Application of a Multi-Functional Acrylic-Based Varnish Reinforced with Nanoparticles in the Preservation of Oil Paintings

تطبيق ورنيش أكريلي متعدد الوظائف مدعم بالجزيئات النانوية للحفاظ على اللوحات الزيتية

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Abstract

This study aims to develop an efficient and eco-friendly acrylic-based varnish reinforced with nanoparticles (AVRN) to protect the surfaces of historical oil paintings against light and biodeterioration. Simulated mock-ups (SMs) were used to assess the AVRN, which integrated 5% and 1% nanomaterial (SiO_2/TiO_2) with 7% acrylic varnishes (Paraloid B72/Plexisol P550) in toluene. X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) were used in the characterization of the nanomaterials. SMs were prepared using celadonite, lemon yellow, and ivory black pigments in linseed oil, then thermally aged and treated with four formulas (F1, F2, F3, and F4) of the AVRN. A set of the AVRN-treated SMs was infected by UV-O3, and another set was aged by *P. aeruginosa*, *B. cereus*, and *A. flavus*. SEM, TEM, colorimeter, and inhibition zone were used to assess the efficiency of treatments. The obtained results revealed that the four formulas of the AVRN improved the properties of the treated SMs to varying degrees. The F4 (SMs treated with TiO_2-NPs 1% suspended in Plexisol P550 7%) showed the optimum results, and the F4-treated SMs demonstrated superior stability under UV-O3 and microbial aging. Finally, TiO_2-NPs 1% showed better results than SiO_2-NPs 5%, ivory black showed better stability than celadonite and lemon yellow against aging factors, and Plexisol P550 gave better results in protecting oil painting surfaces than Paraloid B72 at the same concentration. The study recommends the application of the TiO_2-NPs 1% suspended in Plexisol P550 7% for protecting the surfaces of historical oil paintings against light and biodeterioration.

Keywords: Oil painting, Biodeterioration, Acrylic varnishes, Nanoparticles, Colorimeter, Antimicrobial.

الملخص

تهدف هذه الدراسة إلى تطوير ورنيش فعّال وصديق للبيئة قائم على راتنجات الأكريليك ومعزز بمواد نانوية (AVRN) لحماية أسطح اللوحات الزيتية التاريخية من الضوء والتلف البيولوجي. استخدمت الدراسة نماذج محاكاة (SMs) لتقييم AVRN، والذي دُمج 5٪ و1٪ من المواد النانوية (SiO2 / TiO2) مع 7٪ من ورنيش أكريلي (Paraloid B72 / Plexisol P550) في الطولوين. استُخدم حيود الأشعة السينية (XRD) والميكروسكوب الإلكتروني النافذ (TEM) في توصيف المواد النانوية المستعملة. وحُضّر SMs باستخدام المواد الملونة السيلادونيت والأصفر الليموني والأسود العاجي مع زيت بذر الكتان، ثم أُجري التقادم الحراري ومعالجتها بأربع تركيبات (F1 وF2 وF3 وF4) من AVRN. أُجري تقادم مجموعة من SMs المعالجة بـ AVRN باستخدام UV-O3، ومجموعة أخرى باستخدام *P. aeruginosa* و*B. cereus* و*A. flavus*. جرى استخدام الميكروسكوب الإلكتروني الماسح والمجهر الإلكتروني النافذ ومقياس اللون ومساحة التثبيط لتقييم كفاءة المعالجات. أظهرت النتائج التي توصلت إليها الدراسة أن التركيبات الأربع لـ AVRN حسّنت خصائص SMs المعالجة بدرجات متفاوتة. أظهرت F4 (SMs المعالجة بـ TiO2-NPs 1٪ المعلق في Plexisol P550 7٪) أفضل النتائج، وأظهرت SMs المعالجة بـ F4 ثباتًا فائقًا ضد UV-O3 والتلف الميكروبي. أخيرًا، أظهر TiO2-NPs 1٪ نتائج

أفضل من SiO2-NPs 5٪، وأظهر العاج الأسود ثباتًا أفضل من السيلادونيت والأصفر الليموني ضد عوامل التقادم، وأظهر Plexisol P550 نتائج أفضل في حماية أسطح الصور الزيتية من Paraloid B72 بنفس التركيز. توصي الدراسة باستخدام TiO2-NPs 1% المعلقة في Plexisol P550 7% لحماية أسطح اللوحات الزيتية التاريخية من الضوء والتلف البيولوجي.

الكلمات الدالة: اللوحات الزيتية، التلف البيولوجي، الورنيشات الاكريلية، الجسيمات النانوية، مقياس اللون، المقاومة الميكروبية.

1. Introduction

The varnish is the final and finishing layer of the painting and one of the most sensitive layers because of its composition, large surface area, and minimal thickness[1]. Over time, it is likely affected by many deterioration factors, such as dirt, climate, light and colonization of microorganisms, mechanical stresses, and restoration works. These factors result in varying changes, including yellowing, gray discoloration, fine cracks, craquelure, and crazing [2,3]. Although most traditional paintings have a transparent layer of varnish coating, this layer was mainly aesthetic with a limited protective role[4]. The ideal varnish for the painting should remain transparent and colorless in the long term, possess adequate elasticity, provide protection for the paint layer, have suitable mechanical properties of strength and flexibility, be easily cleaned from dust and dirt, and be removable using a gentle nonpolar solvent, if necessary[5] .

Varnishes had been based for centuries on natural products, primarily natural resins, such as mastic and dammar resins. These resins turn yellow over time, eventually lose their transparency, and may crack because they are highly unstable exudates and can be stabilized only under favorable circumstances and to a limited extent using stabilizing additives [6,7]. Therefore, varnishes must be removed and replaced rather often using a harsh treatment that can damage the painting[8]. Several commercially available synthetic resins (e.g., polyvinyl acetate, polyesters, acryloid,

[1] Abd El-Kareem, M. S., Rabbih, M. A. E. F., Selim, E. T. M., Elsherbiny, E. A. E. M., & El-Khateeb, A. Y. *Application of GC/EIMS in combination with semi-empirical calculations for identification and investigation of some volatile components in basil essential oil.* International Journal of Analytical Mass Spectrometry and Chromatography, 2016. 4(1): p. 14-25.

[2] Bergeon, S., *Painting technique: priming, coloured paint film and varnish.* Scientific Examination of Easel Paintings, 1986: p. 35-62.

[3] Lomax, S.Q. and S.L. Fisher, *An investigation of the removability of naturally aged synthetic picture varnishes.* Journal of the American Institute for Conservation, 1990: p. 181-191.

[4] De la Rie, E.R., *Old master paintings: a study of the varnish problem.* Analytical chemistry, 1989. 61(21): p. 1228A-1240A

[5] Knut, N., *The restoration of paintings.* Köln, Könemann, 1999, p:120

[6] Maines, C.A. and E.R. de la Rie, *Size-exclusion chromatography and differential scanning calorimetry of low molecular weight resins used as varnishes for paintings.* Progress in organic coatings, 2005. 52(1): p. 39-45.

[7] Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., & Van Hooydonk, GVa*Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art.* Analytica Chimica Acta, 2000. 407(1-2): pp. 261-274.

[8] Frigione, M. and M. Lettieri, *Novel attribute of organic–inorganic hybrid coatings for protection and preservation of materials (stone and wood) belonging to cultural heritage.* Coatings, 2018. 8(9): p. 319.

ketone) have been investigated for their suitability as varnishing materials[9], and some are used by painting conservators. Over the years, research aimed at finding more stable products[10,11].

Resins and polymers, such as Beva 371, Plexisol P550, and Paraloid B72 (a copolymer of ethyl methacrylate and methyl acrylate), have been commonly used in painting conservation since the 1930s. The biodeterioration of synthetic polymers is of particular concern to conservators when used for the long-term protection of painting collections. The choice of a resin for the conservation of a particular object must be made after considering the properties required for the material in situ[12]. Additives are used to give resins certain characteristics. Some polymers, such as Beva 371, Plexisol P550, and Paraloid B72, are the most frequent retardants for fungal deterioration of linen fabric among the tested polymers. Results showed that these tested polymers can be used to enhance and reinforce the museum linen textiles but not to protect them against fungal deterioration. Therefore, the study recommends being aware of potential biodeterioration problems with these polymers. Attempts should be made to replace these polymers with more resistant ones or to combine them with a fungicide[13]. Consequently, much research addressed the properties of nanocomposites with unique properties resulting from the nano-scale structures. Some investigations showed that nanomaterials could improve the properties of the polymers[14].

In the last decades, coatings, including polymeric nano-composites based on nano-sized inorganic (aluminum oxide, zinc oxide, calcium carbonate, silica, and titanium dioxide) particles dispersed in a polymeric matrix have increasingly become a viable alternative to commercial polymeric coatings for cultural heritage[15,16] due to their superior properties, especially the higher resistance to temperatures, harsh

[9] Carretti, E., L. Dei, and P. Baglioni, *Solubilization of acrylic and vinyl polymers in nanocontainer solutions. Application of microemulsions and micelles to cultural heritage conservation.* Langmuir, 2003. 19(19): p. 7867-7872.

[10] Von der Goltz, M., Proctor, R. G., Whitten, J., Mayer, L., Myers, G., Hoenigswald, A., & Swicklik, M. *Varnishing as part of the conservation treatment of easel paintings*, in *Conservation of Easel Paintings*. 2020, Routledge. p. 654-676.

[11] de la Rie, E.R., *Stability and function of coatings used in conservation.* Polymers in conservation, 1992: p. 62-82.

[12] Horie, C.V., *Materials for conservation*. 2013: Routledge.

[13] Cappitelli, F., E. Zanardini, and C. Sorlini, *The biodeterioration of synthetic resins used in conservation.* Macromolecular bioscience, 2004. 4(4): pp. 399-406.

[14] Kariminejad, M., Zibaei, R., Kolahdouz-Nasiri, A., Mohammadi, R., Mortazavian, A. M., Sohrabvandi, S., & Khorshidian, N., *Chitosan/polyvinyl alcohol/SiO2 nanocomposite films: Physicochemical and structural characterization.* Biointerface Research in Applied Chemistry, 2022. 12(3): p. 3725-3734.

[15] orcione, C.E., R. Manno, and M. Frigione, *Sunlight curable boehmite/siloxane-modified methacrylic nano-composites: An innovative solution for the protection of carbonate stones.* Progress in Organic Coatings, 2016. 97: p. 222-232.

[16] Fufa, S. M., Jelle, B. P., Hovde, P. J., & Rørvik, P. M.*Coated wooden claddings and the influence of nanoparticles on the weathering performance.* Progress in organic coatings, 2012. 75(1-2): p. 72-78.

environments, and flame, being easy-to-apply, being non-toxic, and durable performance[17,18] .

Titanium dioxide (TiO_2) has been studied and tested for the restoration and preservation of cultural heritage materials that need more resistance against corrosion and photocatalytic activity[19]. TiO_2 nanoparticles (NPs) are precious semiconductor transition metal oxides with unique characteristics, such as simple control, low cost, non-toxic, and great resistance to chemical erosion. They have proved to be efficient catalysts for the degradation of organic pollutants[20] and a strong absorber of UV light[21]. Furthermore, they protect the historic structures from biodeterioration (both gram-positive and gram-negative bacteria, fungi, etc.)[22]. Some nano-inorganic particles are demonstrated to have the ability to reduce friction and improve the wear resistance of polymers[23]. One of the nanoparticles that is used to reinforce polymers is SiO_2 which can improve its tribological properties because of its rigidity and high stability. Nano-sized silica powders have widely been used to improve the properties of polymer matrix composite materials[24,25].

Many studies showed that polymeric surface coatings reinforced with different nanoparticles, such as TiO_2, SiO_2, cellulosic nano/macro fillers, and clays, can provide improvements in the mechanical, surface, barrier, and biological properties of the

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[17] Chobba, M. B., Weththimuni, M. L., Messaoud, M., Sacchi, D., Bouaziz, J., De Leo, F., ... & Licchelli, M. *Multifunctional and durable coatings for stone protection based on Gd-doped nanocomposites.* Sustainability, 2021. 13(19): p. 11033.

[18] Zuena, M., Ruggiero, L., Della Ventura, G., Bemporad, E., Ricci, M. A., & Sodo, A., *Effectiveness and compatibility of nanoparticle based multifunctional coatings on natural and man-made stones.* Coatings, 2021. 11(4): p. 480

[19] Rahimi, H.-R. and M. Doostmohammadi, *Nanoparticle synthesis, applications, and toxicity.* Applications of nanobiotechnology, 2019. 10.

[20] Yadav, S. and G. Jaiswar, *Review on undoped/doped TiO2 nanomaterial; synthesis and photocatalytic and antimicrobial activity.* Journal of the Chinese Chemical Society, 2017. 64(1): p. 103-116.

[21] Norbutus, A.J., *New approaches for the preservation of outdoor public murals: The assessment of protective coatings for mural paintings and painted architectural surfaces*. 2012: University of Delaware.

[22] La Russa, M. F., Rovella, N., de Buergo, M. A., Belfiore, C. M., Pezzino, A., Crisci, G. M., & Ruffolo, S. A., *Testing the antibacterial activity of doped TiO2 for preventing biodeterioration of cultural heritage building materials.* International Biodeterioration & Biodegradation, 2014. 96: p. 87-96.

[23] Aly, A. A., Zeidan, E. S. B., Alshennawy, A. A., El-Masry, A. A., & Wasel, W. A., *Friction and wear of polymer composites filled by nano-particles: a review.* World Journal of Nano Science and Engineering, 2012. 2(01): p. 32.

[24] Ai, N. A., Hussein, S., Jawad, M. K., & Al-Ajaj, I .,*Effect of Al2O3 and SiO2 nanopartical on wear, hardness and impact behavior of epoxy composites.* Chemistry and materials Research, 2015. 7(4): p. 34-40.

[25] Dan, S., Bagheri, H., Shahidizadeh, A., & Hashemipour, H., *Performance of graphene Oxide/SiO2 Nanocomposite-based: Antibacterial Activity, dye and heavy metal removal.* Arabian Journal of Chemistry, 2023. 16(2): p. 104450.

coatings [26]. Nanoparticle coatings have been proposed to protect painting from biological and environmental weathering. In addition, enhanced mechanical superficial characteristics (resistance against abrasion and wear), impact strength and fracture toughness, and improved resistance to flame, fire, and moisture can be achieved with the introduction of inorganic nanoparticles in a protective organic coating.[27]

Nano-coatings containing nano-TiO_2 are efficient materials for preventing the bio-deterioration of heritage materials [28] because of their durability, affordability, and ability to photo decompose pollutants under ultraviolet (UV) irradiation due to their toxicity and inhibition mechanism on bacteria and fungi [29,30]. The antibacterial-coated surfaces exhibit high transmittance, excellent mechanical properties, noncytotoxic, and inhibition ratios against *escherichia coli* (gram-negative) and *streptococcus mutans* (gram-positive) of 94.3 and 80.6%[31]. It had been reported that the hydrophobic coating of a methyl-modified silica hybrid fluorinated Paraloid B72 was prepared to protect the brick from the erosion of polluted rainwater and ultraviolet aging. Treated surfaces showed better permeability to water vapor, chemical corrosion, and ultraviolet resistance, helped protect ancient bricks from damage, and reduced repair and replacement costs[32].

Therefore, many efforts have been made to improve its mechanical properties and realize its potential applications. Blending is one of the most effective ways to provide a new and desirable composition for film-forming applications. So, blending of two polymers could benefit the resulting composites, such as good mechanical properties, and can provide more effective protection against abiotic factors[33].

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[26] Oliveira, R. R. D., Oliveira, T. A. D., Silva, L. R. C. D., Barbosa, R., Alves, T. S., Carvalho, L. H. D., & Rodrigues, D. T., *Effect of reprocessing cycles on the morphology and mechanical properties of a poly (propylene)/poly (hydroxybutyrate) blend and its nanocomposite.* Materials Research, 2021. 24: p. e20200372.

[27] Oliveira, R. R. D., Oliveira, T. A. D., Silva, L. R. C. D., Barbosa, R., Alves, T. S., Carvalho, L. H. D., & Rodrigues, D. T., *Photocurable resin/nanocellulose composite coatings for wood protection.* Progress in Organic Coatings, 2017. 106: p. 128-136. 24: p. e20200372.

[28] Azadi, N., H. Parsimehr, and A. Ershad-Langroudi, *Cultural heritage protection via hybrid nanocomposite coating.* Plastics, Rubber and Composites, 2020. 49(9): p. 414-424.

[29]Li u, S., Wang, Q., Liu, W., Tang, Y., Liu, J., Zhang, H., & Wang, L., *Multi-scale hybrid modified coatings on titanium implants for non-cytotoxicity and antibacterial properties.* Nanoscale, 2021. 13(23): p. 10587-10599.

[30] Meenatchisundaram, N., Chellamuthu, J., Jeyaraman, A. R., Arjunan, N., Muthuramalingam, J. B., & Karuppuchamy, S, N., *Biosynthesized TiO2 nanoparticles an efficient biogenic material for photocatalytic and antibacterial applications.* Energy & Environment, 2022. 33(2): p. 377-398.

[31] Wang, K., Bu, N., Zhen, Q., Liu, J., & Bashir, S., *Modified nano-SiO2/TiO2 hybrid fluorinated B72 as antimicrobial and hydrophobic coatings for the conservation of ancient bricks.* Construction and Building Materials, 2023. 365: p. 130090.

[32] Wang, K., Bu, N., Zhen, Q., Liu, J., & Bashir, S.*Methyl-modified silica hybrid fluorinated Paraloid B72 as hydrophobic coatings for the conservation of ancient bricks.* Construction and Building Materials, 2021. 299: p. 123906.

[33] Kariminejad, M., Biointerface Research in Applied Chemistry, 2022. 12(3): p. 3725-3734.

2. Materials and Methods

2.1. Preparation of silica nanoparticles (SiO_2-NPs)

Sodium silicate (Na_2SiO_3), sodium chloride (NaCl), cetyltrimethylammonium bromide (CTAB), hydrochloric acid (37%), and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich, USA. All the purchased chemicals were used without further purification. Microporous SiO_2-NPs were synthesized using sodium metasilicate (SMS) as a precursor and hydrochloric acid through the precipitation method[34]. Four grams of CTAB were dissolved in 200 mL SMS (1.5%), and then the temperature was adjusted to 55°C under constant stirring. In addition, the mixture was treated with HCl at a concentration of 2.5% through two steps. The first step included the addition of HCl dropwise until the formation of semigelatic point, which could be prepared at pH 9-9.5, followed by stirring for a further 10 min without hydrochloric acid addition. The second step included an additional amount of HCl to the previous mixture until the pH value ranged from 3 to 3.5. Furthermore, ten milliliters of NaCl (10%) were added under continuous stirring for an additional 20 min. Finally, the wet gel of the prepared silica was incubated for 24 hrs. at 50°C, followed by washing well using distilled water and centrifugation at 5000 rpm. The prepared silica wet gel was washed completely after removing the chloride ions from the mixture, which was detected using 0.1M $AgNO_3$ solution. The wet gel was then dried using a microwave oven (800 Watts) for 10 min. The drying process was repeated seven times with interval duration of 5 min after each time. The dried silica was calcined for 3 hrs. at 650°C in a furnace and milled to obtain fine powder.

2.2. Preparation of titanium dioxide nanoparticles (TiO_2-NPs)

Titanium tetrachloride (1.5 mL) was added dropwise to ethanol (15 mL). Then, an excess of hydrogen chloride (HCl) was exhausted in the reaction vessel during the mixing step. A light yellow color was then observed, and the solution was gelatinized to obtain solgel. In addition, the solgel was dried at 80 °C until complete dryness, followed by calcination at 600 °C for 3 hrs. to obtain TiO_2-NPs[35].

2.3. Preparation of the AVRN:

Paraloid B72 and Plexisol P550 (supplied by CTS, Italy) were dissolved in pure toluene (supplied by Sigma-Aldrich, USA) with a concentration of 7% using ultrasonic magnetic stirring (Elmasonic S S30H Ultrasonic bath, Germany) for 60 minutes to ensure the complete dissolution of the polymer in the solvent. Then, 1% TiO_2 and 5% SiO_2 were suspended into the prepared solutions of Paraloid B72 and Plexisol P550 to form the

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[34] Abou Abou Rida, M. and F. Harb, *Synthesis and characterization of amorphous silica nanoparitcles from aqueous silicates uisng cationic surfactants.* Journal of Metals, Materials and Minerals, 2014. 24(1).

[35] Zhu, Y., Zhang, L., Gao, C., & Cao, L., *The synthesis of nanosized TiO2 powder using a sol-gel method with TiCl4 as a precursor.* Journal of Materials Science, 2000. 35: p. 4049-4054.

AVRN coating[36]. Both Paraloid B72 and Plexisol P550 are commonly used in treatments of paintings[37] due to their stability in different conditions, and they have good properties for retardation in fungal deterioration[38].

2.4. Preparation of painting simulated mock-ups (SMs)

Many sets of paint-simulated mock-ups (SMs) were made based on the identified components of the case study that were previously studied and published and according to the traditional painting techniques[39], which successfully reproduced the samples after artificial aging. A ground layer made of lead white and animal glue was prepared and then brushed on the linen fabric after sizing with animal glue solution. The pigment layer was obtained by mixing 1 g of celadonite, lemon yellow, and ivory black with 0.5 ml of linseed oil to obtain homogenous mixtures suited to be applied uniformly with brushes on the preparation ground. The samples (1 cm ×3 cm ×1 mm) were prepared[40]. After drying in ambient conditions, the SMs underwent thermally accelerated aging at 105 ± 1°C, away from light[41], using binder ED115 Germany. The duration of the thermal aging process extended for a total of 357 hours, aiming to replicate accelerated aging conditions that simulate prolonged exposure to elevated temperatures [42,43].

2.5. SMs treatment

After preparation and aging, SMs were immersed in the AVRN with different formulas as follows: F1 (SiO_2-NPs 5% + B72 7%), F2 (SiO_2-NPs 5% + P550 7%), F3 (TiO_2-NPs 1% + B72 7%), and F4 (TiO_2-NPs 1% + P550 7%). Different sets of SMs

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[36] Prati, S., Sciutto, G., Volpi, F., Rehorn, C., Vurro, R., Blümich, B., ... & Mazzeo, R.., *Cleaning oil paintings: NMR relaxometry and SPME to evaluate the effects of green solvents and innovative green gels.* New Journal of Chemistry, 2019. 43(21): p. 8229-8238.

[37] Stoveland, L. P., Stols-Witlox, M., Ormsby, B., & Streeton, N. L., *Mock-ups and materiality in conservation research.* 2021.

[38] Zumbühl, S., Knochenmuss, R., Wülfert, S., Dubois, F., Dale, M. J., & Zenobi, R. *A, A graphite-assisted laser desorption/ionization study of light-induced aging in triterpene dammar and mastic varnishes.* Analytical Chemistry, 1998. 70(4): p. 707-715.

[39] Zhang, Y., Eveno, M., Gallier, F., Camaiti, M., Lattuati-Derieux, A., Salvini, A., & Lubin-Germain, N., *Synthesis of novel partially perfluorinated C-glycosides and their application in blanching easel painting restoration.* Journal of Cultural Heritage, 2023. 62: p. 493-500.

[40] Armen, L., *Biodeterioration of acrylic polymers Paraloid B72 and B-44: Report on field trials.* Anatolian Archaeological Studies, 2016. 15: p. 283-289.

[41] Krmpotić, M., Jembrih-Simbürger, D., Siketić, Z., Anghelone, M., & Radović, I. B., *Study of UV ageing effects in modern artists' paints with MeV-SIMS.* Polymer Degradation and Stability, 2022. 195: p. 109769.

[42] Tan, H. and R. Dang, *Review of lighting deterioration, lighting quality, and lighting energy saving for paintings in museums.* Building and Environment, 2022. 208: p. 108608.

[43] Elsayed, Y., Shabana, Y., Elmitwalli, H., Rashad, Y., Sreenivasaprasad, P., & Mabrouk, N., *Analytical Assessment of Some Essential Oils against Common Fungi Isolated from Egyptian Heritage Part I: Textiles and Oil Paintings.* Sci. Cult, 2023. 9: p. 113-125.

immersed in each formula were prepared for testing against UV-O_3 aging and microbial infestation.

2.6. UV-O_3 aging

The aim of UV-O_3 aging is to assess the improvement in a group of SMs after treatment with the AVRN against UV and ozone aging. A high-intensity, low-pressure mercury lamp without an outer envelope with wavelength 184.9 nm model LRF 02971 of 200-watt, 220 volts was used as the UV and ozone source in a special box for 150 hours. The temperature and humidity were at about 30◦C and 50%, respectively. After UV-O_3 aging, the SMs were kept at room temperature for 72 hours before measurement[44].

2.7. Microbial aging

The aim of microbial aging is to assess the improvement in another group of SMs after treatment with the AVRN against *P. aeruginosa* (gram-negative bacteria), *B. cereus* (gram-positive bacteria), and *A. flavus* (fungus). These microbes were chosen based on literature related to the biodeterioration of oil paintings [45,46]. These strains were taken from the Agricultural Biotechnology Dept., Faculty of Agriculture, Damietta University. The cultivation methods were carried out according to the previous studies [47,48]. SMs were inoculated with the tested microbes to assay the improvement of the treated SMs after treatment with the AVRN against microbial growth.

2.8. Characterization of NPs

2.8.1. X-ray diffraction (XRD)

NPs' crystalline nature was determined and characterized using an X-ray diffractometer (Bruker, D8 ADVANCE, Karlsruhe, Germany).

2.8.2. Transmission electron microscopy (TEM)

The size and morphology of the prepared TiO_2-NPs and SiO_2-NPs were characterized using a transmission electron microscope (Talos L 120C, Thermo Fisher, England) at 120 Kev. In addition, the size of the pores inside the synthesized SiO_2-NPs was measured to confirm the synthesis of microporous SiO_2-NPs. In this respect, NPs

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[44] Yasuda K., Okazaki Y., Abe Y. and Tsuga K., Effective UV/ozone irradiation method for decontamination of hydroxyapatite surfaces, Heliyon, 3, e 00372 (2017).

[45] Mabrouk, N., Rashad, Y., Elmitwalli, H., Shabana, Y., Sreenivasaprasad, P., & Elsayed, Y., *Assessment of some green fungicides against fungi isolated from different heritage sites and museums in Egypt.* Scientific Culture, 2023. 9(3): p. 101-112

[46] El sayed, Y., El-Kadi, S., El-Rian, M., & Mabrouk, N., *The efficiency of microbial culture extracts as green antimicrobial products against some microorganisms colonizing the historic oil paintings.* Scientific Culture, 2023. 9(2): p. 127-143

[47] Elsayed, Y.E. and K.A. Sayed-Ahmed, *A Novel Approach of Using Green Synthesized Tellurium Nanoparticles to Protect Historical Oil Paintings from Bacterial Degradation.* Shedet, 2024.

[48] Abou Elmaaty, T., El-Nagare, K., Raouf, S., Abdelfattah, K., El-Kadi, S., & Abdelaziz, E. J. R. A., *One-step green approach for functional printing and finishing of textiles using silver and gold NPs.* RSC advances, 2018. 8(45): p. 25546-25557.

powders were sonicated in ethanol, and then a drop of colloidal solution was loaded on a 400-mesh copper grid, which was coated with an amorphous carbon film. Additionally, the solvents were evaporated at room temperature[49].

2.9. Evaluating the SMs treatments

2.9.1. Antimicrobial activities

The subject of this study scrutinized the antibacterial activity of the SMs by the good diffusion method against *P. aeruginosa*, *B. cereus*, and *A. flavus*[50]. The inhibition zone assays the area around the SMs where microbial growth was inhibited due to the presence of AVRN. The larger the inhibition zone, the stronger the antimicrobial activity[51].

2.9.2. Scanning electron microscopy (SEM)

The surface morphology of synthesized TiO_2-NPs and SiO_2-NPs was examined using a scanning electron microscope SEM (JEOL JSM-6510LB, Tokyo, Japan) attached to the energy dispersive spectrum (EDX) to determine elemental composition.

2.9.3. Transmission electron microscopy (TEM)

The samples were analyzed using the transmission electron microscopy (L120C TEM for life science, ThermoFisher, USA). Initially, the specimens were fixed in a phosphate-buffered 3% glutaraldehyde solution at pH 6.8. Post-fixation was performed with phosphate-buffered 1% osmium tetroxide, followed by dehydration through a graded ethanol series. Mycelial plugs were then embedded in plastic resin. Ultra-thin sections were prepared using a Reichert ultramicrotome, stained with uranyl acetate and lead citrate, and subsequently examined using the TEM.

2.9.4. Color properties

Color measurements were carried out using a spectrophotometer (PCE-CSM 2 Germany) in the CIE Lab color space. Light exposure can degrade pigments, increasing microbial colonization and surface irregularities, which alter light reflection and pigment appearance. Color parameters (L*, a*, b*) were recorded after AVRN treatment, after UV-O3 aging, and after microbial aging. Changes in lightness/ darkness (ΔL), green/red shift (Δa), and blue/yellow shift (Δb) were measured, with ΔE quantifying overall color stability using the formula $\Delta E= (\Delta L)^2+ (\Delta a)^2+ (\Delta b)^2]^{1/2}$ [52].

3. Results and Discussions

[49] Kubavat, K. K., Trivedi, P. G., Ansari, H. I., & Sindhav, G. M., *Green Molecule Mediated Synthesis of Silver Nanoparticles: Antioxidant, Antibacterial, Cytotoxic and DNA Interaction Study.* Chemistry & Biology Interface, 2019. 9(5).

[50] Balouiri, M., M. Sadiki, and S.K. Ibnsouda, *Methods for in vitro evaluating antimicrobial activity: A review.* Journal of pharmaceutical analysis, 2016. 6(2): p. 71-79.

[51] Ruyter, I., K. Nilner, and B. Möller, *Color stability of dental composite resin materials for crown and bridge veneers.* Dental Materials, 1987. 3(5): p. 246-251.

[52] Prodan, D. A., Gasparik, C., Mada, D. C., Miclăuş, V., Băciuţ, M., & Dudea, D., *Influence of opacity on the color stability of a nanocomposite.* Clinical Oral Investigations, 2015. 19(4): p. 867-875.

3.1. Characterization of SiO_2 and TiO_2-NPs

3.1.1. XRD analysis

The XRD patterns of the prepared SiO_2-NPs are presented in Fig. 1. SIO_2-NPs displayed a broad peak, ranging from 19.68° to 27.32°, which referred to the synthesis of amorphous nano silica [53,54]. In addition, the single and weak peak, which appeared at 27.88°, might correspond to a small quantity of crystalline silica. The amorphous NPs could be changed to be in the crystalline phase due to the high stability of the crystalline phase that gave a sharp and strong peak at 27°[55]. The crystallinity of TiO_2-NPs was confirmed using XRD. The peaks obtained around 24.92°, 37.36°, 47.74°, 53.84°, 54.82°, and 62.42° were attributed to the tetragonal crystal planes of (101), (200), (105), (211), and (204), respectively, which agreed with the TiO_2 peaks in the anatase phase (JCPDS file 73-1764)[56].

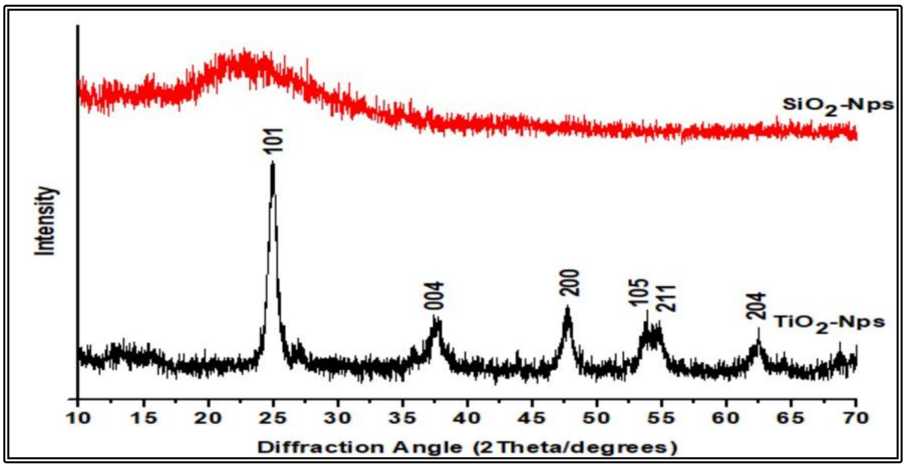

Fig. 1. XRD pattern of the prepared SiO_2-NPs and TiO_2-NPs

3.1.2. TEM analysis

The morphology and size of the synthesized NPs were examined and measured using TEM analysis. The size of the prepared microporous SiO_2-NPs ranged from 15 nm to 120 nm (Fig. 2 a, b, c). Porous materials included three categories based on the diameter range of pores found inside their microstructure as follows: Macroporous (more than 50 nm), mesoporous in the range of 2–50 nm, and microporous (less than

[53] Ghani, N., M.A. Saeed, and I.H. Hashim, *Thermoluminescence (TL) response of silica nanoparticles subjected to 50 Gy gamma irradiation.* Malays J Fundam Appl Sci, 2017. 13(3): p. 178-180.

[54] Tsukimura, K., Miyoshi, Y., Takagi, T., Suzuki, M., & Wada, S. I., *Amorphous nanoparticles in clays, soils and marine sediments analyzed with a small angle X-ray scattering (SAXS) method.* Scientific Reports, 2021. 11(1): p. 6997.

[55] Toro, G., Diab, M., de Caro, T., Al-Shemy, M., Adel, A., & Caschera, D., *Study of the effect of titanium dioxide hydrosol on the photocatalytic and mechanical properties of paper sheets.* Materials, 2020. 13(6): p. 1326.

[56] Jafari, S., Derakhshankhah, H., Alaei, L., Fattahi, A., Varnamkhasti, B. S., & Saboury, A. A., *Mesoporous silica nanoparticles for therapeutic/diagnostic applications.* Biomedicine & Pharmacotherapy, 2019. 109: p. 1100-1111.

2 nm)[57]. Pores observed inside the microstructure of the prepared SiO_2-NPs were in the range of 1-2 nm, confirming the sufficient formation of the microporous SiO_2-NPs. The porous nature of SiO_2-NPs enhanced capillary action more than traditional silica[58]. In addition, the micrographs of TiO_2-NPs obtained from TEM analysis (Fig. 2 d, e, f) showed that their diameters were in the range of 3-17 nm and were spherical. TiO_2-NPs were well dispersed in the colloidal solution.

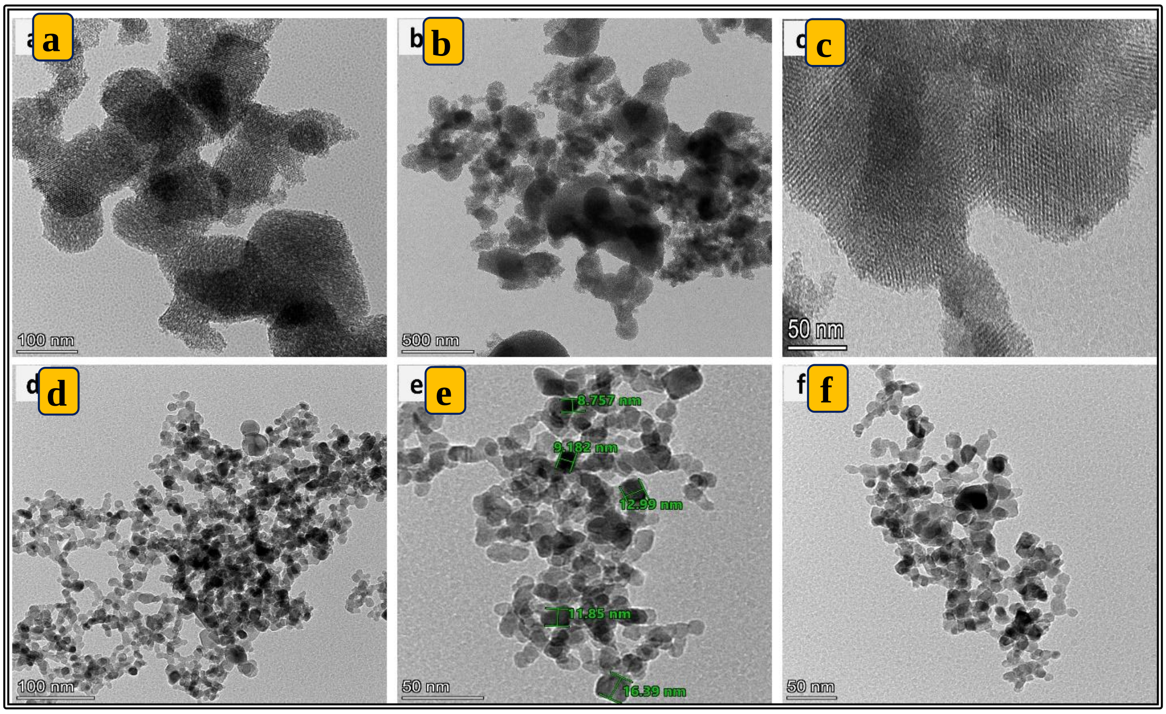

Fig. 2. TEM micrographs of a, b, c; microporous SiO_2-NPs, and d, e, f; TiO_2-NPs at different scales

3.2. Evaluating the SMs treated with AVRN

3.2.1. Antimicrobial activities

The results of the surface morphology of the AVRN-treated SMs after microbial aging are presented in Table 1 and Fig 3. The plate agar method was used to determine the antimicrobial activity. Inhibition zones were carefully measured. All AVRN-treated SMs had inhibitory and killing effects on the growth of different microorganisms, but with various degrees of inhibition and damage according to the type of polymer, nanoparticles, and microbial strain [59,60].

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57 Gu, Y., B. Li, and M. Chen, *An experimental study on the cavitation of water with effects of SiO2 nanoparticles.* Experimental Thermal and Fluid Science, 2016. 79: p. 195-201.

58 Darwish, S., *Microbial studies to evaluate biodeterioration of oil painting and its prevention.* مجلة الإتحاد العام للآثاريين العرب, 2010. 11(1): p. 102-128.

59 Bahaa, A., S. Darwish, and H. Abed el Hamid, *MICROBIAL STUDIES TO EVALUATE BIODETERIORATION OF OIL PAINTING AND ITS PREVENTION.* Magazine General Union of Arab Archaeologists, 2010(11).

60 Patel, B., T. Marar, and M. Bhat, *Study of Biological Activities and Characterization of the Crude Orange Pigment isolated from A Distinct Salinicoccus Sp. MKJ997975.* IOSR J Biotechnol Biochem, 2016. 2: p. 58-61.

The maximum inhibition zone was 702 mm^2 (11.1%) in treatment No. F4 (TiO_2-NPs 1% + P550 7%) against *P. aeruginosa***.** The maximum inhibition zone in the case of *B. cereus* was 396 mm^2 (6.2%) in both F1 (SiO_2-NPs 5% + B72 7%) and F4 (TiO_2-NPs 1% + P550 7%), regarding the optimum results against *A. flavus*. F4 also showed 455mm^2 (7.2%) as the top. The most inefficient treatment was 77mm^2 (1.2%) in the case of F1 against *A. flavus*. The effects of different formulas could be attributed to the specific interactions between the nanoparticles, the polymer matrices, and the microbial cells. Some polymers, such as B72 and Plexisol P550, increased the degree of resistance of coating materials against microbial degradation because the polymers themselves might contain some biocides that played a role in increasing the resistance of the polymer against microbial degradation[61]. After adding nanomaterials, such as SiO_2 and TiO_2, to these polymers, their efficiency increased[62, 63].

Table 1. Antimicrobial performance of SiO_2 / TiO_2 NPs and B72/ Plexisol P550 7%

AVRN treatment	**Antimicrobial activity by inhibition zone**					
	P. aeruginosa		*B. cereus*		*A. flavus*	
	Inhibition zone		Inhibition zone		Inhibition zone	
	mm^2	%	mm^2	%	mm^2	%
F1 (SiO_2-NPs 5% + B72 7%)	225	3.5	372	5.8	77	1.2
F2 (SiO_2-NPs 5% + P550 7%)	308	4.8	396	6.2	110	1.7
F3 (TiO_2-NPs 1% + B72 7%)	476	7.4	352	5.6	377	5.9
F4 (TiO_2-NPs 1% + P550 7%)	702	11.1	396	6.2	455	7.2

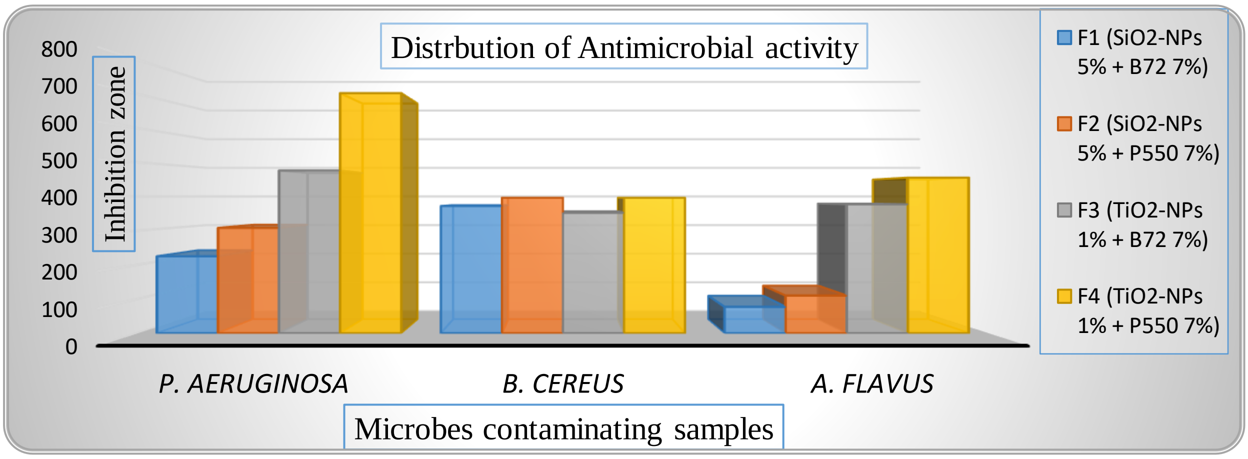

Fig. 3. Distribution ratio of Antimicrobial activity of (AVRN) treatment of SiO_2 / TiO_2 NPs and B72/ Plexisol P550 7% on infested MPs against three microbes' *P. aeruginosa*, *B. cereus* and *A. Flavus* based on the diameter of the inhibition zone (mm) by the agar-well-plate diffusion.

[61] Gunatillake, P., Mayadunne, R., & Adhikari, R. *Recent developments in biodegradable synthetic polymers*. *Biotechnology annual review*, (2006), *12*, 301-347.

[62] Patel, B., T. Marar, and M. Bhat, *Study of Biological Activities and Characterization of the Crude Orange Pigment isolated from A Distinct Salinicoccus Sp. MKJ997975.* IOSR J Biotechnol Biochem, 2016. 2: p. 58-61.

[63] Vroman, I., & Tighzert, L. Biodegradable polymers. Materials, (2009). 2(2), 307-344.

3.2.2. Microscopy results

The most significant SEM and TEM micrographs showing the efficiency of each formula against each microbe were selected. As for the micrographs of *P. aeruginosa* (Fig. 4), the SEM micrographs of the untreated control SMs (Fig. 4a) confirmed the normal growth of *P. aeruginosa* as a filamentous bacterium and implied that it was metabolically active. TEM micrographs revealed a granulated hyphal cytoplasm, which contained numerous lipid bodies[64]. Other AVRN-treated SMs with different formulas showed variant antimicrobial activity against *P. aeruginosa*. F4 (TiO_2-NPs 1% + Plexisol P550) (Fig. 4 a4) showed the optimum antimicrobial activity among all treatments. A complete collapse of organelles, the disappearance of the mitochondria, and lysis in the internal component of the cells were shown due to the efficiency of both nanoparticles and polymer matrix, which proved a useful method for developing tailored antimicrobial treatments[65]. F1 (SiO_2-NPs 5% + B72 7%) showed inefficient antimicrobial activity and little collapsed organelles.

As for the micrographs of *B. cereus* (Fig. 5), the SEM micrographs of the control SMs (Fig. 5 a) confirmed the super bacterial growth of *B. cereus*. TEM micrographs revealed a granulated hyphal cytoplasm and regular bacterial cells. Other SMs treated with the AVRN in different formulas showed variant efficiency against *B. cereus.* F4 (Fig. 5 a4) showed the optimum antimicrobial results. The disappearance of the mitochondria and the rupture in cell walls were observed, which revealed the efficiency of the components of the F4[66]. F1 also showed inefficient antibacterial activity; swollen bacterial cells with slight lysis in internal components were observed. No noticeable morphological alteration was noticed[67].

Regarding the micrographs of *A. flavus* (Fig. 6), the SEM micrographs of the control SMs (Fig. 6a) confirmed the regular fungal growth of *A. flavus*. The cluster of normal conidia with wrinkled surfaces was noted as unaffected ones. TEM micrographs revealed a granulated hyphal cytoplasm and regular bacterial cells. Other SMs treated with the AVRN in different formulas showed variant efficiency against *B. cereus.* F4 (Fig. 6 a4) showed the optimum antifungal activity. The mitochondria disappeared and the hyphae

[64] Elsayed, Y., and Shabana, Y. (2018). The effect of some essential oils on *Aspergillus Niger* and *Alternaria Alternata* infestation in archaeological oil paintings. *Mediterranean Archaeology and Archaeometry*, *18*(3), pp. 71-87

[65] Wang, K., Bu, N., Zhen, Q., Liu, J., & Bashir, S., Construction and Building Materials, 2023. 365: p. 130090.

[66] Zahrouni, A., Benammar, I., Harzallah, O., Bistac, S., & Salhi, R., *Effect of Sol–Gel Derived TiO2-SiO2 Binary Nanoparticles on Thermomechanical Property of Polymer Matrix Composite.* Journal of Inorganic and Organometallic Polymers and Materials, 2023. 33(12): p. 4052-4067.

[67] Zhou, B., X. Zhao, and Y. Liu, *The latest research progress on the antibacterial properties of TiO2 nanocomposites.* The Journal of The Textile Institute, 2024: p. 1-27.

collapsed and twisted due to the efficiency of the TiO_2 and the polymer in the F4[68]. In the case of *A. flavus*, F1 showed inefficient antibacterial activity and intact cell wall and plasma membrane. Normal mitochondria surrounded with debris of lytic organelles were observed[69].

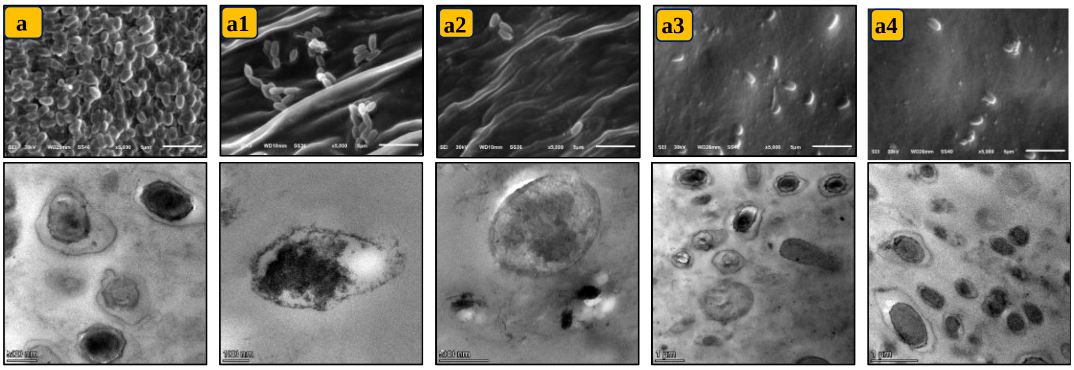

Fig. 4 SEM and TEM micrographs of the *P. aeruginosa* treatments; the control SMs only aged by *P. aeruginosa* (**a**); F1-treated SMs (**a1**); F2-treated SMs (**a2**); F3-treated SMs (**a3**); F4-treated SMs (**a4**) then aged by *P. aeruginosa*

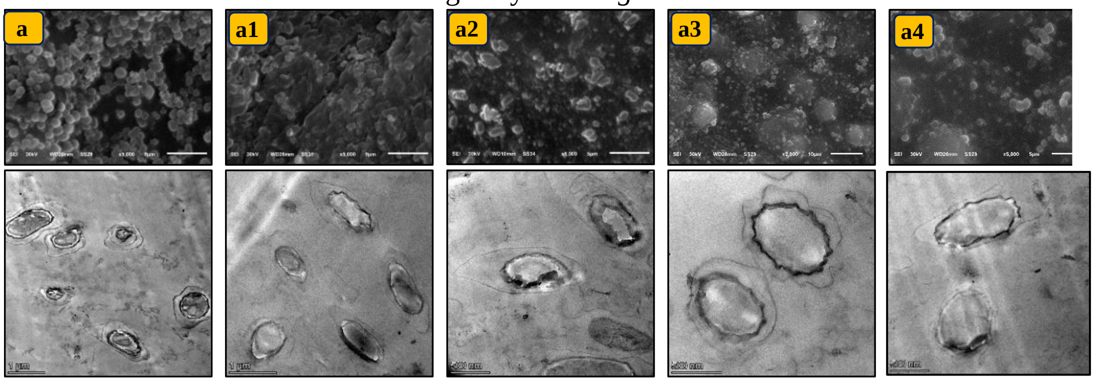

Fig. 5 SEM and TEM micrographs of the *B. cereus* treatments; the control SMs only aged by *B. cereus* (**a**); F1-treated SMs (**a1**); F2-treated SMs (**a2**); F3-treated SMs (**a3**); F4-treated SMs (**a4**) then aged by *P. aeruginosa*

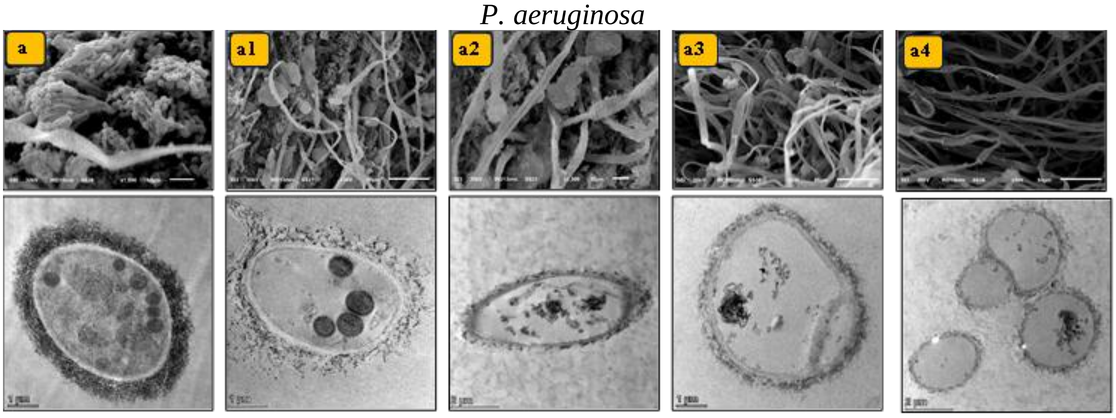

Fig. 6 SEM and TEM micrographs of the *A. Flavus* treatments; the control SMs only aged by *A. flavus* (**a**); F1-treated SMs (**a1**); F2-treated SMs (**a2**); F3-treated SMs (**a3**); F4-treated SMs (**a4**) then aged by *P. aeruginosa*

[68] Elsayed, Y., and Shabana, Y. (2018).
The effect of some essential oils on *Aspergillus Niger* and *Alternaria Alternata* infestation in archaeological oil paintings. *Mediterranean Archaeology and Archaeometry*, *18*(3), pp. 71-87

[69] Timofeeva, L. and N. Kleshcheva, *Antimicrobial polymers: mechanism of action, factors of activity, and applications.* Applied microbiology and biotechnology, 2011. 89: p. 475-492

3.2.3. Color measurements

The results of CIELab color changes (Table 2, Fig 7) showed the color difference (ΔL, Δa, and Δb) and the total color difference (ΔE) of the SMs painted with celadonite, lemon yellow, and ivory black then immersed in the different formulas (F1, F2, F3, and F4) of the AVRN. It is important to understand the effects of the tested microbes and UV-O3 on pigments. The exposure of surfaces to both UV radiation and microbes can lead to accelerated degradation[70,71].

Results of UV-O_3 aging:

The results of UV-O_3 aging revealed that all treatments generally protected the SMs from aging. The total color difference (ΔE) varied generally between the "not detectable" to the "small" chromatic difference. It is known that the values of chromatic difference are classified as follows: 0–1 (not detectable by the human eye), 1–3 (slight chromatic difference), 3–6 (detectable difference), and > 6 (large difference)[72]. The TiO_2-based AVRN (F3 and F4) generally showed better results than the SiO_2-based AVRN (F1 and F2), especially F4, due to the efficiency of both TiO_2 and Plexisol P550 polymers.

Ivory black showed the lowest ΔE values after UV-O_3 aging. Its values varied from 2.02 in F1 to 1.36 in F4. It may reflect the efficiency of TiO_2 NPs and Plexisol P550 in protecting the ivory black color. Moreover, it demonstrates that ivory black is generally stable against light, but longer exposure to UV light can result in some fading or discoloration. In contrast, lemon yellow tended to be more susceptible to fading and color change due to its chemical composition. It is susceptible to light exposure despite the protective effect of different formulas, especially F2, which showed ΔE=2.44, and F1, which showed 4.12. The ΔE results of celadonite showed moderate protective efficiency. Some color shifting commonly appeared depending on the degree of reaction with the environmental effects[73].

Table 2: Colorimetric results of the AVRN-treated SMs after UV-O3 and microbial aging

Pigment	Treatments	After UV-O3 aging				After microbial aging			
		ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
Celadonite	Control	-8.54	5.38	9.3	13.72	-14.03	-10.44	18	25.10
	F1	-3.03	0.5	1.15	3.28	-5.5	5.8	5	9.43
	F2	-1.67	1.67	1.03	2.58	-6	1.4	3.5	7.09
	F3	-1.8	0.69	0.8	2.09	-6.5	2.3	1.12	6.99
	F4	-0.9	0.87	0.5	1.35	-4.9	4.2	0.7	6.49
	Control	13.4	9.33	-8.31	18.32	-23.08	-16.46	16.27	32.69

[70] Fairchild, M.D., *Color appearance models*. 2013: John Wiley & Sons.

[71] Yousif, E. and R. Haddad, *Photodegradation and photostabilization of polymers, especially polystyrene.* SpringerPlus, 2013. 2: p. 1-32.

[72] Drzewinska, E., *Instrumentalna ocena bieli wytworów papierowych.* Przegląd Papierniczy, 2002. 58(12): p. 724-730.

[73] Coccato, A., L. Moens, and P. Vandenabeele, *On the stability of mediaeval inorganic pigments: a literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments.* Heritage Science, 2017. 5: p. 1-25.

Lemon yellow	F1	2.1	2.41	-2.6	4.12	5.7	-5.8	8.3	11.62
	F2	1.4	1.2	-1.6	2.44	7.3	-4.2	4.7	9.64
	F3	1.9	3.08	-1.2	3.81	4.2	-5.4	2.9	7.43
	F4	2.1	1.51	-1.23	2.86	3.2	-4.8	3.9	6.96
Ivory black	Control	-7.64	4.77	-6.29	10.99	-15.98	-12.01	11.39	23.01
	F1	1.25	1.23	-1	2.02	5.7	-2	0.5	6.06
	F2	1.03	1.02	-0.6	1.57	4.5	-2.7	4.2	6.72
	F3	1.2	1.23	-0.5	1.79	3.6	-2.82	3.37	5.68
	F4	0.7	1.05	-0.5	1.36	3.4	-0.8	3.2	4.74

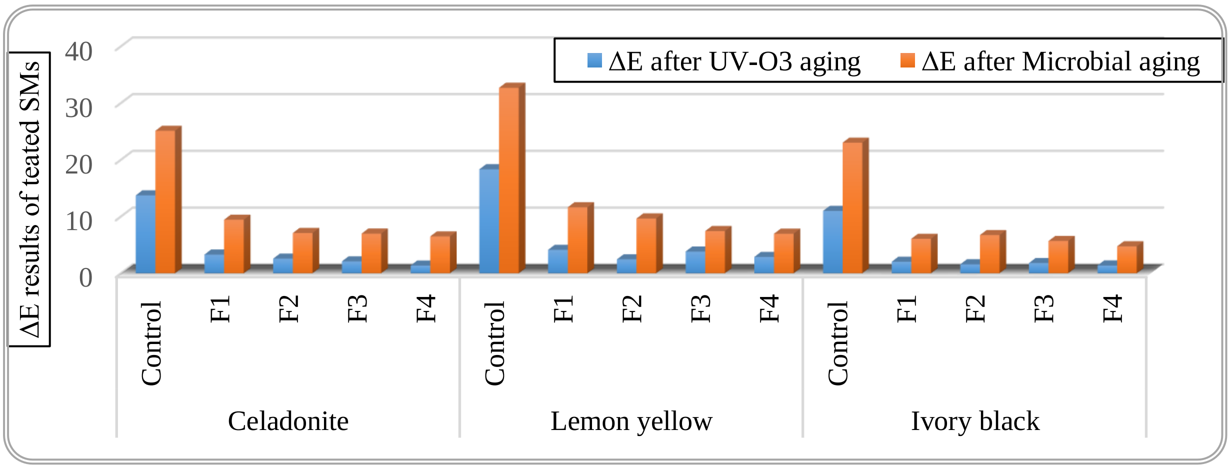

Fig. 7: ΔE results of the AVRN-treated SMs after UV-O_3 and microbial aging

Results of the microbial aging:

It is noteworthy that microbial aging had more crucial effects than UV-O_3 aging. The minimum effects of the microbial aging in ivory black F4 (ΔE=4.74) were stronger than the maximum effects of the UV-O_3 aging in lemon yellow F1 (ΔE=4.12). **Microbial aging** commonly results in material or tangible microbial residues, which increase the color difference. Microbial growth can create an uneven surface that affects light reflection, potentially leading to visible changes in the appearance of the pigment color[74,75].

Ivory black showed the minimum color change after the microbial aging of F4 (ΔE=4.74). This reflects the stability of ivory black pigments against microbial aging in comparison with the tested other pigments. These color differences are commonly attributed to the interaction of microbes with the pigment, which affects its stability and appearance in several ways. Lemon yellow showed the maximum color change after the microbial aging of F1 (ΔE=11.62). This reflects the less stability of lemon yellow

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[74] Pastorelli, G., Cucci, C., Garcia, O., Piantanida, G., Elnaggar, A., Cassar, M., & Strlič, M., *Environmentally induced colour change during natural degradation of selected polymers.* Polymer degradation and stability, 2014. 107: p. 198-209.

[75] Haug, S.P., C.J. Andres, and B.K. Moore, *Color stability and colorant effect on maxillofacial elastomers. Part III:* The Journal of prosthetic dentistry, 1999. 81(4): p. 431-438.

pigment against microbial aging due to the nature and vulnerability of the lemon yellow[76,77].

4. Conclusions

This research highlights the effectiveness of applying Paraloid B72 and Plexisol P550 reinforced with SiO_2 and TiO_2 nanoparticles in protecting oil paintings from UV radiation and microbial contamination. Four treatments (F1, F2, F3, and F4) were evaluated for their efficiency. They showed various degrees of protection against each type of aging. F4 (TiO_2-NPs 1% suspended in Plexisol P550 7%) showed the most effective protection layer, significantly reducing discoloration on coating surfaces, and offering superior defense against tested microbes. This combination proved its efficiency at low concentrations of nanoparticles, reflecting its potential for applications in heritage conservation.

The results demonstrated that ivory black was the most durable pigment, with minimal color change against UV-O_3 and microbial aging. Celadonite had average results, with treatments being more effective against microbial contamination than light exposure. Lemon yellow showed an unacceptable performance, with significant fading and color change under UV rays, due to poor light fastness. Overall, the use of nanoparticle-reinforced varnishes showed a promising ability to protect painting surfaces from microbial aging and color changes and enhance the durability of oil paintings against these environmental factors. These results suggest that incorporating nanoparticles like SiO_2 and TiO_2 into acrylic polymer coatings can substantially improve the preservation of cultural heritage artifacts.

5. Acknowledgments

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6. References

1) Abd El-Kareem, M. S., Rabbih, M. A. E. F., Selim, E. T. M., Elsherbiny, E. A. E. M., & El-Khateeb, A. Y. *Application of GC/EIMS in combination with semi-empirical calculations for identification and investigation of some volatile components in basil essential oil.* International Journal of Analytical Mass Spectrometry and Chromatography, 2016. **4**(1): p. 14-25.

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[76] Aksu, S., Kelleci, O., Aydemir, D., & Istek, A., *Application of acrylic-based varnishes reinforced with nano fillers for conservation of weathered and worn surfaces of the historical and cultural wooden buildings.* Journal of Cultural Heritage, 2022. 54: p. 1-11.

[77] Allen, N., *Photofading and light stability of dyed and pigmented polymers.* Polymer Degradation and Stability, 1994. 44(3): p. 357-374.

2) Abou Elmaaty, T., El-Nagare, K., Raouf, S., Abdelfattah, K., El-Kadi, S., & Abdelaziz, E. J. R. A.*One-step green approach for functional printing and finishing of textiles using silver and gold NPs.* RSC advances, 2018. 8(45): p. 25546-25557.
3) Aksu, S., Kelleci, O., Aydemir, D., & Istek, A., *Application of acrylic-based varnishes reinforced with nano fillers for conservation of weathered and worn surfaces of the historical and cultural wooden buildings.* Journal of Cultural Heritage, 2022. 54: p. 1-11.
4) Alia, J., H. Edwards, and F. Garcia-Navarro, FT-Raman and powder XRD analysis of the Ba (SO4) x (CrO4) 1− x solid solution. Talanta, 1999. 50(2): p. 391-400.
5) Alrubaie, S., Introduction to the contemporary art in Arab land. 2014: AuthorHouse.
6) Al-Sharouni, S., Museum in a book 1ed. Vol. 1. 1998, Egypt: Alshrok House.
7) Aly, A. A., Zeidan, E. S. B., Alshennawy, A. A., El-Masry, A. A., & Wasel, W. A.*Friction and wear of polymer composites filled by nano-particles: a review.* World Journal of Nano Science and Engineering, 2012. 2(01): p. 32.
8) Bellei, S., Multi-analytical approach for the study of modern semiconductor pigments. 2017.
9) Bonaduce, I., Colombini, M. P., Degano, I., Di Girolamo, F., La Nasa, J., Modugno, F., & Orsini, S.*Mass spectrometric techniques for characterizing low-molecular-weight resins used as paint varnishes.* Analytical and Bioanalytical Chemistry, 2013. **405**: p. 1047-1065.
10) Bouchard, M. and D.C. Smith, Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2003. 59(10): p. 2247-2266.
11) Burgio, L. and R.J. Clark, Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2001, 57(7), p. 1491-1521.
12) Burgio, L., A. Cesaratto, and A. Derbyshire, Comparison of English portrait miniatures using Raman microscopy and other techniques. Journal of Raman Spectroscopy, 2012. 43(11): p. 1713-1721.
13) Burnstock, A. and K.J. van den Berg, Twentieth century oil paint. The interface between science and conservation and the challenges for modern oil paint research. Issues in contemporary oil paint, 2014: p. 1-19.
14) Cappitelli, F., THM-GCMS and FTIR for the study of binding media in Yellow Islands by Jackson Pollock and Break Point by Fiona Banner. Journal of Analytical and Applied Pyrolysis, 2004. 71(1): p. 405-415.
15) Cataldi, A., Corcione, C. E., Frigione, M., & Pegoretti, A. , *Photocurable resin/nanocellulose composite coatings for wood protection.* Progress in Organic Coatings, 2017. 106: p. 128-136. 24: p. e20200372.
16) Chaplin, T.D., R.J. Clark, and M. Martinón-Torres, A combined Raman microscopy, XRF and SEM–EDX study of three valuable objects–A large painted leather screen and two illuminated title pages in 17th century books of ordinances of the Worshipful Company of Barbers, London. Journal of Molecular Structure, 2010. 976(1-3): p. 350-359.
17) Chobba, M. B., Weththimuni, M. L., Messaoud, M., Sacchi, D., Bouaziz, J., De Leo, F., & Licchelli, M. *Multifunctional and durable coatings for stone protection based on Gd-doped nanocomposites. Sustainability*, 2021. 13(19): p. 11033.
18) Dan, S., Bagheri, H., Shahidizadeh, A., & Hashemipour, H., *Performance of graphene Oxide/SiO2 Nanocomposite-based: Antibacterial Activity, dye and heavy metal removal.* Arabian Journal of Chemistry, 2023. 16(2): p. 104450.

19) Edwards, H. and M. Falk, Fourier-transform Raman spectroscopic study of frankincense and myrrh. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 1997. 53(13): p. 2393-2401.
20) Edwards, H., D. Farwell, and D. Webster, FT Raman microscopy of untreated natural plant fibres. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 1997. 53(13): p. 2383-2392.
21) Elayed, Y., Shabana, Y., Elmitwalli, H., Rashad, Y., Sreenivasaprasad, P., & Mabrouk, N.*Analytical Assessment of Some Essential Oils against Common Fungi Isolated from Egyptian Heritage* Part I: Textiles and Oil Paintings. Sci. Cult, 2023. 9: p. 113-125.
22) Elsayed, Y., Conservation of a historic panel oil-painting coated with an ancient varnish layer. Shedet, 2019. 6(6): p. 238-256.
23) El sayed, Y., El-Kadi, S., El-Rian, M., & Mabrouk, N. *The efficiency of microbial culture extracts as green antimicrobial products against some microorganisms colonizing the historic oil paintings.* Scientific Culture, 2023. 9(2): p. 127-143
24) Elsayed, Y., Identification of oil media in five canvas paintings at the Agricultural Museum in Egypt. J. of Faculty of Archaeology (Qena), 2015. 10: p. 60-92.
25) Elsayed, Y.E., Identification of the painting materials of a unique easel painting by mahmoud sa'id. Egyptian Journal of Archaeological and Restoration Studies, 2019. 9(2): p. 155-169.
26) Fremout, W. and S. Saverwyns, Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library. Journal of Raman spectroscopy, 2012. 43(11): p. 1536-1544.
27) Fufa, S. M., Jelle, B. P., Hovde, P. J., & Rørvik, P. M.*Coated wooden claddings and the influence of nanoparticles on the weathering performance.* Progress in organic coatings, 2012. **75**(1-2): p. 72-7.
28) Gražėnaitė, E., Inorganic green pigments: investigation of historical and synthesis of novel pigments by sol-gel method. 2018, Vilniaus universitetas.
29) Ielo, I., Galletta, M., Rando, G., Sfameni, S., Cardiano, P., Sabatino, G., ... & Plutino, M. R.. *Design, synthesis and characterization of hybrid coatings suitable for geopolymeric-based supports for the restoration of cultural heritage*. in *IOP Conference Series: Materials Science and Engineering*. 2020. IOP Publishing.
30) Izzo, F.C., 20th century artists' oil paints: a chemical-physical survey. 2011.
31) Jafari, S., Derakhshankhah, H., Alaei, L., Fattahi, A., Varnamkhasti, B. S., & Saboury, A. A.*Mesoporous silica nanoparticles for therapeutic/diagnostic applications.* Biomedicine & Pharmacotherapy, 2019. 109: p. 1100-1111.
32) Kariminejad, M., Zibaei, R., Kolahdouz-Nasiri, A., Mohammadi, R., Mortazavian, A. M., Sohrabvandi, S., & Khorshidian, N*Chitosan/polyvinyl alcohol/SiO2 nanocomposite films: Physicochemical and structural characterization.* Biointerface Research in Applied Chemistry, 2022. **12**(3): p. 3725-3734.
33) Keune, K. and J.J. Boon, Imaging secondary ion mass spectrometry of a paint cross section taken from an early Netherlandish painting by Rogier van der Weyden. Analytical Chemistry, 2004. 76(5): p. 1374-1385.
34) Krmpotić, M., Jembrih-Simbürger, D., Siketić, Z., Anghelone, M., & Radović, I. B.., *Study of UV ageing effects in modern artists' paints with MeV-SIMS.* Polymer Degradation and Stability, 2022. 195: p. 109769.
35) Kubavat, K. K., Trivedi, P. G., Ansari, H. I., & Sindhav, G. M.*Green Molecule Mediated Synthesis of Silver Nanoparticles: Antioxidant, Antibacterial, Cytotoxic and DNA Interaction Study.* Chemistry & Biology Interface, 2019. 9(5).
36) Kühn, H. and M. Curran, Chrome yellow and other chromate pigments, in Artists' pigments; A handbook of their history and characteristics. 1986. p. 187-217.

37) La Russa, M. F., Rovella, N., de Buergo, M. A., Belfiore, C. M., Pezzino, A., Crisci, G. M., & Ruffolo, S. A., *Nano-TiO2 coatings for cultural heritage protection: The role of the binder on hydrophobic and self-cleaning efficacy.* Progress in Organic Coatings, 2016. 91: p. 1-8.
38) Li u, S., Wang, Q., Liu, W., Tang, Y., Liu, J., Zhang, H., & Wang, L., *Multi-scale hybrid modified coatings on titanium implants for non-cytotoxicity and antibacterial properties.* Nanoscale, 2021. 13(23): p. 10587-10599.
39) Li, T., Fan, Y., Wang, K., Song, S., Liu, X., Bu, N., & Bashir, S.*Methyl-modified silica hybrid fluorinated Paraloid B72 as hydrophobic coatings for the conservation of ancient bricks.* Construction and Building Materials, 2021. 299: p. 123906.
40) Lomax, S.Q. and T. Learner, A review of the classes, structures, and methods of analysis of synthetic organic pigments. Journal of the American Institute for conservation, 2006. 45(2): p. 107-125.
41) Mabrouk, N., Rashad, Y., Elmitwalli, H., Shabana, Y., Sreenivasaprasad, P., & Elsayed, Y., *Assessment of some green fungicides against fungi isolated from different heritage sites and museums in Egypt.* Scientific Culture, 2023. 9(3): p. 101-112
42) McLeave, H., The Last Pharaoh: Farouk of Egypt. (No Title), 1970.
43) Meenatchisundaram, N., Chellamuthu, J., Jeyaraman, A. R., Arjunan, N., Muthuramalingam, J. B., & Karuppuchamy, S, N., *Biosynthesized TiO2 nanoparticles an efficient biogenic material for photocatalytic and antibacterial applications.* Energy & Environment, 2022. 33(2): p. 377-398.
44) Mills, J. and R. White, Organic chemistry of museum objects. 2012: Routledge.
45) Nakamoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds: Theory and applications in inorganic chemistry. 2008: Wiley.
46) Oberlin, A., Carbonization and graphitization. Carbon, 1984. 22(6): p. 521-541.
47) O'Hanlon, G., Green Earth Pigments in Art—Uses, Properties and Colors.
48) Oliveira, R. R. D., Oliveira, T. A. D., Silva, L. R. C. D., Barbosa, R., Alves, T. S., Carvalho, L. H. D., & Rodrigues, D. T., *Effect of reprocessing cycles on the morphology and mechanical properties of a poly (propylene)/poly (hydroxybutyrate) blend and its nanocomposite.* Materials Research, 2021. 24: p. e20200372.
49) Panaitescu, D., Ciuprina, F., Iorga, M., Frone, A., Radovici, C., Ghiurea, M., & Plesa, I.*Effects of SiO2 and Al2O3 nanofillers on polyethylene properties.* Journal of Applied Polymer Science, 2011. 122(3): p. 1921-1935.
50) Pastorelli, G., Cucci, C., Garcia, O., Piantanida, G., Elnaggar, A., Cassar, M., & Strlič, M., *Environmentally induced colour change during natural degradation of selected polymers.* Polymer degradation and stability, 2014. 107: p. 198-209.
51) Prasad, P., A. Pradhan, and T. Gowd, In situ micro-Raman investigation of dehydration mechanism in natural gypsum. Current Science, 2001: p. 1203-1207.
52) Prati, S., Sciutto, G., Catelli, E., Ashashina, A., & Mazzeo, R., *Development of innovative embedding procedures for the analyses of paint cross sections in ATR FITR microscopy.* Analytical and bioanalytical chemistry, 2013. 405: p. 895-905
53) Prati, S., Sciutto, G., Volpi, F., Rehorn, C., Vurro, R., Blümich, B., ... & Mazzeo, R. *Cleaning oil paintings: NMR relaxometry and SPME to evaluate the effects of green solvents and innovative green gels.* New Journal of Chemistry, 2019. 43(21): p. 8229-8238.
54) Prodan, D. A., Gasparik, C., Mada, D. C., Miclăuş, V., Băciuţ, M., & Dudea, D., *Influence of opacity on the color stability of a nanocomposite.* Clinical Oral Investigations, 2015. 19(4): p. 867-875.
55) Rossell, J., B. King, and M.J. Downes, Detection of adulteration. Journal of the American Oil Chemists' Society, 1983. 60(2Part2): p. 333-339.

56) SCHILLING, M.R. and H.P. KHANJIAN, GAS CHROMATOGRAPHIC ANALYSIS OF AMINO ACIDS AS ETHYL CHLOROFORMATE DERIVATIVES. 1996.
57) Smith, G.D. and R.J. Clark, Raman microscopy in archaeological science. Journal of archaeological science, 2004. 31(8): p. 1137-1160.
58) Smith, G.D. and R.J. Clark, Raman microscopy in art history and conservation science. Studies in Conservation, 2001. 46(sup1): p. 92-106.
59) *Stoveland, L. P., Stols-Witlox, M., Ormsby, B., & Streeton, N. L.., Mock-ups and materiality in conservation research.* 2021.
60) Toro, G., Diab, M., de Caro, T., Al-Shemy, M., Adel, A., & Caschera, D.., *Study of the effect of titanium dioxide hydrosol on the photocatalytic and mechanical properties of paper sheets.* Materials, 2020. 13(6): p. 1326.
61) Tosatti, B.S., Trattati medievali di tecniche artistiche. Vol. 778. 2007: Editoriale Jaca Book.
62) Tsukimura, K., Miyoshi, Y., Takagi, T., Suzuki, M., & Wada, S. I., *Amorphous nanoparticles in clays, soils and marine sediments analyzed with a small angle X-ray scattering (SAXS) method.* Scientific Reports, 2021. 11(1): p. 6997.
63) Van den Berg, J., Analytical chemical studies on traditional oil paints. Amsterdam: University of Amsterdam, 2002.
64) Van Den Berg, J.D., K.J. Van Den Berg, and J.J. Boon. Chemical changes in curing and ageing oil paints. in Triennial meeting (12th), Lyon, 29 August-3 September 1999: preprints. Vol. 1. 1999.
65) Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., & Van Hooydonk, GVa*Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art.* Analytica Chimica Acta, 2000. **407**(1-2): p. 261-274.
66) Von der Goltz, M., Proctor, R. G., Whitten, J., Mayer, L., Myers, G., Hoenigswald, A., & Swicklik, M. *Varnishing as part of the conservation treatment of easel paintings*, in *Conservation of Easel Paintings*. 2020, Routledge. p. 654-676.
67) Wang, K., Bu, N., Zhen, Q., Liu, J., & Bashir, S.*Modified nano-SiO2/TiO2 hybrid fluorinated B72 as antimicrobial and hydrophobic coatings for the conservation of ancient bricks.* Construction and Building Materials, 2023. 365: p. 130090.
68) Zahrouni, A., Benammar, I., Harzallah, O., Bistac, S., & Salhi, R.., *Effect of Sol–Gel Derived TiO2-SiO2 Binary Nanoparticles on Thermomechanical Property of Polymer Matrix Composite.* Journal of Inorganic and Organometallic Polymers and Materials, 2023. 33(12): p. 4052-4067.
69) Zhang, Y., Eveno, M., Gallier, F., Camaiti, M., Lattuati-Derieux, A., Salvini, A., & Lubin-Germain, N. *Synthesis of novel partially perfluorinated C-glycosides and their application in blanching easel painting restoration.* Journal of Cultural Heritage, 2023. 62: p. 493-500.
70) Zhu, Y., Zhang, L., Gao, C., & Cao, L., *The synthesis of nanosized TiO2 powder using a sol-gel method with TiCl4 as a precursor.* Journal of Materials Science, 2000. 35: p. 4049-4054.
71) Zuena, M., Ruggiero, L., Della Ventura, G., Bemporad, E., Ricci, M. A., & Sodo, A., *Effectiveness and compatibility of nanoparticle based multifunctional coatings on natural and man-made stones.* Coatings, 2021. 11(4): p. 480.
72) Zumbühl, S., Knochenmuss, R., Wülfert, S., Dubois, F., Dale, M. J., & Zenobi, R. *A graphite-assisted laser desorption/ionization study of light-induced aging in triterpene dammar and mastic varnishes*. Analytical Chemistry, 70(4), 707-715.