Photo-catalytic degradation of binding media of ultramarine blue containing paint layers. A new perspective on the phenomenon of "ultramarine disease" in paintings.

E. René de la Rie,[a,b] Anne Michelin,[b] Manuela Ngako,[b] Eleonora Del Federico,[c] Chelsey Del Grosso[d]

a University of Amsterdam, Faculty of Humanities, Conservation and Restoration of Cultural Heritage, Johannes Vermeerplein 1, 1071 DV Amsterdam, The Netherlands
b Sorbonne Universités, Centre de recherche sur la conservation (CRC, USR 3224), Muséum national d'Histoire naturelle, Ministère de la Culture et de la Communication, CNRS ; CP21, 36 rue Geoffroy-Saint-Hilaire, 75005 Paris, France.
c Pratt Institute, Department of Mathematics and Science, 200 Willoughby Avenue, Brooklyn, NY 11205, USA
d TU Delft, Faculty of Aerospace Engineering, The Adhesion Institute, Kluyverweg 1, 2629 HS Delft, The Netherlands

Abstract

Failure of ultramarine blue paint layers in historic as well as modern paintings has been reported in the literature many times and is often referred to as "ultramarine disease" or "ultramarine sickness." The pigment itself is known to degrade hydrolytically when exposed to acids, but whether this is the primary cause of the failure remains unclear. This paper describes a study in which ultramarine blue paints using linseed oil and a urea-aldehyde resin as binding media were aged under simulated indoor conditions. The paints were analyzed using reflectance spectroscopy, scanning electron microscopy, and Raman and nuclear magnetic resonance spectroscopy. The urea-aldehyde resin binding medium was analyzed using size exclusion chromatography and Fourier-transform infrared spectroscopy. The study provides evidence of photo-catalytic degradation of binding media of ultramarine blue paint layers via free-radical processes, causing changes in reflectance while the pigment itself remains intact. It is believed that this is the primary process behind the degradation of ultramarine blue paint layers in paintings.

Keywords

Ultramarine disease; photo-catalytic degradation; acid hydrolysis; binder; paint; painting; linseed oil; urea-aldehyde resin; free radical process; hindered amine light stabilizer

Introduction

Fading, “blanching,” “whitening” or “greying” of ultramarine blue in paintings has been reported by many and the term “ultramarine disease” or “ultramarine sickness” has often been used to describe the phenomena, although a clear explanation has never been put forward. There are also many examples of well-preserved ultramarine blue paint layers in paintings that are hundreds of years old. The pigment is known to be sensitive to acids and this has often been offered as the reason for the optical changes, but whether this is true remains unclear.[1]

Boissonnas distinguished between “ultramarine sickness” caused by acids, and discoloration (“blanching”) caused by micro fissures that scatter light.[2] He describes being able to restore the original color by rubbing the painting with a solution of acrylic resin and pine oil. Wyld *et al*. also define true “ultramarine sickness” as discoloration caused by acids, but state that it is rare, possibly due to protection by alkaline lead white, with which it is often mixed. They do mention “blanching” of ultramarine paint layers, specifically in paintings by Claude.[3] Fading of ultramarine paint in paintings by 20th century Swiss artists caused by loss of the oil binder was described by Bosshard.[4] The color could be restored by application of solvent and oil although not with great ease. Klaas described “ultramarine sickness” from the viewpoint of “acid degradation” and “micro cracks” in the binder. He concludes that these micro cracks, causing separation from the pigment particles and hence scattering of light, are the main mechanism responsible for the blanching of the paint, something that apparently had been observed by Pettenkofer as early as 1870.[5] Binding medium degradation in ultramarine blue paints was also noted in a couple of recent studies.[6,7]

Ultramarine blue has been considered light stable but extremely sensitive to acids. Dilute HCl, HNO_3, and H_2SO_4 rapidly destroy the pigment, while producing hydrogen sulfide.[1] Acetic acid attacks the pigment at a much lower rate than mineral acids. Modern synthetic ultramarine is often coated with silica to make it more resistant to acid attack.[8] Both natural (lapis lazuli) and synthetic ultramarine have an aluminosilicate structure known as sodalite with the general formula $[Al_6Si_6O_{24}]_6$ and is a form of zeolite. The aluminosilicate network is known as a β-cage and is capable of encapsulating various chemical species. Within the cage, cations such as K^+ and Na^+, anions such as Cl^- and OH^-, and neutral species such as CO_2 and H_2O may be ‘enclathrated’ or entrapped. The small pore size of the cage (ca. 2 Å) when compared to the molecular radius of these compounds or ions ensures that the enclathrated species remain inside the structural framework.[9,10] The cage traps and stabilizes, specifically in ultramarine blue, the polysulfur radical anions $S_2^{-\cdot}$ and $S_3^{-\cdot}$. The radical anion $S_3^{-\cdot}$ is primarily responsible for the pigment’s blue color. Cations act as counter ions and may also play a role in the color of the pigment.[11,12,13,14] Only at high temperature can the extremely reactive polysulfur radical anions move in and out of the cage. At room temperature, they cannot escape from the sodalite cage due to their size and this explains the stability of the pigment. But the cage is destroyed easily by acids and fading of the pigment as a result of this as well as exposure to alkali has been described in recent publications.[15,16] Loss of color of ultramarine blue paint in 20th century paintings due to removal of aluminum from the cage has also been described.[17]

During a previous study of the stability of paints used for the conservation and restoration of cultural objects it was found that those containing ultramarine blue pigment degraded faster during aging under light than most other paints.[18] In that study, newly developed paints for art conservation prepared using Laropal® A81 (BASF), a low molecular weight urea-aldehyde resin, as a binder were compared to other commonly used retouching media, such as poly(vinyl acetate) and acrylic resins. These are all solvent-based paint binders, that is they are non-crosslinking resins that dry by solvent evaporation. Urea-aldehyde resins are used industrially for the preparation of pigment pastes and have excellent pigment wetting capacity due to the presence of secondary amide groups and other polar functional groups.[19,20] Low molecular weight binding media, with weight-average molecular weights of a few thousand, provide paints with low viscosity. Such paints dry with smoother surfaces that scatter less light and hence give more color saturation than polymeric binders when applied over microscopically rough surfaces. This is important for paints used in the conservation of paintings (retouching paints), where more color saturation may be required for darker passages and in glazes.[21,22] The urea-aldehyde resin paints were deemed stable alternatives for commonly used retouching paints based on natural resins, which are unstable.[23]

The degradation of ultramarine blue containing paints was further investigated in the present study. This paper describes changes observed during accelerated aging under light of paints containing synthetic ultramarine blue, both silica coated and uncoated, prepared with a linseed oil binder, which dries by oxidative polymerization and with a urea-aldehyde resin binder, which dries by solvent evaporation. For comparison, paints with ochre (iron oxide) as pigment and a urea-aldehyde resin binder were also prepared and aged. The paints as well as the unbound pigments were aged in a xenon arc cabinet using simulated indoor conditions, that is by filtering out wavelengths absorbed by window glass (wavelengths below ca. 320 nm). Some aging was also carried out under exclusion of all UV radiation below 400 nm. The paints were analyzed using reflectance spectroscopy in the UV-vis range, scanning electron microscopy (SEM), and Raman and nuclear magnetic resonance (NMR) spectroscopy. Changes in soluble binding media were observed using size exclusion chromatography (SEC) and Fourier-transform infrared spectroscopy (FTIR).

Materials and Methods

Materials

Ultramarine blue paints were prepared especially for this study by Gamblin Artists Colors (www.gamblincolors.com) on a small 3-roll mill. The paints were prepared at relatively high pigment mass concentration (around 60%). The following pigments and binding media were used: ultramarine blue (EP-62) and coated ultramarine blue (Nubicoat HWR – high weather resistant) (www.nubiola.com); Kremer ultramarine blue 45030) (for NMR spectra of acid-degraded ultramarine blue only) (www.kremer-pigmente.com); Hoover 113NO ochre (iron oxide) (www.hoovercolor.com); Tinuvin® 292 (a mixture of *bis*(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate, a hindered amine light stabilizer (HALS) (www.basf.com); urea-aldehyde resin (Laropal® A81) (www.basf.com); refined linseed oil (www.gamblincolors.com).

Unbound (no binder), coated and uncoated ultramarine blue pigment were pressed into pellets. Around 100-150 mg of each pigment was pressed into 13 mm diameter pellets using a Perkin-Elmer hydraulic press using a pressure of 8 t. The pellets were attached to glass slides with double sided tape.

The paints were applied to glass slides using a 4-sided film applicator at a thickness of 60 µm.

Accelerated aging

Accelerated aging under light was carried out in a Xenotest ALPHA+ chamber (www.atlas-mts.com) under simulated indoor conditions, that is by simulating daylight through window glass. The samples were placed on a specimen rack that rotates around a xenon lamp with a 3 mm-thick glass filter (Xenochrome 320), which blocks radiation below 320 nm. Some samples were also aged behind a UV filter blocking radiation below 400 nm. The irradiance level was set to 50 W/m^2 in the range of 300-400 nm. The black-standard temperature (BST) was 59 ± 3 °C, the test chamber temperature (CHT) was 34 ± 3 °C and the relative humidity was 50 ± 2 %. The samples were exposed to light continuously for ca. 1500 hours. Acid-degraded ultramarine blue pigment for NMR studies was prepared by digesting 1 g of pigment in 250 ml of a 25 mM solution of HCl, for 6 hours or until no color change was observed. This was followed by titration to neutrality with 0.5 M Na_2CO_3. The degraded pigment was then gravity filtrated, rinsed with distilled water and dried at 50% RH for one week.

Reflectance Spectroscopy

Diffuse reflectance (DR-UV-vis) spectra were recorded in the range of 250-2500 nm (only data between 300 and 800 nm are reported here) using an Agilent Cary 5000 UV-vis-NIR spectrophotometer equipped with an integrating sphere (polytetrafluoroethylene (PTFE) coating). The specular reflectance component was excluded by an inserted gloss trap. The spot size was 1 cm x 0.5 cm and the spectral resolution was 1 nm. A PTFE white standard (Spectralon® Reflectance Standards, Labsphere Inc.) was used for baseline correction before reflectance measurement.

Raman spectroscopy

Raman spectra were obtained using an InVia Reflex Renishaw® spectrometer equipped with a frequency-doubled Nd:YAG laser emitting at 532 nm and a 1800 grating. Analyses were performed under a Leica x50/0.75 microscope objective in order to focus the beam on a 1 micrometer diameter area. A spectral window between 100 and 3200 cm^{-1} was used and the spectral resolution was 2 cm^{-1}. To avoid thermal degradation of the samples by laser heating, the laser power was kept below 100 μW under x50 objective.

^{27}Al MAS NMR Spectroscopy

^{27}Al nuclear magnetic resonance (NMR) magic angle spinning (MAS) spectra were obtained using a Bruker AV-750 spectrometer (17.6 T) at a larmor frequency of 195.460 MHz. The samples were finely ground and packed into a 4 mm zirconia solid-state NMR rotors. The spectra were obtained with 64 accumulations, a 90º pulse length of 2 μs, and a repetition delay of either 1 or 3 s. The spectral window used was 1276.7 ppm and 4096 points were acquired. The samples were spun at 15 kHz MAS rate. The spectra were processed with an exponential multiplication window function with 100 Hz line broadening.

SEC

Size exclusion chromatography (SEC) of the binder was carried out after re-dissolving the paint in 2-propanol, centrifugation and transfer of the supernatant, followed by evaporation of the solvent. The analysis was done on a Shimadzu Prominence Ultra Fast Liquid Chromatography system equipped with a Shodex GPC LF-804 column (8.0 x 300.0 mm)) and refractive index detector. The samples were dissolved at 1 mg/mL in unstabilized tetrahydrofuran (THF) and run at 1 mL/min with tetrahydrofuran (THF) as the eluent. The instrument was maintained at 40°C.

FTIR

The binder samples used for SEC were also analyzed using attenuated total reflectance - Fourier-transform infrared spectroscopy (ATR-FTIR). The samples were analyzed using a PerkinElmer Spectrum 100 FTIR spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory and a ZnSe crystal. The binder sample solutions were deposited onto the crystal and spectra were collected on the remaining films after solvent evaporation. Data were collected at 16 scans with a resolution of 4 cm^{-1}.

FEG-SEM

Field-emission gun scanning electron microscopy (FEG-SEM) was performed on a JSM-7800F with the PC-SEM version 5.1.0.1 software (JEOL). Small fragments of paint samples were placed on aluminum stubs with double sided carbon tape. In order to minimize charging of the sample surface, the samples were coated with a thin layer of Pt/Pd coating (approximatively 8 nm in thickness). Secondary electron (SE) images were collected at 5 kV with a probe current of ca. 8–10 pA and a working distance of about 4 mm.

Results and Discussion

Unless specifically stated otherwise, the results below are for the *uncoated* pigment. Likewise, unless specifically indicated that a UV filter was used, all aging was done with the UV component of the light source included.

Unbound ultramarine blue pigment

Aging in the xenon arc instrument for ca. 1500 hours of the *unbound* (no binder) ultramarine blue pigment pellets caused virtually no changes in the reflectance spectrum between 300 and 800 nm, whether the pigment is coated or not (Figure 1). The spectra show a broad absorption band centered around 600 nm, which is attributed to $S_3^{-\cdot}$.[11] A slight increase in reflectance around 350 nm can be observed in both cases. The origin of this change is not known but it could be due to breakdown of a small organic impurity.

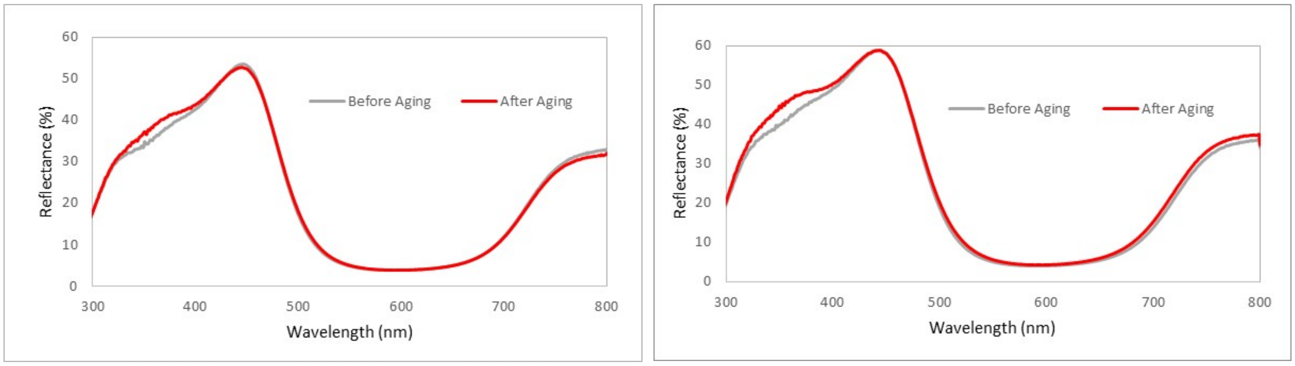

Figure 1 DR-UV-vis reflectance spectra of uncoated (left) and coated (right) unbound ultramarine blue pigment before aging and after aging for ca. 1500 hours in a xenon arc chamber.

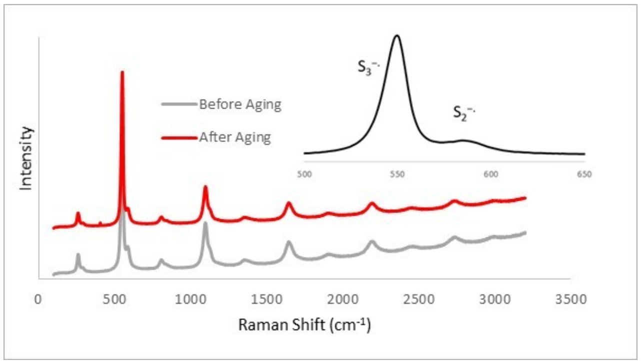

Figure 2 Raman spectra of unbound uncoated ultramarine blue pigment, before aging and after aging for ca. 1500 hours in a xenon arc chamber. The expansion shows the $S_3^{-\cdot}$ and $S_2^{-\cdot}$ bands.

The Raman spectrum of uncoated, *unbound* ultramarine blue pigment show no change after aging (Figure 2). The spectra show the characteristic bands for $S_3^{-\cdot}$ and $S_2^{-\cdot}$ at 550 cm^{-1} and 590 cm^{-1}, respectively, as well as overtone bands. The fact that the spectrum does not change after aging indicates that no change occurs in the makeup of the color centers.[14] The Raman spectrum of the coated ultramarine blue pigment is identical to that of the uncoated pigment and also shows no change after aging (not shown).

Ultramarine blue in linseed oil

Aging of ultramarine blue *paint* prepared with a linseed oil binder produced dramatic changes in the reflectance spectrum (Figure 3). The spectrum of the unaged paint shows low reflectance, in accordance with the low refractive index of the pigment, which approaches that of the binding medium.[1] Despite the dramatic change in the reflectance spectrum no change is observed in the Raman spectrum, indicating that the pigment remains intact (Figure 3).

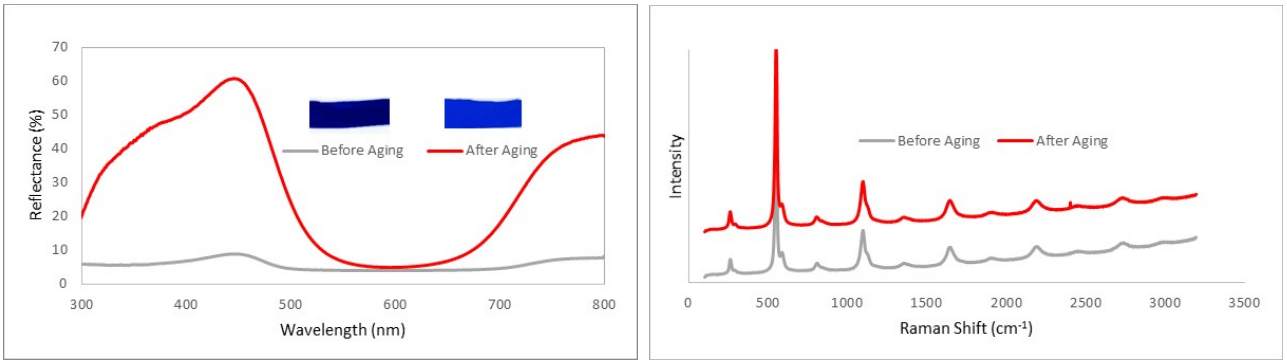

Figure 3 DR-UV-vis reflectance spectra (left) and Raman spectra (right) of ultramarine blue in linseed oil before aging and after aging for ca. 1500 hours in a xenon arc chamber. Photographs of the paints before and after aging have been inserted.

Severe binding medium erosion at the paint surface can be observed in the FEG-SEM images of ultramarine blue in linseed oil, when the surface before aging is compared with that after aging (Figure 4). Before aging, a homogenous film of binder with dispersed pigments can be observed. After aging, this film is not visible anymore and only small remnants of the binder remain at the surface. Erosion of the binder at the surface causes an increase in microscopic surface roughness, light scattering and hence a loss of color saturation. The effect is akin to the removal of a varnish from an old painting, which may expose an eroded surface that scatters light and leaves desaturated colors.[22,22]

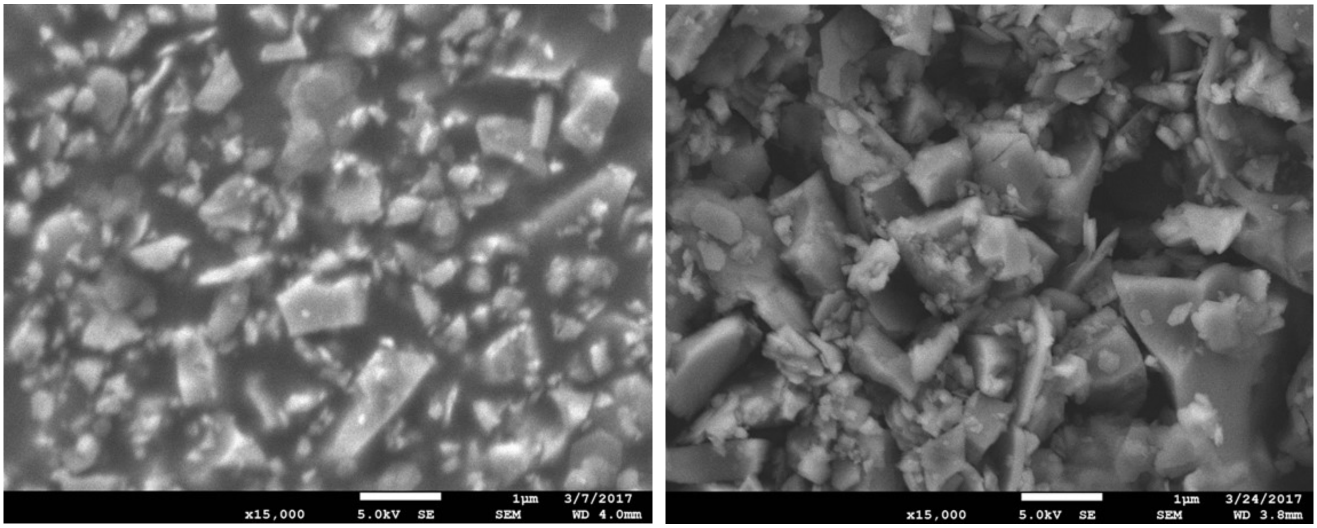

Figure 4 FEG-SEM images of ultramarine blue in linseed oil, before aging (left) and after aging for ca. 1500 hours in a xenon arc chamber (right).

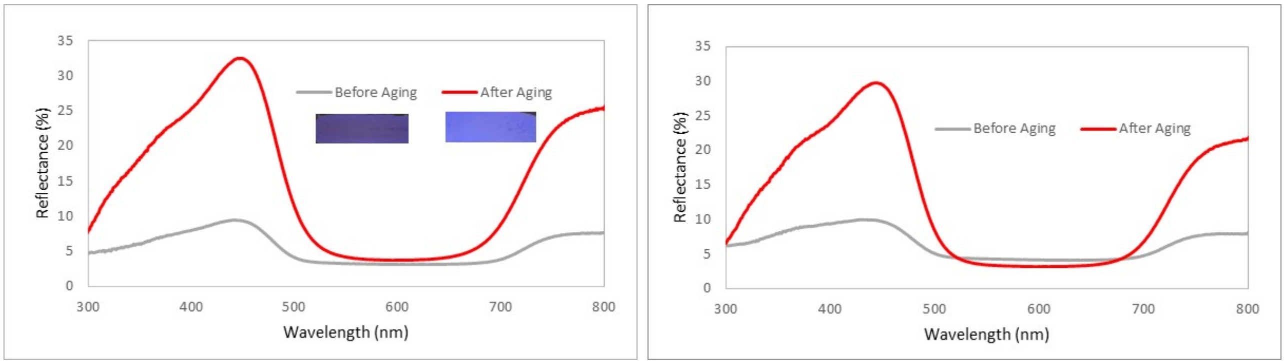

Figure 5 DR-UV-vis reflectance spectra of uncoated (left) and coated (right) ultramarine blue in a urea-aldehyde resin binder before aging and after aging for ca. 1500 hours in a xenon arc chamber. Photographs of the paints before and after aging have been inserted (uncoated pigment only).

Ultramarine blue in urea-aldehyde resin

The phenomena were further investigated using a urea-aldehyde resin binder. Aging of paint prepared using coated and uncoated ultramarine blue pigment in urea-aldehyde resin again caused significant changes in the reflectance spectra. No noteworthy differences were observed between the coated and uncoated pigment upon aging (Figure 5).

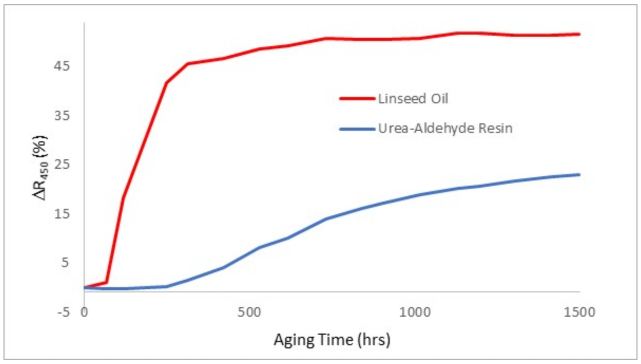

Figure 6 Change in reflectance at 450 nm vs. aging time for ultramarine blue in urea-aldehyde resin and in linseed oil.

The spectrum of the aged paint shows a sharp increase in reflectance and, again, looks more like that of the unbound pigment (Figure 1), suggesting extensive binder degradation. When the increase in reflectance at 450 nm (R(t)-R(0)) is plotted against aging time, it can be observed that there is an induction time of about 250 hours in the case of the urea-aldehyde resin. This induction time is significantly shorter in the case of linseed oil and the change is also much more severe. The maximum value is furthermore reached within a few hundred hours in the case of linseed oil, while the increase is much more gradual in the case of the urea-aldehyde resin (Figure 6).

The Raman spectrum of ultramarine blue in urea aldehyde resin shows no change after aging, despite the substantial change in the reflectance spectra, indicating that the pigment remains unchanged. The spectra (not shown) are identical to that of the unbound pigment and that of the linseed oil paint (Figures 2 and 3).

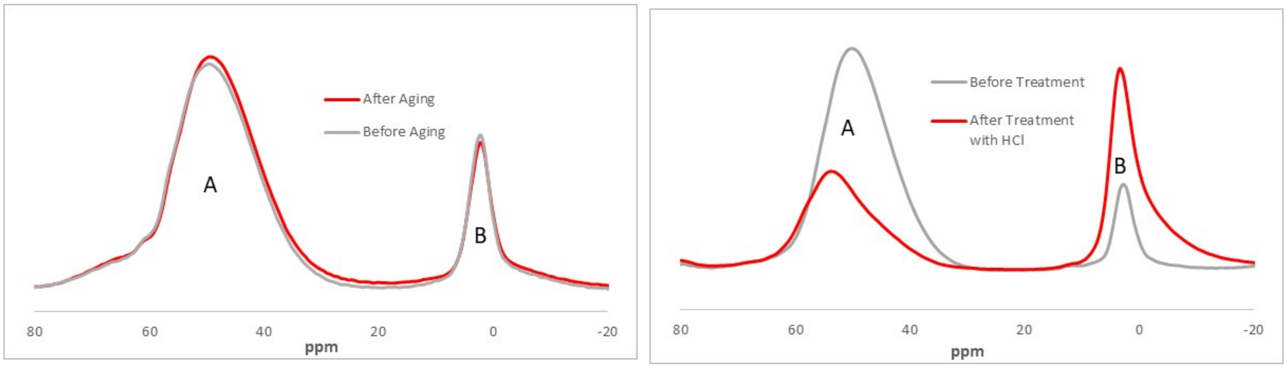

Figure 7 ^{27}*Al NMR MAS spectra of ultramarine blue in a urea-aldehyde resin before aging and after aging for ca. 1500 hours in a xenon arc chamber (left) and ultramarine blue before and after hydrolytic degradation using a dilute HCl solution (right)*

^{27}Al nuclear magnetic resonance (NMR) magic angle spinning (MAS) spectra provide further evidence of the fact that the pigment remains unchanged. The spectra display two broad peaks (Figure 7). The more-intense peak A is characteristic of tetrahedrally-coordinated framework Al, and the less intense peak B is distinctive of octahedrally coordinated non-framework

Al.[24,25] Both peaks are expected to be broad due the presence of the paramagnetic chromophores $S_3^{-\cdot}$ and $S_2^{-\cdot}$ and the fact that ^{27}Al is quadrupolar (spin 5/2).[26,27,28] There is no significant difference between the spectra for the aged and unaged sample, indicating that there is no change in the zeolite framework. Moreover, the fact that there is no change in the linewidth and position of peak A indicates that there is no change in the $S_3^{-\cdot}$ or $S_2^{-\cdot}$ paramagnetic chromophores. The loss of $S_3^{-\cdot}$ and $S_2^{-\cdot}$ would both sharpen peak A and shift it to lower field due to the loss of framework Al in close contact with the paramagnetic chromophores.[16,16] Such a change can be observed when ultramarine blue is exposed to a dilute HCl solution (Figure 7). The hydrolytic degradation leads to an increase of peak B and a decrease, sharpening and left shift of peak A. This is the result of framework destruction along with de-alumination and the loss of the paramagnetic chromophores $S_3^{-\cdot}$ or $S_2^{-\cdot}$.

The size exclusion chromatograms (SEC) of resin extracted from ultramarine blue in a urea-aldehyde resin binder shows a shift to lower molecular weights after aging when compared to the unaged resin, confirming degradation of the resin (Figure 8). Urea-aldehyde resins are known to shift to lower molecular weights upon aging.[20] For Fourier-transform infrared (FTIR) analysis, a small amount of the solution that was also used for the SEC analysis was placed on the attenuated total reflectance (ATR) crystal of the instrument. A spectrum was obtained after solvent evaporation and compared to that of the unaged resin. The spectrum of the aged resin shows significant changes in the carbonyl (1600-1800 cm^{-1}) and hydroxyl (3000-3600 cm^{-1}) regions, indicating oxidation (Figure 8). It must be noted that

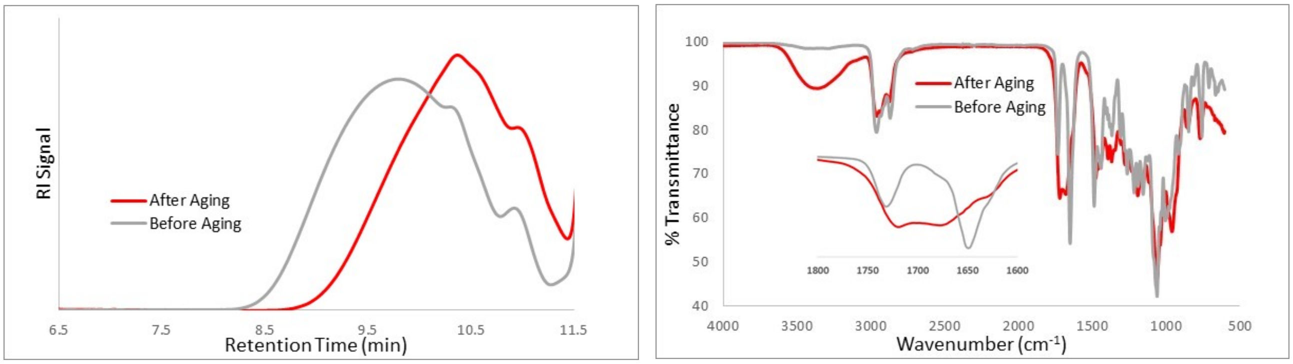

Figure 8 SEC (left) and FTIR spectrum (right) of resin extracted from ultramarine blue in urea-aldehyde resin binder after aging for ca. 1500 hours in a xenon arc chamber, compared to those of unaged urea-aldehyde resin. The insert in the FTIR spectrum shows an expansion of the carbonyl region.

since both the SEC and FTIR analyses were obtained on solvent extracts of the paints, they represent the bulk of the resin and not necessarily the changes occurring at the surface, which may be much more severe. It was necessary to extract the resin from the paint for ATR analysis, as the spectrum of the whole paint sample is dominated by the pigment.

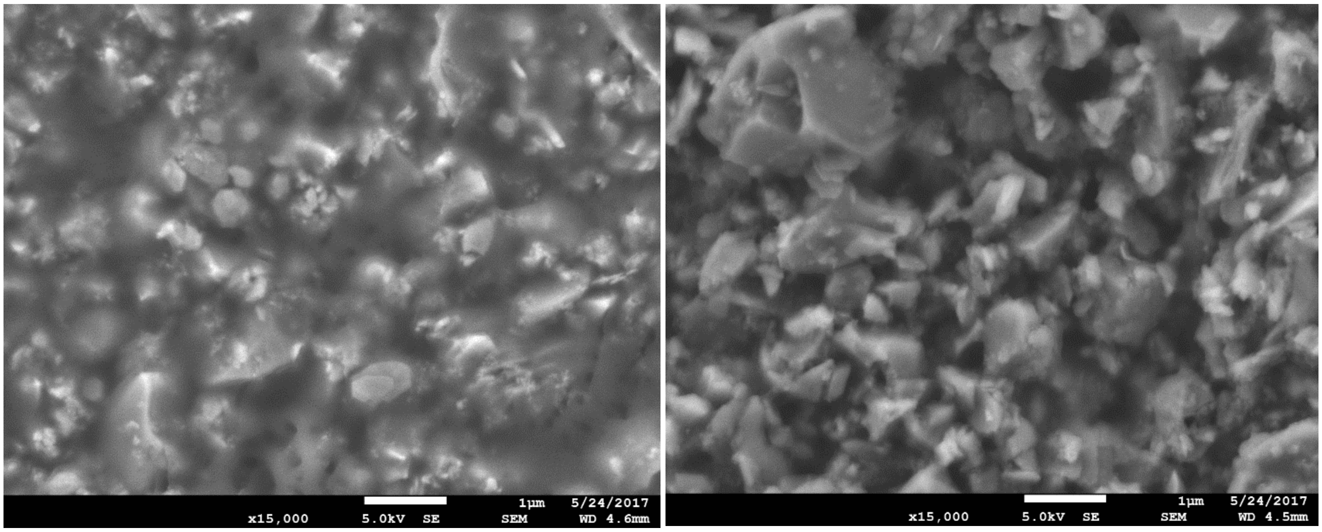

Figure 9 FEG-SEM images of ultramarine blue in urea-aldehyde resin, before aging (left) and after aging for ca. 1500 hours in a xenon arc chamber (right).

Binding medium erosion at the paint surface can be observed in the FEG-SEM images of ultramarine blue in urea-aldehyde resin, when the surface before aging is compared with that after aging (Figure 9). The erosion is similar to that observed with linseed oil (Figure 4) although less severe, in agreement with the respective changes in reflectance (Figures 3, 5 and 6). Binder erosion at the surface again causes an increase in microscopic surface roughness, light scattering and hence a loss of color saturation.

Ultramarine blue in urea-aldehyde resin aged behind a UV filter

When ultramarine blue in urea-aldehyde resin is aged behind a UV filter (eliminating radiation below 400 nm) little change is observed in the reflectance spectrum, indicating that UV radiation is necessary for the degradation to occur (Figure 10).

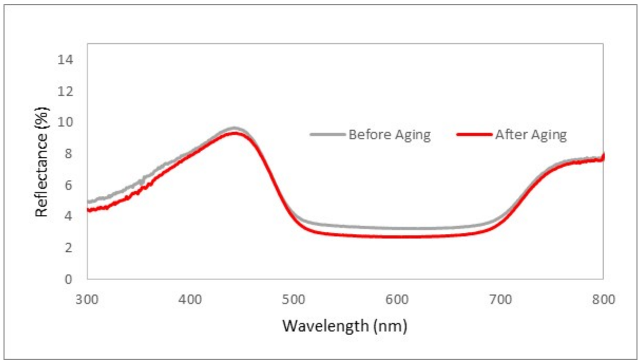

Figure 10 DR-UV-vis reflectance spectra of ultramarine blue in a urea-aldehyde resin binder before aging and after aging for ca. 1500 hours in a xenon arc chamber behind a UV filter.

Ultramarine blue in urea-aldehyde resin with HALS

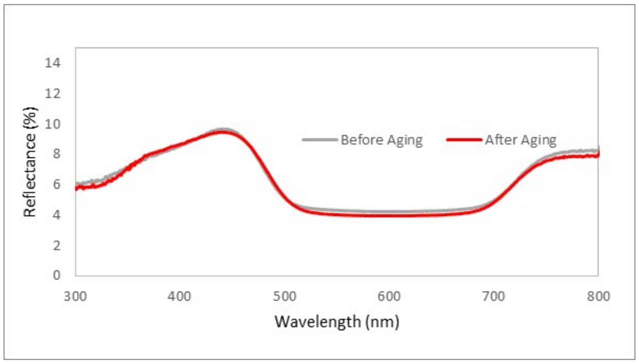

Figure 11 DR-UV-vis reflectance spectra of ultramarine blue in a urea-aldehyde resin with addition of HALS before aging and after aging for ca. 1500 hours in a xenon arc chamber.

To provide evidence that the catalytic action of ultramarine blue is free radical initiated, the hindered amine light stabilizer (HALS) Tinuvin® 292 was added at 1% (weight to weight of binder) to ultramarine blue in urea-aldehyde resin. The reflectance spectrum of this paint shows no change after aging (Figure 11). The SEC and the FTIR spectrum of resin extracted from this paint also show that degradation is largely inhibited by the presence of the HALS. The molecular weight distribution remains largely unchanged and there is little indication of oxidation in the FTIR spectrum (Figure 12). Addition of the free radical scavenger therefore inhibits the ultramarine blue catalyzed degradation, indicating that the process is free radical initiated.

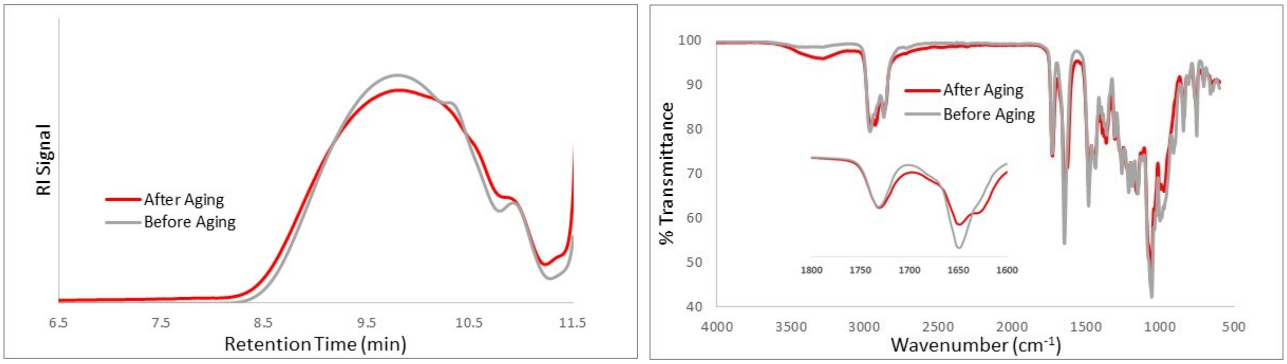

Figure 12 SEC (left) and FTIR spectrum (right) of resin extracted from ultramarine blue in urea-aldehyde resin to which a HALS was added, after aging for ca. 1500 hours in a xenon arc chamber, compared to those of unaged urea-aldehyde resin. The insert in the FTIR spectrum shows an expansion of the carbonyl region.

Ochre (iron oxide) in urea-aldehyde resin

For comparison, paint prepared with ochre (iron oxide) in a urea-aldehyde resin binder was aged under the same circumstances. The reflectance spectrum shows no change upon aging (Figure 13). SEC of resin extracted from the aged ochre paint also shows little change in the molecular weight distribution and only minor changes in the FTIR spectrum (Figure 14). No obvious erosion of binder at the surface is observed after aging in the FEG-SEM images of ochre in urea-aldehyde resin (Figure 15). About as much of the binder film can be observed after aging as before. Ochre, composed of natural iron oxides and not being a photo-catalyst, behaves as an inert pigment and does not generate binder degradation.

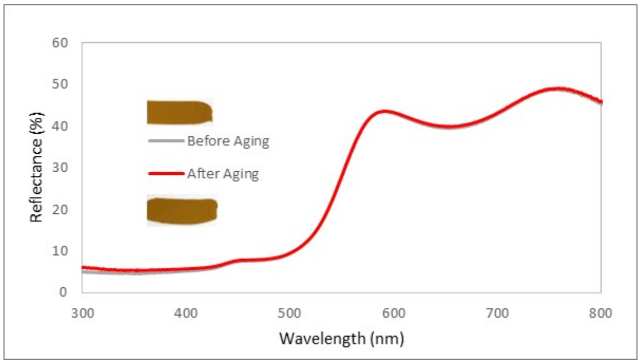

Figure 13 UV-vis reflectance spectra of iron oxide (ochre) in a urea-aldehyde resin binder, before aging and after aging for ca. 1500 hours in a xenon arc chamber. Photographs of the paints before and after aging have been inserted.

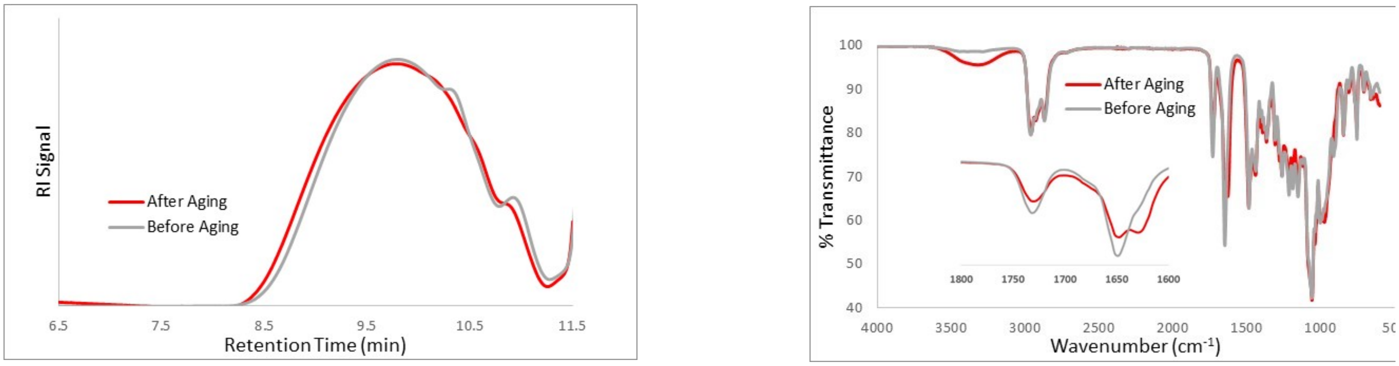

Figure 14 SEC (left) and FTIR spectrum (right) of resin extracted from iron oxide (ochre) in a urea-aldehyde resin after aging for ca. 1500 hours in a xenon arc chamber, compared to those of unaged urea-aldehyde resin. The insert in the FTIR spectrum shows an expansion of the carbonyl region.

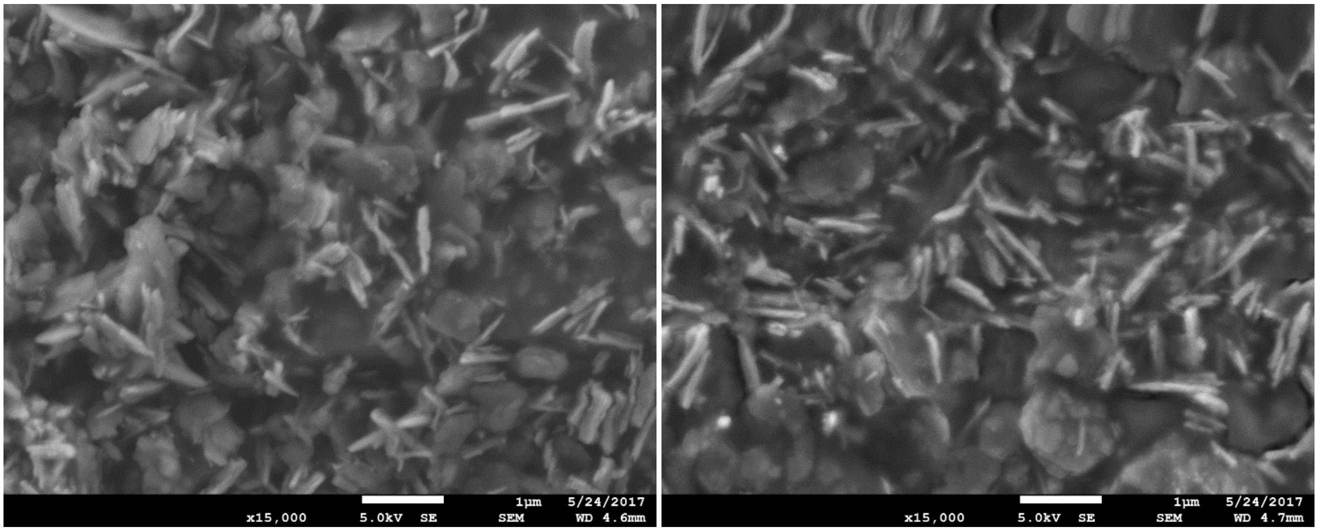

Figure 15 FEG-SEM images of ochre (iron oxide) in urea-aldehyde resin, before aging (left) and after aging for ca. 1500 hours in a xenon arc chamber (right).

General Discussion

From these results, it is clear that ultramarine blue acts as a photo-catalyst and therefore may cause degradation of binding media. Binder degradation causes microscopic roughness and light scattering at the surface, resulting in color desaturation and an appearance that is closer to that of the unbound pigment. It can be compared to the difference between an unvarnished and a varnished painting, albeit in a more extreme form.[21] No changes in the pigment itself could be determined using Raman spectroscopy and NMR.

These results were obtained in a simulated indoor environment (daylight through window glass). The effect may be more severe in an outdoor environment. Addition of a hindered amine light stabilizer (HALS), a free radical scavenger, stops the degradation in the urea-aldehyde resin binder, providing evidence of a free radical process. Furthermore, UV radiation appears to be necessary for the degradation process to occur. The photo-oxidation of urea-aldehyde resins has been investigated previously, as has been the inhibiting effects of antioxidants and other stabilizing additives.[29,19,19] The photo-oxidation of polymers and its inhibition by hindered amine light stabilizers and other stabilizers have been reported widely in the literature.[30] Drying oils such as linseed oil polymerize by means of a free radical oxidative mechanism and therefore already contain reactive oxygen species after drying. These may be further activated by the presence of ultramarine blue.

Whether the polysulfur radical anions trapped in the sodalite cage play a role in the degradation process is, of course, a crucial question. As they are not likely to escape the cage at room temperature, they could only play a role if smaller species are able to move in and out of the cage. However, sodalite, and zeolites in general, are known to catalyze chemical reactions on their surfaces. Many of these are ionic in nature but free radical reactions are known to occur as well. Natural and synthetic aluminosilicate structures, such as zeolites, have been reported to catalytically rupture C-C bonds in hydrocarbons at high temperature via a free radical mechanism and trapped sulfur radical anions have been reported to play a role in this. This is, however, unlikely to occur at room temperature.[31,32] There is in fact overwhelming evidence in the literature for photochemical reactions on zeolite surfaces. Zeolites, with their high surface area, internal active sites and excellent adsorption capability, have been shown to be photo-catalysts without the participation of trapped radical species.[33,34,35] The mechanism of catalytic activity of zeolites is still not completely understood but impurities within the zeolite structures are not essential for their catalytic activity and free radical cations may be formed easily on their surfaces and within their cavities. Free radical anions may also be formed on their surfaces, such as superoxide, $O_2^{-\cdot}$. Free radical reactions induced by UV or visible irradiation have been demonstrated in a great variety of organic molecules and polymers adsorbed onto zeolite surfaces or trapped into their cavities.[36] The channels and pores of zeolites, therefore, facilitate free radical reactions produced by photochemical excitation of absorbed organic molecules. In particular, photochemical reactions of ketones generate reactive carbon-centered radicals.[37]

It can therefore be expected that ultramarine blue catalyzes free radical reactions in molecules adsorbed on the surface of its molecular structure or within its pores. Secondary amide groups in the urea-aldehyde resin molecules, while not normally as photo-active as the ketone group, may be activated when the molecules are adsorbed to the sodalite surface. The resin has other functional groups that may play a role in the process, but its structure is not known in detail.[20] Both linseed oil and urea-aldehyde resin are severely affected by ultramarine blue due to photo-catalytic degradation.

Photo-oxidation of the binding medium of ultramarine blue paint layers is most likely the primary cause of the optical changes known as "ultramarine disease.” Fading of the pigment due to breakdown of the sodalite cage as a result of exposure to acids is much less likely.

Conclusions

Ultramarine blue pigments photo-catalyze paint binding medium degradation when UV radiation is present via a free radical process. This, and not acid hydrolysis, is likely to be the primary cause of the phenomenon generally described as “ultramarine disease” or “ultramarine sickness.” The formation of micro cracks or micro fissures mentioned in the literature can also be explained as being the result of binder degradation. Severe erosion of the binder at the surface leads to light scattering and the observed changes in reflectance. This also explains why the color can be restored by application of oil or resin to the surface. As is evident from these results, the ultramarine blue pigment itself remains intact during photo-oxidation of the binding medium. Hydrolytic breakdown of the pigment itself is much less likely in a non-acidic environment. Coating of the pigment, although probably reducing hydrolytic breakdown of the sodalite cage when exposed to acids, does not inhibit the pigment’s photo-catalytic activity. Inhibition of the process by a hindered amine light stabilizer provides evidence for a free radical process. As the polysulfur radical anions are too large to migrate in and out of the sodalite cage, they can only play a role in the process if smaller species migrate in and out of the cage. A more likely explanation is a free radical process catalyzed at the surface or within the pores of the sodalite cage, for which there is ample evidence in the literature.

Addition of white pigments, such as white lead, to ultramarine blue paint may inhibit binder degradation due to absorption or reflection of UV radiation. This should be further investigated but it may be one explanation for the survival of ultramarine paint layers in many Old Master paintings, in which ultramarine blue was often mixed with a white pigment. Limited exposure to UV radiation may be another reason for the survival of many ultramarine blue containing paint layers.

Exclusion of UV radiation, as is already implemented in many museums, is highly recommended. Incorporation of a hindered amine light stabilizer is recommended for new applications when exposure to UV radiation is anticipated, such as in outdoor settings. This, however, is not a viable option for binding media that dry by an oxidative free radical process, such as drying oils.

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