efficacy of the colour protectors were evaluated.

Figure 1. (**A**,**B**): different views of the *A Guarda Escrita nas Estrelas* mural, in which the different tones of the paints can be seen. (**C**): detail showing the blue base (BLB) paint on which the other paints were applied by stencilling; in this case the blue (BL) and brown (BR) paintwork can be seen; note the variable roughness of the concrete substrate. (**D**): application of a protector in a monitored area with orange (OR) paint. (**E**): concrete mock-up with yellow (YE) paint, used in the outdoor exposure test. (**F**): panel of mock-ups in the outdoor exposure test.

Table 1. Paints used in the mural and selected colour protectors, with the corresponding identification code (ID). Manufacturers' specifications and composition determined by XRD (mineralogical) and FTIR (binder nature) are included. n.d., not detected.

	ID	Trade Name (Manufacturer)	Mineralogical Composition	Binder Type
Paint	BL	MTN 94 Freedom Blue RV 151 (Montana Colors)	TiO_2	Alkyd
	BR	MTN 94 Safari Brown RV 135 (Montana Colors)	TiO_2, crocoite and goethite	Alkyd
	GR	MTN 94 Valley Green RV 6018 (Montana Colors)	TiO_2 and goethite	Alkyd
	PI	MTN 94 Tutti Frutti RV 151 (Montana Colors)	TiO_2	Alkyd
	OR	MTN 94 Orange RV 2004 (Montana Colors)	TiO_2 and goethite	Alkyd
	YE	MTN 94 Light Yellow RV 1021 (Montana Colors)	TiO_2, talc and goethite	Alkyd
	BLB	Montokril Liso S 5540r90b (Montó Pinturas)	Calcite and talc	Acrylic
Protector	PR	BV0000 (Proa)	n.d.	Acrylic
	EG	CARLUX EGA-352-M00-01-FT (Ega)	SiO_2 (opal)	Acrylic

2.3. Evaluation of the Colour Protectors' Performance in the Mural

Three months after the mural was completed (December 2018), the colour protectors were applied to previously selected areas painted with each of the paints (Figure 1D). A control area without protector was also established. The protective coatings were applied by brush following the manufacturers' recommendations, as outlined in the technical specifications of the products. The processes were carried out with the express permission of the artists and the owner of the harbour structure (the port authorities).

The impact of the protectors on the original colour of the 7 paints and the durability of the protective effect were evaluated by measuring the differences in colour in the paintwork with and without protector. The colour was measured in the CIELab and CIELCH colour spaces [52] using a spectrophotometer (Minolta CM-700d) with a pulsed xenon lamp and an integrating sphere of diameter 40 mm. The measurements (10 random shots per area and time) were made in specular component excluded (SCE) mode, with a spot diameter of 3 mm, illuminant D65 and observer angle of 10°. The following parameters were recorded: lightness L* (range 0, representing black, to 100, representing white); a* (colour position between red and green, with positive and negative values, respectively); b* (colour position between yellow and blue, with positive and negative values, respectively); chroma C* and hue h. This method was used to record the colour of the painted surfaces with and without protector, 15 days after application of the products, then once a month for 12 months (between December 2018 and December 2019) and finally, 25 months after the application (January 2021). The changes in colour were evaluated by calculating the ΔL^*, Δa^*, Δb^*, ΔC^*_{ab} and ΔH^* colour differences and the total colour difference (ΔE^*_{ab}). In order to evaluate the impact of the protectors on the colour of the paint, the original colour of the paint (without protective coating) was used as a reference value, and to evaluate the durability, the initial colour of the paint with protector, measured at the start of the monitoring period, was used as the reference value.

During the colour monitoring period (December 2018 to January 2021, in total 25 months), the mean monthly temperature was 13.4 °C. The monthly thermal range varied between 6 °C (in winter) and 12 °C (in summer), reflecting a greater effect of continentality during the summer months. Throughout the whole monitoring period, freezing conditions were only recorded on 4 days, in January 2021. During the same period, a total of 3206.8 L/m^2 of rainfall was recorded (annual mean, 1474 L/m^2), indicating a high degree of seasonality (the rainfall volume was four times higher in winter than in summer). Considering these two climatic parameters (temperature and precipitation), this zone corresponds to a temperate-humid ombrothermic regime [53], and following the Köppen–Geiger climate classification system, to an oceanic type Cfb climate [54]. The wall on which the mural is painted is oriented E26° S; the mean monthly global irradiation was 1425 kJ/m^2 (max-min: 2907–400 kJ/m^2) during the study period. Owing to the orientation, the mural is predominantly affected by easterly winds, originating from the mainland. However, although the mural is protected from waves and from the rain and wind associated with sea storms (direction SSW), exposure to aerosols is maximal. This was demonstrated in a previous study characterizing the total deposition at a point located 10 km to the north of A Guarda [55], whose geographical and topographical positions can be considered similar to those of the study area, regarding marine influences. In a period of only 4 months, almost 8 g of chloride and 1 g of sulphate were collected [55].

2.4. Evaluation of the Colour Protectors' Performance under Natural Outdoor Exposure and UV-Radiation Aging Tests

The efficacy of the colour protectors was also evaluated in two different aging tests: natural outdoor exposure with marine influence and exposure to ultraviolet radiation, as explained in detail below.

In both tests, mock-ups of 4 of the 7 paints used in the real mural were prepared: green (GR), pink (PI), orange (OR) and yellow (YE). A concrete base substrate was prepared with granite aggregate (particle size 20–40 µm) and Portland cement (Cosmos CEM II/B-M (VL) 32.5 N) in a ratio of 3:1 (by weight). Once the concrete has set (30 days), test specimens of 7 × 7 × 2 cm were cut from the block. The specimens were washed and brushed to remove dust from the surface, dried at 40 ± 1 °C to constant weight and stored under laboratory conditions (15 ± 5 °C; RH 60 ± 10%) until use. Finally, the spray paints were applied following the manufacturers' recommendations (Figure 1E). Fifteen days later, the protectors were applied to batches of specimens (one batch per protector), and a third batch was left without protector (controls). The resulting mock-ups, with and without protector, were held for 30 days in laboratory conditions (15 ± 5 °C; 60 ± 10% RH). After this period, and with the aim of evaluating the impact of the protector on the original colour of the paints, the colour of the painted surfaces of all mock-ups was measured following the previously described protocol. The colour was measured at six randomly selected points on the surface of each mock-up, and the ΔL^*, Δa^*, Δb^*, ΔC^*_{ab} and ΔH^* colour differences and the total colour difference (ΔE^*_{ab}) were calculated, relative to the original colour of the mock-ups without protector. The mock-ups were then subjected to the tests described in Sections 2.4.1 and 2.4.2.

2.4.1. Natural Outdoor Exposure

This test consists of exposing the mock-ups with and without protectors for 12 months (December 2018 to December 2019) in a panel situated on one of the exterior walls in a building on the Island of Toralla (Vigo, NW, Spain), with orientation N45° W and at a distance of about 20 m from the coastline (Figure 1F). During the 12-month exposure period, the average monthly global irradiation was 16,420 kJ/m^2 (max-min: 26,050–5550 kJ/m^2), average monthly RH, 76% (max-min: 86–68%), average monthly mean temperature, 16.1 °C (max-min: 20.5–10.9 °C), maximum temperature, 30.6 °C and the minimum temperature, 3.6 °C.

As in the real mural, the durability of the protectors was evaluated by measuring the colour of the painted surfaces of all mock-ups monthly during 12 months, using the same equipment and conditions described above and recording the colour at 6 randomly selected points on each surface. The ΔL^*, Δa^*, Δb^*, ΔC^*_{ab} and ΔH^* colour differences and the total colour difference (ΔE^*_{ab}) were calculated relative to the initial values of the colour coordinates on the mock-ups with and without protector. The colour was only able to be measured on 10 occasions as at two of the monitoring times, the samples were not dry enough for measurements to be made, owing to the continuous heavy rainfall.

2.4.2. UV Radiation Exposure

The painted mock-ups with and without protector were irradiated using OSRAM Ultra Vitalux 300 W UV lamps (radiation power 13.6 W of UV-A and 1.3 W of UV-B) positioned at a vertical distance of 50 cm from the surfaces of the mock-ups and at a distance from each other of 30 cm to ensure equal irradiation of all samples. The mock-ups were exposed to 210 cycles each of 22 h of irradiation and 2 h of darkness (total, 4620 h of irradiation).

The efficacy and durability of the protectors was also evaluated by measuring the colour expressed in the CIELab and CIELCH colour spaces, using the same equipment and conditions described above, and recording the colour of the mock-ups (6 random measurements per sample) after every 330 h of irradiation.

2.5. Analytical Techniques Used to Characterize the Materials before and after the Aging Tests

The paints and protectors were applied (single coat) to aluminium foil and allowed to dry for 30 days under laboratory conditions in order to obtain samples for characterization, which was performed following these types of analysis:

(1) X-ray Diffraction (XRD), using a SIEMENS D5000 (Cu-Kα radiation with a Ni filter, voltage of 45 kV and intensity of 40 mA) and applying the random powder method. Each mineral phase was identified using the X'Pert HighScore software.

(2) Fourier Transform Infrared spectroscopy (FTIR) in diamond crystal attenuated total reflection (ATR) mode, using a Spectrum 100 instrument with a diamond crystal (Perkin Elmer, Waltham, MA, USA), in the infrared spectral region between 650 cm^{-1} to 4000 cm^{-1}, at a 4 cm^{-1} resolution over 16 scans.

In order to determine the causes of the colour changes, samples of the paintwork with and without protector were obtained from the real mural and the mock-ups used in the outdoor and UV radiation exposure tests, before and after the colour monitoring. The samples were analysed using the following protocol:

1. Stereomicroscopic visualization using a Nikon SMZ800 microscope. Samples were studied by observing both the paint surface and cross-sections of samples, for which

purpose specimens were embedded in epoxy resin (EpoThin 2 epoxy resin and EpoThin 2 epoxy hardener), cut and polished.

2. Micromorphological and compositional analysis by means of Scanning Electron Microscopy with an Energy-Dispersive X-ray microprobe (SEM-EDX), using a QUANTA FEI 200 with backscattered electron (BSE) and secondary electron (SE) detectors. Observations were conducted with a working distance of 9–11 mm and an accelerating potential of 20 kV. Both paint surfaces and cross-sections of samples were observed.
3. Chemical characterization (molecular) by Fourier Transform Infrared spectroscopy (FTIR) of selected samples, using the method and equipment described above.

3. Results and Discussion

3.1. Pre-Test Characterization of Paints and Protectors

Table 1 shows details of the mineralogical phases detected by XRD in the paints and protectors and the nature of the organic base by FTIR. The Montana spray paints GR, PI, OR and YE were characterized in a previous study [19]: XRD analysis detected rutile (TiO_2) in all of these paints, talc in YE and traces of goethite in YE, GR and OR; the rutile and talc would be included in the paints as fillers and the goethite as an inorganic pigment, being common in red and yellow paints. In the same study, FTIR analysis confirmed the alkyd nature of these paints, as the typical fingerprint bands of the functional groups of this type of resin were identified [19].

In the present study, analysis of the BR, BL and BLB paints revealed the presence of rutile, crocoite ($PbCrO_4$) and goethite in BR, calcite and talc in BLB and rutile in BL.

FTIR analysis of the samples (Figure 2) confirmed the alkyd nature of the BR and BL paints, by detection of bands at 3600–3100 cm^{-1} -ν(O-H)- [56,57], 2925 and 2854 cm^{-1} -ν(C-H) doublet- [56,58], 1720 cm^{-1} -ν(C=O)- [56,58], 1600 and 1581 cm^{-1} -ν(C=C) aromatic group doublet- [59], 1450 cm^{-1} -ν(CH2)- [58], 1252, 1114 and 1066 cm^{-1} -ν(C-O)- [58] and 750–728 cm^{-1} -ρ(C-H)- [56,58].

The BLB paint is consistent with an acrylic resin modified by styrene; in the doublet corresponding to ν(C-H), in addition to two intense bands at 2925 and 2854 cm^{-1}, two small shoulders were distinguished at 2955 and 2871 cm^{-1} [56,58], with ν(C=O) at 1728 cm^{-1} [56,58] and ν(C-O) at 1250 and 1150 cm^{-1} [58]. The presence of styrene was confirmed by the positions of the bands at 3080 cm^{-1} -ν(C-H)- and 668 cm^{-1} -ρ(C-H)- [58].

FTIR analysis also confirmed the nature of the inorganic fillers detected by XRD: rutile was identified in the BR and BL paints by a band at 690 cm^{-1} (Ti-O) [60]; calcite was identified in the BLB paint by bands at 1420 cm^{-1} -ν(C-O)- and 875 cm^{-1} -ν(C=O)- [56]; talc was identified in the BLB paint by bands at 3670 cm^{-1} -ν(O-H)- [56,61] and 1018 cm^{-1} (Si-O) [56], and goethite was identified in the BR paint by a band at 908 cm^{-1} -δ_{deform}(O-H) of Fe-OOH- [62,63].

Regarding characterization of the colour protectors, XRD analysis only detected poorly crystalline SiO_2 (opal) in the Ega product (Table 1).

FTIR analysis confirmed the acrylic nature of both protectors (Figure 2), via identification of the previously indicated fingerprint bands of these polymers [33,56,58].

In the spectrum of the Ega protector, the presence of polyethoxylated surfactants was detected by identification of the bands assigned to these compounds in previous studies [33,64]: these include an intense absorption band at 1108 cm^{-1} -ν(C-O)- and bands at 1060 cm^{-1} -ν(C-O)-, 1359 and 1344 cm^{-1} -ν(CH_2)-, 1277 cm^{-1} -ν(C-O of alcohol groups-, 2955, 2740 and 2694 cm^{-1} -ν(C-H)-, 964 cm^{-1} -ρ(C-H)-; the bands at 1238 and 1145 cm^{-1} overlapped with ν(C-O) of the acrylic polymer. The complex/structured band in the spectral range between 1200 and 1000 cm^{-1} may also be defined by some ν(Si-O) vibration, which absorbs in this range [56], given that SiO_2 was detected in this product by XRD.

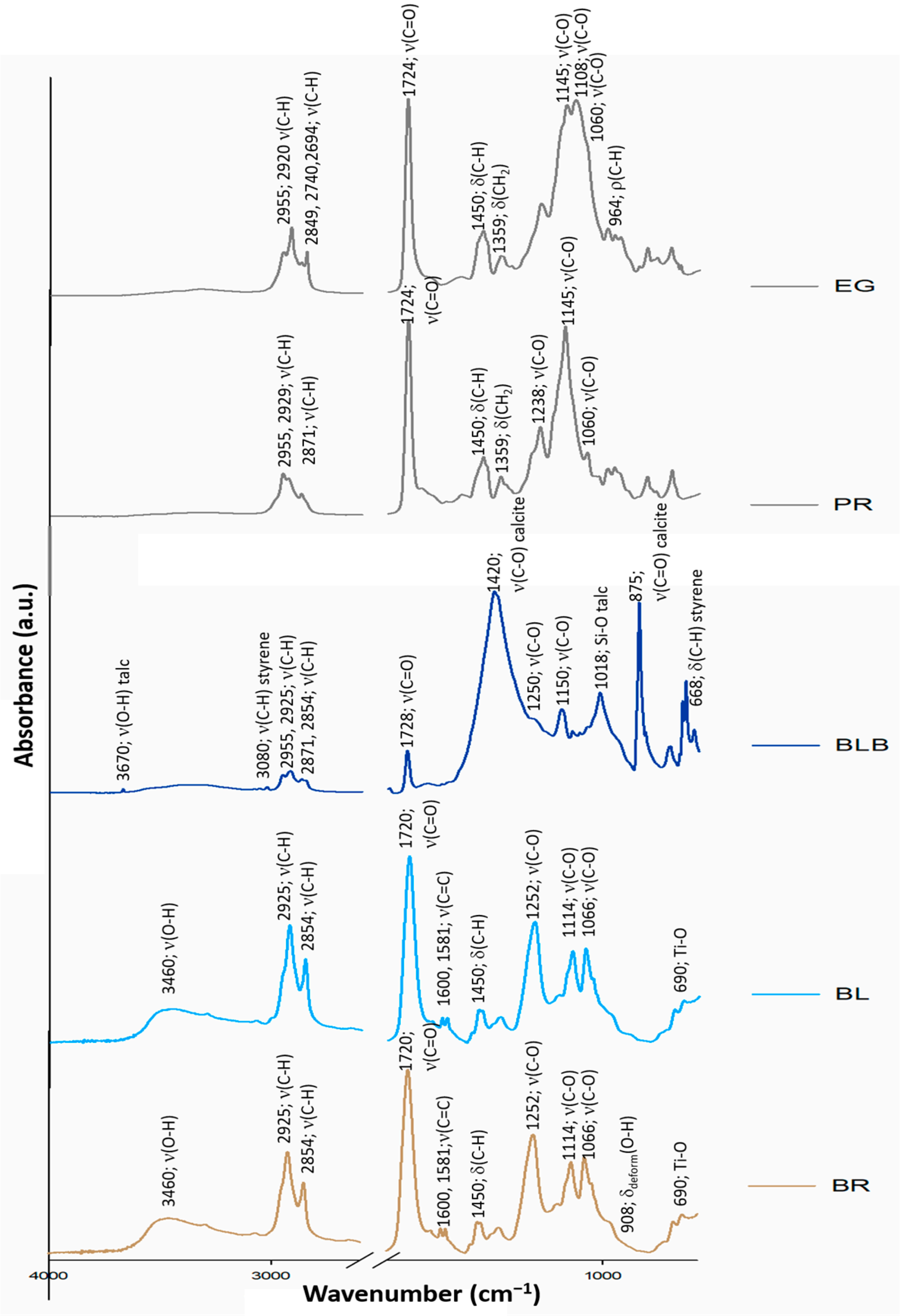

Figure 2. FTIR (absorbance) spectra of paints: brown (BR), blue (BL), base blue (BLB) and the Proa (PR) and Ega (EG) protectors scraped from aluminium foil.

3.2. Impact of the Protectors on the Original Colour of the Paint

The ΔE^*_{ab} values calculated after application of each protector on each paint both in the real mural and in the mock-ups are represented in Figure 3A. In all cases, the protectors caused a change in the original colour of the paints.

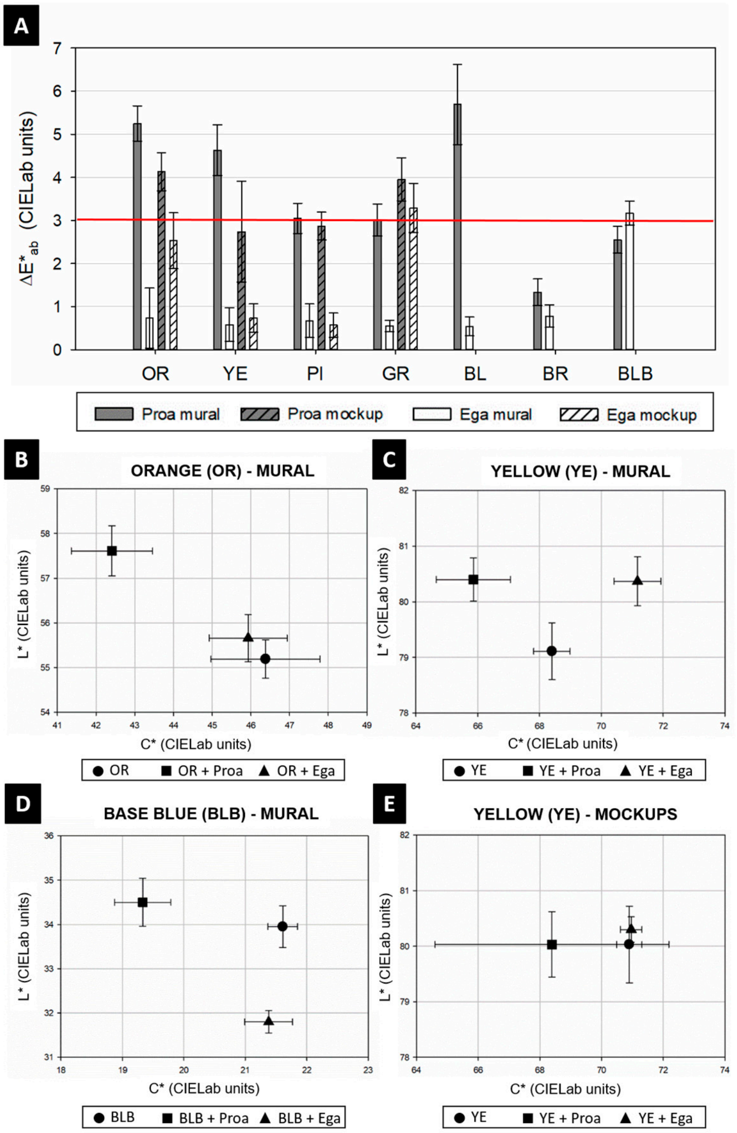

Figure 3. Plots of colour parameters in painted surfaces with protector coatings to analyse the colour change cause by application of the protectors. (**A**): mean values of ΔE^*_{ab} caused by the Proa and Ega protectors on the paints in the mural and in the mock-ups. (**B**–**E**): mean values and error bars for L* and C* parameters in the paints without protector and with the different protectors: orange OR paint in the mural (**B**), yellow YE paint in the mural (**C**), blue base BLB paint in the mural (**D**), and yellow YE paint in the mock-ups (**E**).

3.2.1. Mural

In the mural, the Proa protector produced higher colour changes than the Ega protector in all paints, except the BLB paint, the only acrylic paint among those evaluated. The differences in the ΔE^*_{ab} values corresponding to Proa and Ega were statistically significant. Considering a ΔE^*_{ab} value of three CIELab units as the threshold after which the colour change is perceptible to the human eye [65], the colour change produced by the Proa protector in five of the seven paints will be visible to the human eye; the colour change would not be perceptible in the BR and BLB paints only. However, the Ega protector only produced a visible colour difference in the BLB paint, yielding a ΔE^*_{ab} of 3.17 ± 0.28 CIELab units, although slightly higher than that yielded by the Proa protector (2.55 ± 0.31 CIELab units).

The mean values and standard errors of the parameters L* and C* for three of the paints (OR, YE and BLB) in the mural are graphically represented in Figure 3B to Figure 3D as representative of the type of change that takes place in these parameters. Application of the Proa protector produced an increase in the luminosity and a decrease in the chroma in the OR (Figure 3B), YE (Figure 3C), PI and GR paints, which were therefore paler in colour, but only a decrease in chroma (luminosity was not affected) in the BL and BLB paints (Figure 3D), in which the colour turned greyish. The Ega protector did not produce large changes, except in (1) the BLB paint, in which the luminosity decreased and the chroma remained constant, so that the paint became darker (Figure 3D) and (2) the YE paint, in which Ega caused an increase in luminosity and chroma, so that the paint appeared brighter (Figure 3C). Regarding the ΔH^*, no great changes were observed in any of the paints after application of the protectors (the colour differences ranged between 1.28 and -0.92 units), except in the BLB paint treated with Proa, which yielded a ΔH^* of -2.62 units, indicating that the blue colour was displaced towards green-yellow tones.

The formation of an intense craquelure in the Proa protector a few days after application to the mural may be one of the reasons explaining the intense colour change caused by this product. Thus, it was found that (1) in the BL paint, in addition to the craquelure, the protective layer acquired a yellowish tone (Figure 4A), which explains the high ΔE^*_{ab} value obtained after application of the protector (5.69 ± 0.93 CIELab units) and is reflected by the ΔH^* value of this sample; and (2) in the BR paint, a large area of the craquelure in the protective layer became detached only 15 days after application of the protector (Figure 4B). Loss of the protective layer due to detachment explains the low ΔE^*_{ab} obtained for this paint ($\Delta E^*_{ab} = 1.33 \pm 0.31$ CIELab units, not perceptible to the human eye) and affected (as we will see later) the subsequent measurements of the colorimetric parameters during the monitoring to evaluate the durability of the protection, as the measurements were made on the paint with very little protector remaining. Unlike Proa, the Ega protector is smooth and completely transparent and provides homogenous cover over the surface of the paints in the mural.

3.2.2. Mock-Ups

In the mock-ups, the changes in colour caused by the Proa protector are quantitatively lower than those in the mural, except for the GR paint, in which a higher value was obtained (Figure 3A). By contrast, the changes in colour caused by the Ega protector were greater than in the real mural, except in the PI paint. In any case, the total colour difference yielded by Proa was always higher than that yielded by Ega, although the difference was only statistically significant in the case of the OR and PI paints. In the mock-ups, the colour changes due to the presence of the Proa protector were only visible to the human eye in two of the five paints evaluated—the OR and GR paints—, while the colour change caused by application of Ega was only visible in the GR paint. The standard deviation in the ΔE^*_{ab} values was particularly high for the mock-up with YE paint and the Proa protector (2.74 ± 1.17 CIELab units) (Figure 3A). The high dispersion of values can be attributed to the fact that, in addition to the craquelure formed (with cracks of more than 0.5 cm in width and 3 cm in length), the cover provided by the protector was not homogenous (Figure 4C), with some areas being covered by the protector (yielding a ΔE^*_{ab} of 3.91 CIELab units) and others remaining without protector (yielding a ΔE^*_{ab} of only 1.57 CIELab units); this was also evident in the graph of the mean values and standard errors of the L^* and C^* parameters in the YE paint (Figure 3E) and it was confirmed that the parameter most affected was C^*, for which values of up to 72.18 CIELab units were obtained for areas without the protector and much lower values of around 64.60 units for areas with protector. In the PI paint, craquelure also appeared in the layer of Proa protector (Figure 4D). By contrast, the Ega protector provided a homogenous smooth, transparent layer (Figure 4E).

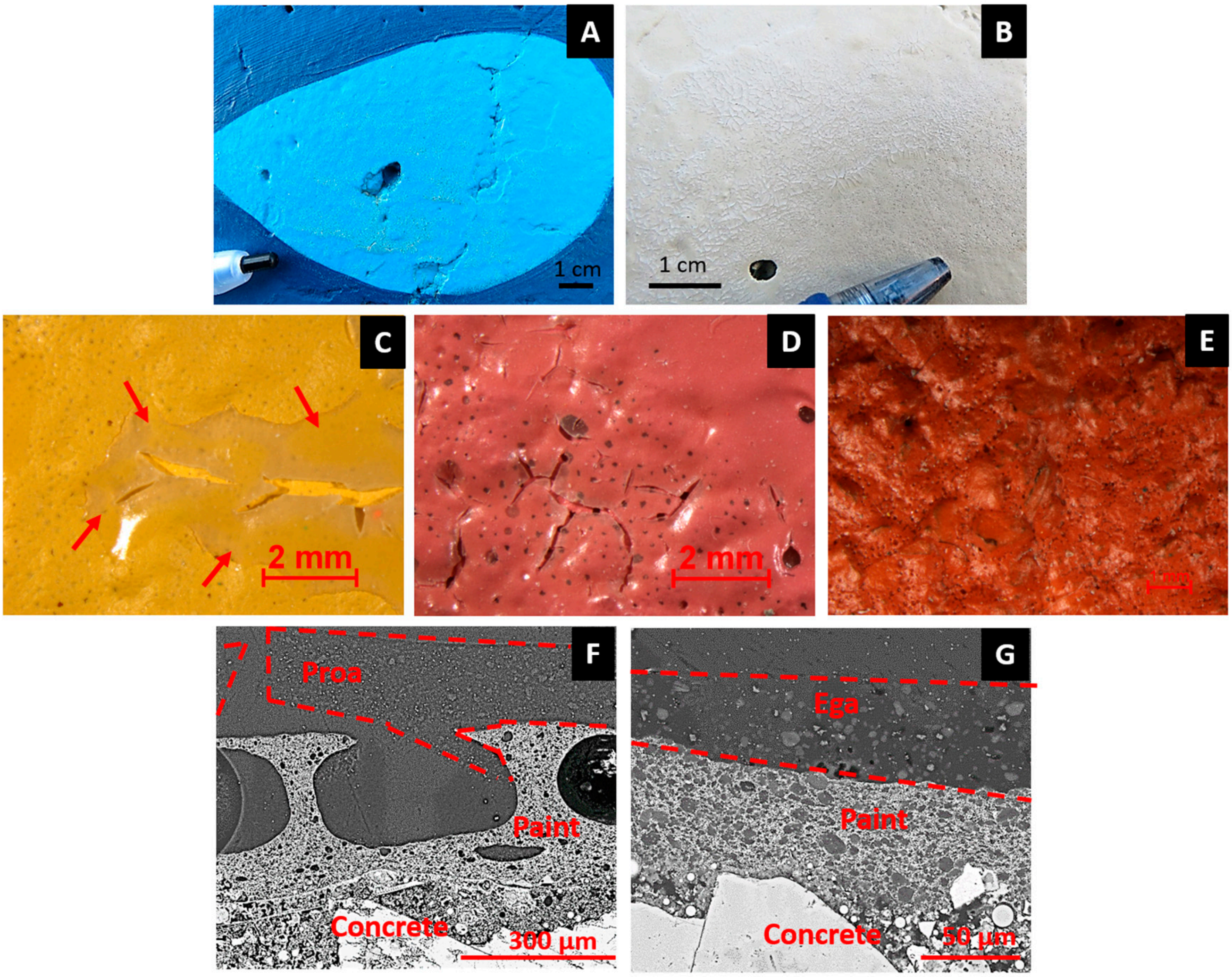

Figure 4. (**A**,**B**): images of the surface of the blue base BLB (**A**) and the brown BR (**B**) paints in the mural after application of the Proa protector. (**C**–**E**): stereomicrographs of mock-up surfaces with Proa protector on yellow YE paint (**C**) proa protector on pink PI paint (**D**) and Ega protector on pink PI paint (**E**). (**F**,**G**): scanning electron micrographs of mock-up cross-sections of the Proa protector on pink PI paint (**F**) and the Ega protector on orange OR paint (**G**).

SEM examination of the cross-sections of the paintwork with and without protector showed that (1) the craquelure affected all depths of the layers of the Proa protector (thickness, 150–200 µm), reaching the paint surface (Figure 4F), and (2) the Ega protector provided a continuous, although thinner, layer (up to 60 µm) than the Proa protector. Numerous Si-rich microparticles of up to 15 µm were detected in the Ega protector (Figure 4G), consistent with the results of the XRD analysis.

Regarding ΔH*, the only notable changes were in the GR paint treated with Ega (ΔH* = 2.34 ± 0.71 CIELab units) and the PI paint treated with Proa (ΔH* = 2.55 ± 0.38 CIELab units); note that in the mural these paints did not undergo significant changes in hue.

The differences in the ΔE^*_{ab} values corresponding to the mural and the mock-ups may be due to various factors such as:

1. The application of the protectors: although the same person applied the protectors to the mural and to the mock-ups following the same procedure and criterion for covering the surfaces, the products were applied on a vertical surface in the mural and on a horizontal one in the mock-ups.

2. The environmental conditions at the time of application: in the laboratory, the mock-ups were held at ambient temperature and relative humidity (15 ± 5 °C and 60 ± 10% RH), whereas the outdoor location of the mural would favour more rapid heating and cooling of the surfaces, which may affect film formation of the protectors and their interaction with the paints.
3. In the mural, the paints were applied on top of the blue base paint, while in the mock-ups they were applied directly on the concrete surface, which may have affected the performance of the protector.
4. The concrete on which the mural is painted is not the same as that used in the mock-ups; the differences in the granulometry of the aggregate (type of aggregate, dosage aggregate-cement, etc.) may influence the drying process of the protective coatings and the interaction between these and the paints. Likewise, although the protectors were applied on a dry, sunny day after a week without any rain, it is possible that the concrete was not completely dry. In addition, the location of the mural beside the sea must also be taken into consideration.

3.3. Protective Performance

The ΔE^*_{ab} values for the unprotected areas of paint in the mural and areas of the same paints with both protectors at 12 and 25 months after treatment are represented graphically in Figure 5A. First, after 25 months, all of the paintwork without protector had undergone colour changes visible to the human eye ($\Delta E^*_{ab} > 3$ CIELab units) except the BR paint; there was an enormous variation in the colour of the PI and OR paints, with much higher ΔE^*_{ab} values (22.97 ± 0.11 and 19.88 ± 0.69 CIELab units, respectively) than for the GR (10.29 ± 0.20 CIELab units), YE (9.85 ± 0.42 CIELab units), BLB (6.89 ± 0.23 CIELab units) and BL (4.00 ± 0.19 CIELab units) paints. Second, after 25 months, all of the paintwork with protector had undergone smaller colour changes than the paints without protector. Considering the degree to which the colour change is visible to the human eye, the protectors only reduced the ΔE^*_{ab} to below three units in the BLB paint, with Proa yielding an ΔE^*_{ab} of 2.86 ± 0.39 and Ega a much lower value, of 0.80 ± 0.24 units.

The greater efficiency of Ega in protecting the colour of the paint in the real mural (Figure 6A) contrasts with the minimal efficacy of both products in protecting the colours of the OR and PI paints (Figure 6B). Intense deterioration of the Proa protector on the BL paint was also evident, with the coating becoming opaque, yellowish in colour and beginning to detach from the surface 9 months after application (Figure 6C). The BR paint was an exception to this pattern, as it underwent minimal colour variations with both protectors and also without them (Figure 5A). However, the Proa protector on this paint formed intense craquelure 15 days after application (Figure 4B) and became completely detached from the surface after 4 months, so that the colour measurements were made directly on the paint surface after this time. Thus, use of a colour protector would be unnecessary with the BR paint owing to its high level of photostability.

The ΔE^*_{ab} values for the paints on the mock-ups with and without protectors (Figure 5B,C) showed some similarities and differences relative to those in the mural. In the outdoor exposure test (Figure 5B), the ΔE^*_{ab} values for the OR paint were similar, and again higher than three CIELab units: without protector, the ΔE^*_{ab} value was 13.94 ± 0.69 units, similar to that obtained in the mural after 12 months and with both protectors. Neither protector was therefore very effective in protecting the colour of this paint in the outdoor environment, as can be seen in the images in Figure 6D, in which the surfaces on the OR paint with and without protector have faded in a similar way. However, in the mock-ups of PI paint with and without protector, the colour change after the outdoor exposure test was different from that in the mural: the ΔE^*_{ab} for the PI paint without protector was only 5.69 ± 0.64 CIELab units (Figure 6B), which is much lower than the value obtained in the mural after the same exposure time (12 months) (22.97 ± 0.11 CIELab units) (Figure 6A). The layer of Proa protector applied to the PI paint in the mock-up reduced the ΔE^*_{ab} to below three CIELab units (Figure 5B) after 12 months, unlike in the mural, in which the corresponding ΔE^*_{ab} was 14.82 ± 0.56 units after the same exposure time (Figure 5A). In the same paint treated with Ega, a visible colour change was observed at the end of the test (Figure 6E) and greatly affecting the inside of the numerous broken bubbles covering the surface (Figure 6E,F). These bubbles were formed during the paint application process, and the protectors were applied on top of them (Figure 6E(1)); during the exposure test, the bubbles burst, leading to detachment of the protective coating and leaving the paint surface exposed and thus causing greater loss of colour than in the rest of the sample (Figure 6E(2),F). Finally, the colour change undergone by the other two paints (GR and YE) with and without protector was quantitatively similar to that observed in the mural after the same period of time.

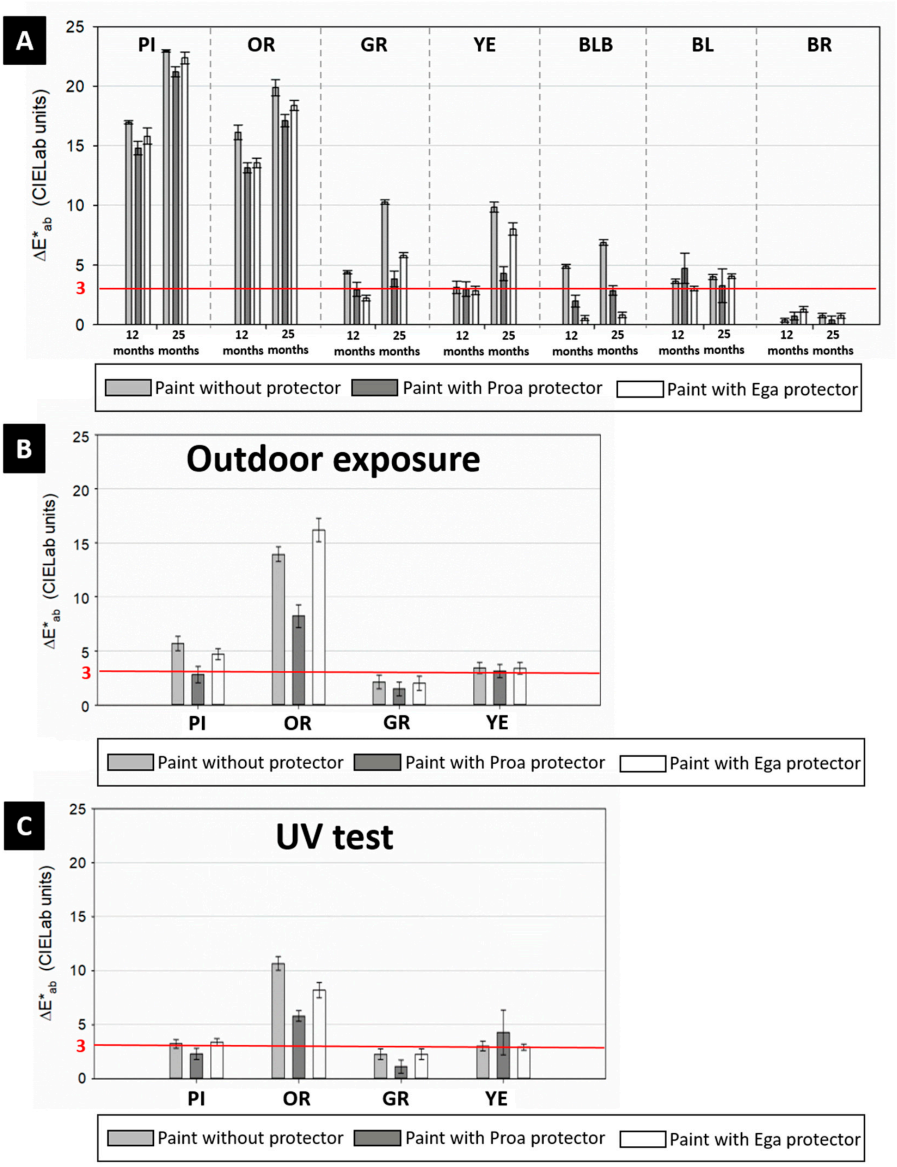

Figure 5. Bar charts of the total colour differences (ΔE^*_{ab}) in the different paints (PI-pink, OR-orange, GR-green, YE-yellow, BLB-blue base, BL-blue, BR-brown), with protector (Proa and Ega) and without protector 12 and 25 months after treatment in the mural (**A**) and in the mock-ups after the outdoor exposure test (**B**) and after the UV test (**C**).

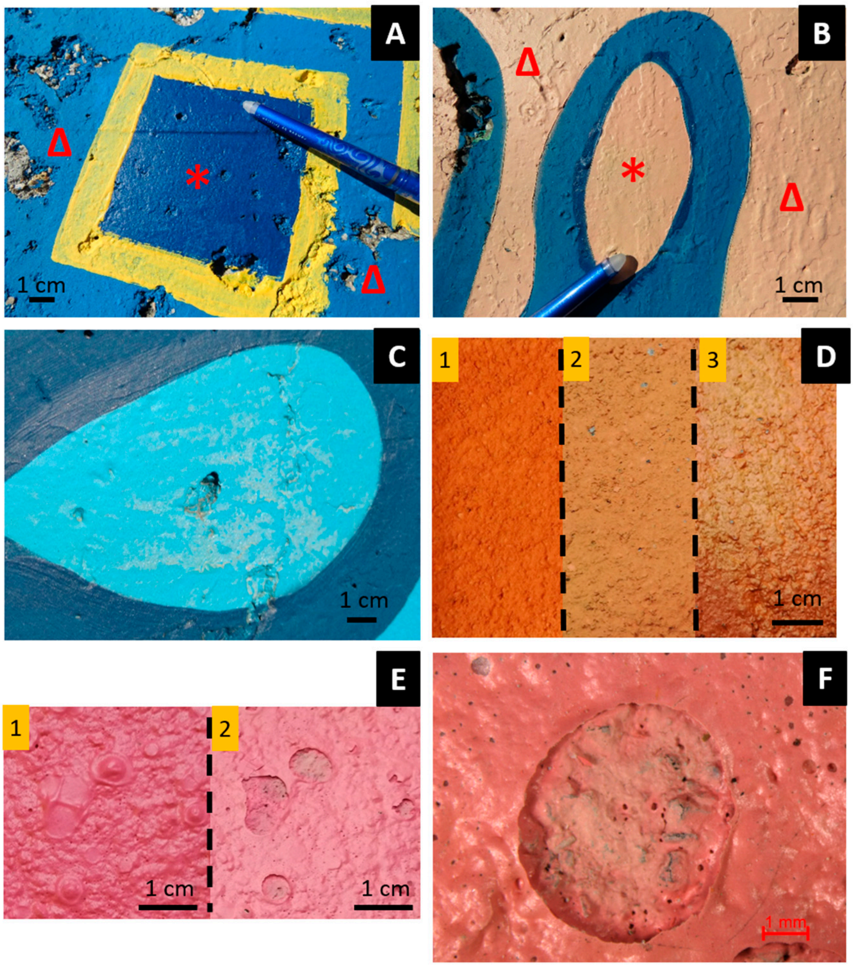

Figure 6. (**A**): BLB paint 25 months after application of Ega 25: note the difference in colour between the unprotected area (indicated by Δ) and the area coated with Ega (inside the square, indicated by *). (**B**): the PI paint 25 months after the application of Ega: note the similarity in the colour of the treated area (indicated by *) and the untreated area surrounding the blue loop (indicated by Δ). (**C**): the BL paint in the mural 9 months after treatment with Proa, showing the change in the appearance of the protective coating, which has become opaque and yellowish. (**D**): comparison of images of the mock-ups with OR paint; (1) without protector, before outdoor exposure, (2) without protector, after outdoor exposure and (3) with the Ega protector, after outdoor exposure. (**E**): comparison of images of the same area of a mock-up with PI paint treated with the Ega protector: (1) before outdoor exposure and (2) after outdoor exposure. (**F**): stereomicrograph of the PI paint coated with Ega, after outdoor exposure.

In the UV exposure test (Figure 5C), the changes were similar to those observed in the outdoor exposure test (Figure 5B), although the ΔE^*_{ab} values were, in all cases, slightly lower.

The surfaces and cross-sections of the mock-ups with and without protectors after the different exposure tests were also examined by SEM and analysed by means EDX coupled to SEM. The following features were observed:

1. The existence of saline deposits on the surface of the mural and the mock-ups exposed outdoors (mural and outdoor exposure test), specifically Na- and Cl-rich crystals with a cubic habit, typical of halite (Figure 7A), and acicular, subidiomorphic Ca- and S-rich crystals (Figure 7B), which would correspond to gypsum; these salts are derived from marine environments, specifically from marine aerosols [25,55]. These deposits will undoubtedly contribute to the colour change; however, greater amounts of deposits

were not found in the samples that changed most in colour. The presence of diatoms, which are common in freshwater surfaces, was also detected.

2. The Proa protector deteriorated considerably, separating from the painted surface in some areas after the outdoor exposure (Figure 7C); the lack of adherence between the Proa coating and the underlying paint surface was also apparent in the cross-sectional samples (Figure 7D). Enrichment of Ti occurred at the edges of the fissures in the protector, which was observed in the backscattered electron images with an intense brightness (Figure 7C). Ti deposits were also observed on the paint surface (Figure 7C), indicating that the paint may have become degraded due to loss of the organic component, which leads to the segregation of the rutile-based fillers at the surface.
3. The Ega protector was also deteriorated, as in some areas it was also observed the paint surface (Figure 7E).

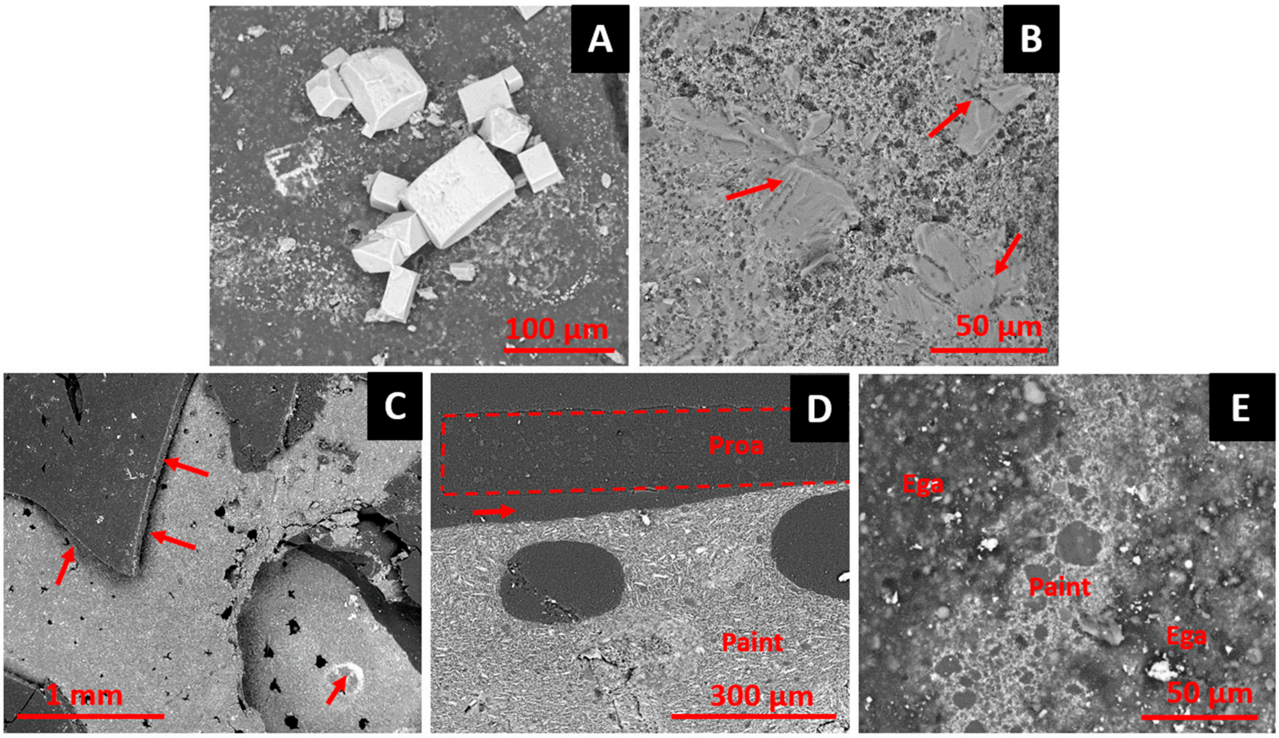

Figure 7. SEM micrographs of the mural and mock-up surfaces after outdoor exposure. (**A**): sodium chloride crystals on the surface of the PI paint treated with the Ega protector after mural exposure. (**B**): gypsum crystals present on the surface of the PI paint treated with Ega after outdoor exposure test. (**C**): surface of the YE paint treated with the Proa protector after outdoor exposure test; arrows indicate Ti accumulations. (**D**): cross-section of the YE paint treated with the Proa protector after outdoor exposure test; the arrow indicates the gap between the protective coating and the paint. (**E**): surface of the OR paint with the Ega protector after outdoor exposure test.

For a more detailed analysis of the colour changes, the values of ΔL^*, ΔC^*_{ab} and ΔH^* were calculated for all the paints with and without protector after exposure for 25 months in the mural and after 12 months exposure of the mock-ups in the outdoor exposure and UV tests (Figure 8). In all paints except the blue ones (BL, BLB) and BR paint, the change in colour was, in general, due to an increase in the L* coordinate, a decrease in C* and an increase in h. These changes indicate that the colours became paler, with a slight change in tone. The effect was strongest in the PI and OR paints, as indicated by the high ΔE^*_{ab} values. In general, the changes in parameters L*, C* and h were also greater in the mural than in the mock-ups used in the aging tests.

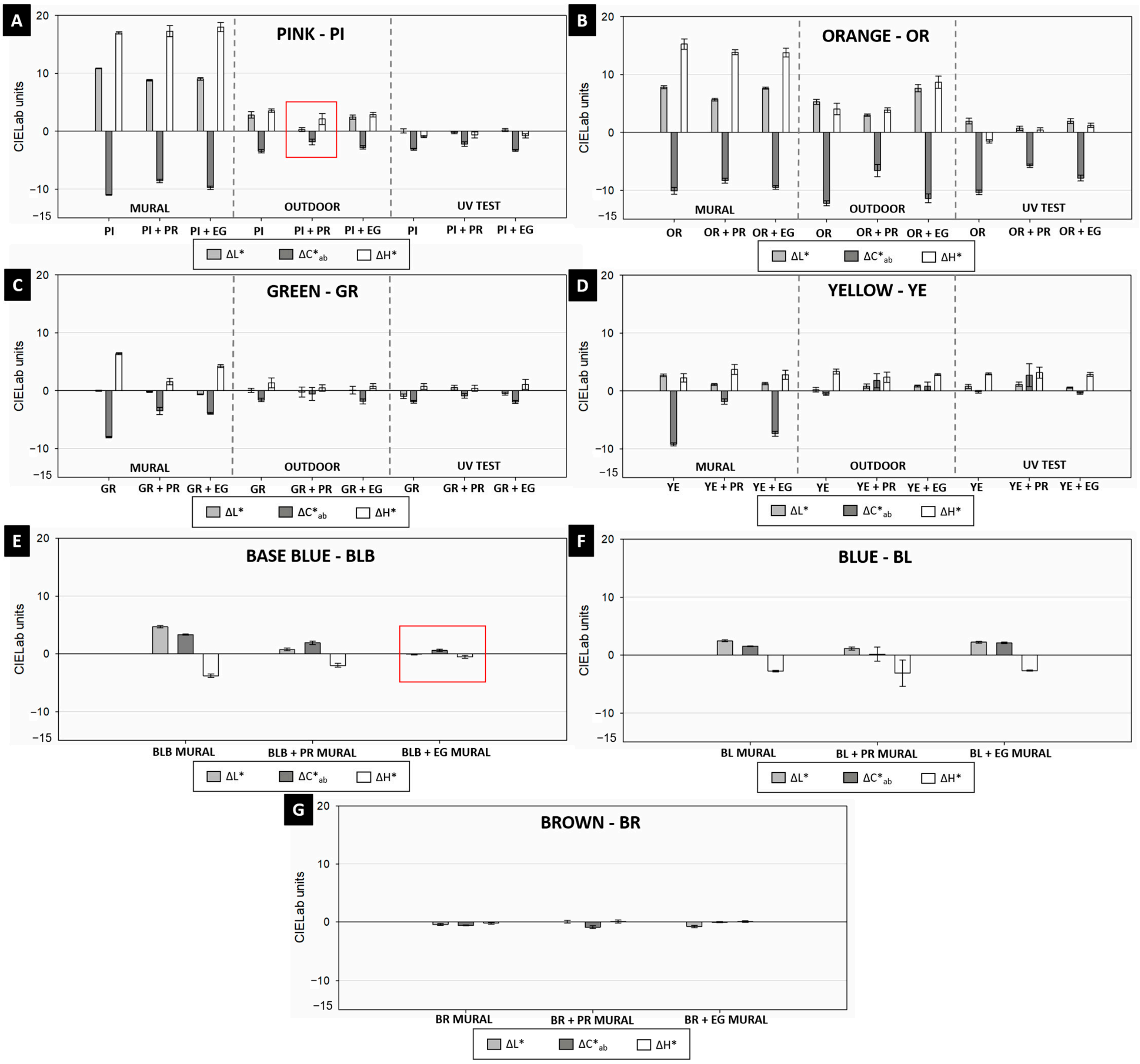

Figure 8. (**A**–**G**): bar charts showing the ΔL*, ΔC*$_{ab}$ and ΔH* values for the paints in the mural after exposure for 25 months and for the mock-ups after exposure for 12 months (outdoor exposure test) and 4620 h of irradiation (UV aging test). Red rectangles indicate cases where the products provided some degree of protection.

In Figure 8, the values of ΔL*, ΔC*$_{ab}$ and ΔH* for the mural correspond to an exposure period of 25 months and are generally higher than the values for the mock-ups (exposure period 12 months), with the following exceptions: (1) the BLB and BL blue paints, in which L* and C* increased (the colours faded) and the h decreased, and (2) the GR paint, in which L* scarcely changed, and when C* changed, it did so to a greater extent (the colour deepened). In those cases in which the ΔE*$_{ab}$ values indicated that the products provided some degree of protection, the ΔL*, ΔC*$_{ab}$ and ΔH* values were lower; this is the case of the BLB paint with the Ega protector, the YE and GR paints with Proa protector in the mural and the mock-ups with PI paint with Proa protector after outdoor exposure after the aging tests. The exception of the BR paint is confirmed, which scarcely changed.

The values of the colour parameters analysed enabled the following to be established:

1. Two of the paints (OR and PI) faded more than the others, especially in the mural; the deterioration in the colour of these paints affected the three colour parameters analysed (L*, C* and h). Previous studies have shown that paints differ in their susceptibility to fade (depending on the original tone of the paint), with orange and reddish tones being the most susceptible [19,28]. The SEM images show some enrichment of Ti at the surface of the paints exposed after detachment of the protector, confirming degradation of the paint. In this case, it is likely that the organic components have degraded, causing a relative enrichment of the inorganic component (the Ti in the rutile used as filler). Without ruling out a possible contribution, it is unlikely that the degradation of the paints is due exclusively to a photocatalytic effect of TiO_2, because the TiO_2 detected in the paints by means XRD was rutile, not anatase—a polymorph with a greater photocatalytic effect [66].
2. The efficacy of the Proa protector depended on the paint to which it was applied. Application of Proa to the green (GR) and yellow (YE) paints in the mural implied much greater resistance to fading, although the colour change in these paints was visually perceptible. In this respect, use of this product would be recommended to slow down the colour change under these conditions. In the case of outdoor exposure and UV aging tests, the product was not required, as the YE and GR paints scarcely underwent any change in colour under the test conditions. However, SEM analysis revealed that the protective coating lost adhesion and became detached from the surface, leaving the paint exposed.
3. The Ega protector was also degraded, as the protective layer disappeared from the surface of the paints in some areas. This protector was only effective on the BLB paint, which by coincidence is the only acrylic paint. The Proa product also provided some degree of protection for this paint, but less than Ega. These findings indicate some relationship between the efficacy of the protector and the chemical nature of the protector and of the paint. Further studies would be of interest to determine the relationship between the alkyl paints under study here and other alkyd-based protectors, as addressed in a previous study [24].

Analysis of the changes in the ΔE^*_{ab} values for the paints with and without protector during exposure time under the three different conditions (Figure 9) revealed some interesting differences between paints, protectors and exposure conditions. For example, the temporal changes in ΔE^*_{ab} in the PI paint were different in the mural and in the mock-ups exposed outdoors: in the mural, the ΔE^*_{ab} initially underwent a rapid increase and then changed gradually over time (Figure 9A); by contrast, in the mock-up in the outdoor exposure test, the ΔE^*_{ab} only began to increase slightly after 7 months (Figure 9B). The difference may be due to the following:

1. As the measurement period was the same in both tests (with the first measurement made in December 2018), the meteorological conditions would have been similar in both the mural and the test panel (separated by a distance of 30 km). The only difference was the orientation: SE in the mural and NW in the test panel. Nonetheless, the PI paint showed similar stability in the outdoor test panel during one year as in the UV test under laboratory conditions, while the OR paint showed a similar deterioration pattern in all three tests (Figure 5).
2. Differences in the layers underneath the paint. In the mock-ups, the paint layer was in direct contact with the concrete substrate, while in the mural, it covers several existing layers of paint. In addition, although the substrate was concrete in both cases, differences in the size and distribution of particles in the aggregate, the aggregate: cement ratio and the presence of some additive may influence the properties of the concretes regarding the transport of gases and water (vapour and liquid) and of the surface properties that determine, e.g., the degree of adhesion of the paint to the substrate and even the penetration of the paint to the interior, which may influence the deterioration of the paint.

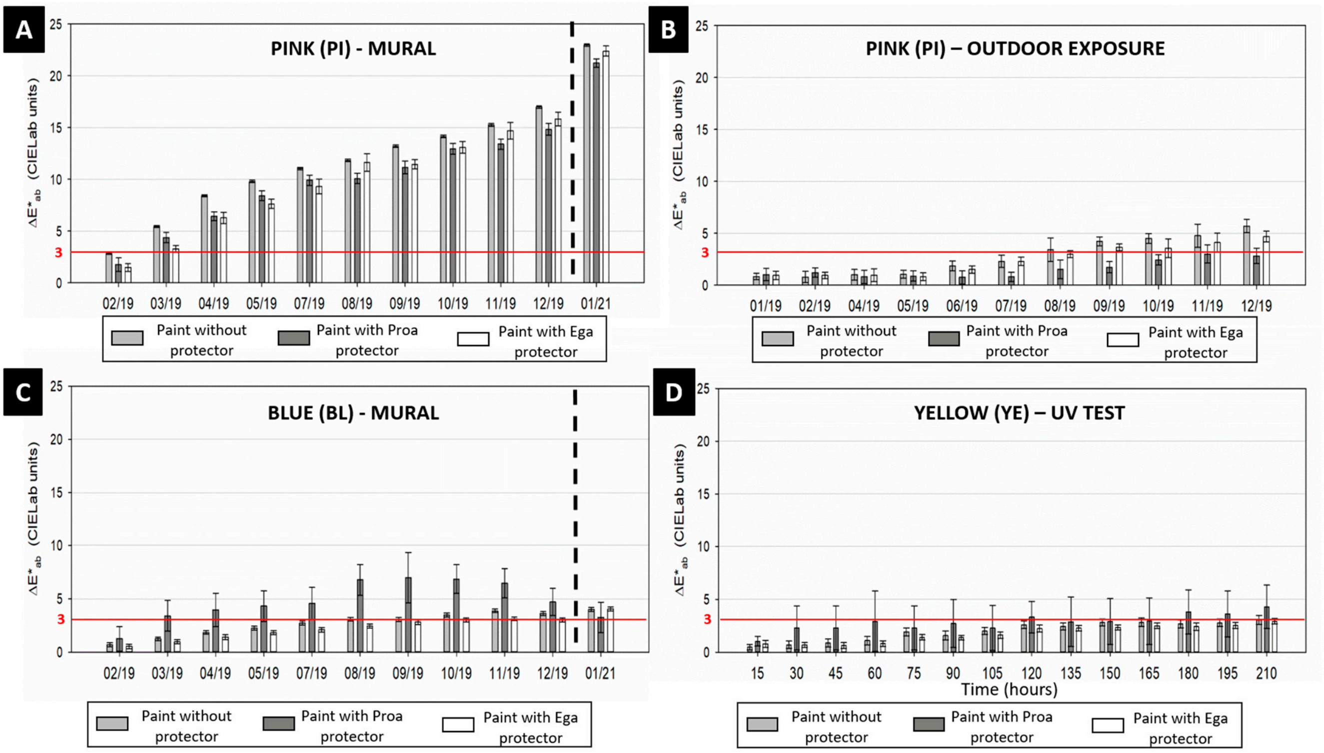

Figure 9. Bar charts showing the temporal evolution of ΔE^*_{ab}. (**A**): pink PI paint in the mural. (**B**): PI paint in the mock-up after outdoor exposure test. (**C**): blue base BLB paint in the mural. (**D**): yellow YE paint after the UV test.

The ΔE^*_{ab} of the OR paint increased gradually during the exposure time in a similar way under the three exposure conditions (mural, outdoor exposure and UV radiation). In the other paints and conditions, the increase in ΔE^*_{ab} did not follow a clear pattern, and in some cases it fluctuated. This occurred in the mural with the BL paint covered with the Proa protector (Figure 9C): the ΔE^*_{ab} increased gradually until 9 months after application, when the ΔE^*_{ab} began to decrease. This fluctuation is related to the deterioration that the Proa protector underwent on this paint. Shortly after application, the protector turned opaque and yellowish in colour, and 9 months after application, it began to become detached from the paintwork (Figure 6C), coinciding with the inflection point in the ΔE^*_{ab} values (Figure 9C). Deterioration of the protective coating was also indicated by the high standard deviation in the measurements, as detachment of the protector is not regular across the whole surface being monitored. High standard deviations in the temporal changes in ΔE^*_{ab} in the YE paint with Proa were also observed (Figure 9D for the UV test) due to the same effect: this protector did not cover the surface of the mock-ups satisfactorily (Figure 4C).

With the aim of studying the possible degradation of the paints and protectors in relation to the total colour differences, two paints were selected for more detailed study of the chemical changes detected by FTIR analysis: the PI paint (belonging to the group of paints for which the greatest changes in colour were observed in the mural) and the YE paint (belonging to the group of paints with smallest changes in colour). The results enable confirmation of the following:

1. Considering only the paints without protector, in the PI paint, the absorption of the bands at 2925 and 2854 cm^{-1} -ν(C-H)-, 1720 cm^{-1} -ν(C=O)- and 1252, 1114 and 1066 cm^{-1} -ν(C-O)-, associated with the polymer, decreased, particularly in the mural samples. The changes therefore corresponded to the intensity of colour changes, which were greater in the mural and lower in outdoor and UV tests. This also occurred in the YE paint (Figure 10A), with the decrease in the absorption of the bands being greater in the mural and lower in the mock-up samples subjected to the UV and outdoor

exposure tests, although these differences are not consistent with the intensity of the colour changes; however, the values obtained were low and similar for the three types of exposure (3.14 ± 0.51 CIELab units for the mural, 3.04 ± 0.43 CIELab units for the mock-up sample in the UV test and 3.42 ± 0.50 CIELab units for the mock-up sample in the outdoor exposure test). In addition, in the spectrum of the YE paint on the mock-up in the UV test, an increase in the absorption band in the -ν(O-H) region (at 3100–3600 cm^{-1}) and a shoulder of the carbonyl absorption extending to wavenumbers above 1750 cm^{-1} were detected (Figure 10A); these observations may be compatible with the formation of oxidation products of the alkyd component [67–69]. In the spectrum of the YE paint there was also a decrease in the absorption of the bands at 1670 cm^{-1} -ν(C=O) amide- and 1515 cm^{-1} -ν(C-N) amide-, with the decrease being greater in the mural; these peaks correspond to azo pigments present in this paint [19,58].

2. The spectra of the paints treated with the Proa protector appeared to remain stable, as no significant changes in relation to the formation of bands were detected; in addition, no new peaks or disappearance of peaks were detected.
3. The following changes were detected in the spectra of the paints treated with the Ega protector: (1) in the PI paint in the mural, the absorption of the band located at 1108 cm^{-1} (corresponding to surfactant) underwent a large decrease (Figure 10B), possibly due to loss of the surfactant [33,64,70], by migration to the surface as the protective coating dried [33,64,70–73], and (2) in both paints and after the three types of tests, a shoulder was observed above 1750 cm^{-1}, corresponding to carbonyl absorption (Figure 10C), indicating photo-oxidation of the protector. This finding may be compatible with the formation of oxidation products such as γ-lactones and anhydrides [74]; the intensity of this shoulder was greater after exposure of the mural and was weaker in the mock-ups after the exposure tests.

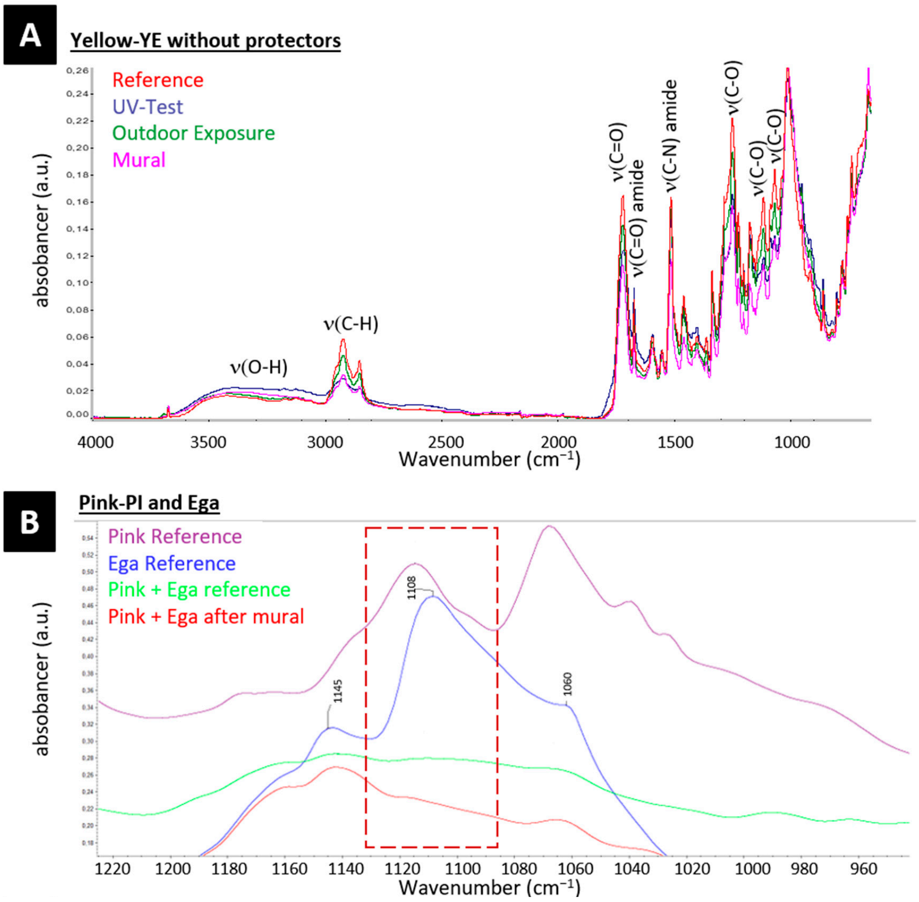

Figure 10. *Cont.*

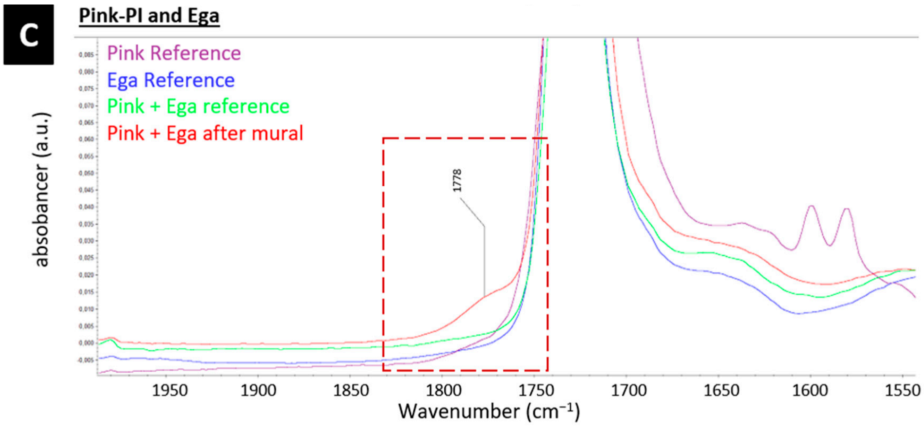

Figure 10. (**A**): FTIR (absorbance) spectra of the yellow YE paint without protector before and after the three exposures; the spectra were normalised to the silicate absorption band at 1018 cm^{-1}, not affected by aging. (**B**,**C**): details of FTIR (absorbance) spectra of the pink (PI) paint and Ega protector in the regions between 1225 and 945 cm^{-1} (**B**) and 1990 and 1540 cm^{-1} (**C**).

4. Conclusions and Future Perspectives

This study evaluated the impact generated by two acrylic-based colour protectors (Proa and Ega) on the colour of six alkyd paints and one acrylic paint and also the durability of the protective performance. The evaluation was conducted in situ, in a real mural, and the results were compared with those obtained in concrete mock-ups subjected to an ultraviolet aging test in the laboratory and to natural exposure in an outdoor environment with marine influence.

Both protectors altered the original colour of the paints, although the impact was much more notable with Proa than with Ega. This occurred in all of the alkyd paints, but not in the acrylic paint (BLB) used in the mural, in which Ega and Proa caused similar changes. This finding indicates that the impact on the colour depends on the chemical composition of the protector and also on the chemical affinity between the paint and the protector: thus, for at least one of the protectors (Proa), application on alkyd paint is not recommended owing to the impact on the colour of the paint. In addition, the formation of craquelure on the Proa (but not Ega) coating also suggests problems related to the physical or chemical affinity between the protective material and the paint. It is also clear that the application conditions (in situ versus laboratory conditions), the complexity of the substrate to which the paint is applied (existence of previous paint layers, type of concrete) and the environmental conditions during the application may contribute to explaining the differences in the degree to which the protectors affect the original colour of the paints under the three different conditions. Thus, Proa had a stronger impact on the mural than on the mock-ups. These results, along with the fact that the performance of Ega is much more difficult to predict, confirm the need to conduct previous colour tests under the same application and environmental conditions and with the same substrate before finally applying the protectors on the artwork. This will enable the selection of the best protectors for each particular paint when the final colour of the selected paints is important to the artists.

The efficacy and durability of the colour protectors were different, but also varied depending on the environmental conditions and the paint tone. In the mural, application of protectors is only recommended for the paints that displayed intermediate susceptibility to colour degradation (GR, YE, BLB); in these cases, the Proa protector appeared to be more effective (except on BLB). The presence of the protective coating on the paints in the mural that displayed extreme susceptibility to colour degradation was totally ineffective, and by contrast, application on the only photostable paint (BR) was completely unnecessary. In the outdoor exposure and UV tests, the fading was much less intense, so that the efficacy of the protectors in retaining the colour of the paint was more evident. Proa was again more effective than Ega, except in specific cases. The results of this part of the study therefore confirm the following: (1) the influence of the chemical composition of the protector and its affinity for the paint: Proa was more effective as a colour protector than Ega in almost all cases, except for the only acrylic paint, for which Ega proved more effective; (2) the clear influence of the susceptibility of the paint to deteriorate on the degree of protection provided by the product: both protectors were totally ineffective for paints that undergo large colour changes, e.g., the PI and OR paints in the mural; (3) the complexity of the environmental conditions in the real mural, defined by multiple deterioration-related factors (temperature, water, soluble salts, wind). Thus, in the mural, a greater deterioration of the colour of the paints without protectors was observed; this deterioration was difficult to prevent with the protectors, which are, in turn, more susceptible to physical deterioration. The presence of abundant salt deposits on the surface of the exposed paints (protected and unprotected), is an invitation to undertake specific studies on the contribution of the crystallisation–hydration processes of soluble salts to the deterioration of urban art paints and to the effectiveness of colour protection products.

The greater efficacy of Proa compared to Ega was also confirmed by FTIR: in the mock-ups with Proa, no significant changes were detected, whereas in the mock-ups with Ega, loss of surfactant was observed and there were signs of photo-oxidation of the polymer. However, examination of the samples by scanning electron microscopy confirmed the physical degradation of both protectors, mainly via loss of adherence to the underlying paint layer.

The convenience of prior evaluation of the colour change generated by the protectors was confirmed, as in some cases the changes in colour can be detected by the human eye. The evaluation should be conducted in the mural itself and under the same conditions of application and environmental and site-specific conditions. The interest in evaluating the performance of these colour protectors under conditions as similar as possible to those in contemporary urban murals was also confirmed. However, the results of this study arouse interest in conducting more detailed investigation of the influence of the chemical affinity between the protectors and the paints. In this respect, the use of simple exposure tests with a small number of variables, such as the UV aging test used in this study, would be the most suitable initial approach.

Given that direct intervention in the materials used in the cultural heritage for their consolidation, waterproofing and/or protection (as is the case) must be reversible, future research considering the removal of the protective coatings for paints would be of great interest.

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