Characterization of morphological and chemical changes

at micro- and nano- scale in contemporary paintings treated with biocides

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Abstract: The growing problems of biodeterioration undergone by commercial artists' paints have increasingly required the application of biocide treatments on contemporary artworks. In most cases, commercial biocides, which have not been created for the purpose of being used in the field of art conservation, are applied in the dosages recommended by the manufacturer without control on the effects of their application on the artwork. From this, a study has been conducted aimed to evaluate the changes induced by the biocide on contemporary paintings of acrylic and PVAc type. Two biocides have been considered, namely, Biotin T® and Preventol RI80®. Chemical changes have been identified by using FTIR spectroscopy and UV-VIS spectrophotometry. The morphological study at micro-scale has been performed by using optical microscopy and SEM-EDX. In a second step chemical and morphological changes at nano-scale have been characterized by using, at first time in the field of the analysis of artworks, the novel technique of electrochemical atomic force microscopy (AFM). Some of the most significant changes observed by microscopy were: appearance of spots and alteration of the brightness of the paint film, as well as, deposits of biocide. A notable delay in the coalescence phase of drying of the acrylic polymer used as binding media was recognized by means of AFM. Spectroscopic analysis results suggest that the application of the biocide causes a significant migration of additives to the surface from the *core* film.

Keywords: biocide, acrylic paints, PVAc paints

Introduction

The major concerns in the field of conservation and restoration of contemporary paintings are all based on the premise not to know precisely how the paint films based on acrylic and polyvinyl acetate (PVAc) type, are formed, and as a result is not known how they interact with the environment and the materials used by conservators in subsequent cleaning and consolidation methods (WITHMORE and COLALUCCA, 1995; LEARNER 2001; LEARNER 2003; OSETE and DOMÉNECH 2006; DOMÉNECH *et al*., 2008; SILVIA *et al.*, 2010). The general issues that arise for a restorer include: the dirt trap capacity of the acrylic mediums, the sensitivity to water and solvents and the growth of microorganisms. Other aspects considered by restorers refer to the loss of low molecular weight species present in the paint films which, in most cases have not been identified, but that are probably surfactants and other additives (PLOEGER *et al*., 2006; WITHMORE *et al.*, 2006; ORMSBY *et al.*, 2006; DOMÉNECH *et al.*, 2010).

The growing problems of biodeterioration undergone by commercial artists' paints have increasingly required the application of biocide treatments on contemporary artworks. In most cases, commercial biocides, which

have not been created for the purpose of being used in the field of art conservation, are applied in the dosages recommended by the manufacturer without control on the effects of their application on the artwork. In many cases can cause significant morphological and chemical damage to the paint surface resulting in chromatic alterations, by the precipitation of the product which changes the visual appearance. (KOESTLER 1988; HEYN 1995; ABDEL-KAREEM 2000; CAPITELLI 2005; DOMÉNECH *et al*., 2007; DOMÉNECH *et al*., 2009)

From this, a study has been conducted aimed' to evaluate the changes induced by the biocide on contemporary paintings of acrylic and PVAc type. Two biocides have been considered, namely, Biotin T® and Preventol RI80®. Chemical changes have been identified by using FTIR spectroscopy and UV-VIS spectrophotometry. The morphological study at micro-scale has been performed by using optical microscopy and SEM-EDX. In a second step chemical and morphological changes at nano-scale have been characterized by using, for the first time in the field of the analysis of artworks, the novel technique of electrochemical atomic force microscopy (ECAFM).

Experimental

Reagents

Two biocides commonly used in the restoration field were selected:

Biotin T® is a liquid preparation of n-octyl-isothiazolinone(OIT) and quaternary ammonium salt. It is a biocide used in Italy and Spain for prevention from microbiological attack on many materials.

Preventol RI80® is a liquid formulation of alkyl benzyl dimethyl ammonium chloride (quaternary salt) and dipropylene glycol methyl ether. It is used in diluted solutions for the elimination of fungi, algae and lichens from finished coated surfaces.

Both manufacturers recommend to use them dissolved in a concentration range of 1-3%; in the case of Biotin T® water and for Preventol RI80® water or alcohol. In addition, the manufacturer recommends to start the treatment by spraying a small amount of solution on the infected surfaces to prevent live spores from spreading around.

Commercial artist's emulsion paints studied

Two different acrylic emulsion paints were selected for this study: burnt umber (PBr7) and phthalocyanine blue (PB15) Liquitex® Heavy Body. Liquitex® paints are prepared with a butyl acrylate-methyl methacrylate-based medium.

In parallel, two PVAc emulsion paints were studied: Egypt violet (PV23) and Natural burnt umber (PY42 + PBr7) Flashe® (distributed by Lefranc & Bourgeois).

Test specimens preparation

The specimens were prepared by applying successive layers of the commercial paint by casting over Mylar® sheets to acquire an average thickness layer of 0.15 mm. The dimensions of the resulting specimens are 3.5

x 4.0 cm for the Flashe® and 3.5 x 3.5 cm for Liquitex®. Paint films were dried under the environmental conditions for one year.

Application of Biocides

Specimens were treated by spraying the biocide 1.5% solution, in deionized water for Biotin T®, from a distance of 15 - 20 cm approximately. Three spray doses of Biotin T® solution were applied ensuring the solution covered the surface evenly.

Preventol RI80® was applied with a nebulizer in a 1.5% solution in pure ethanol; two nebulizations were needed to observe that the solution was homogeneously covering the specimens' surface not dripping.

Instrumentation

Light microscopy

The surface of the specimens was examined under a Leica S8APO microscope using incident light at the x10 to x80 magnification.

Scanning electron microscopy-energy-dispersive X-ray microanalysis (SEM-EDX)

Surfaces and cross section of the film specimens were monitored using a Jeol JSM 6300 scanning electron microscope operating with a Link-Oxford-Isis X-ray microanalysis system. The analytical conditions were 20-kV accelerating voltage and 2 x 10-9 A beam current. Samples were carbon-coated to eliminate charging effects. The working distance is maintained at 15 mm.

FTIR spectroscopy (FTIR)

The infrared (IR) spectra in the in the attenuated total reflectance (ATR) mode for the film specimens were obtained using a Vertex 70 Fourier transforms infrared spectrometer with an fast-recovery deuterated triglycine sulphate, temperature-stabilised coated detector and an MKII Golden Gate ATR accessory. A total of 30 scans were collected at a resolution of 4 cm-1, and the spectra were processed using the OPUS/IR software.

Spectrophotometry UV-VIS (UV-VIS)

The spectra in the UV and visible regions were obtained using a Perkin Elmer Lambda 35 recording double-beam spectrophotometer. Reflectance measurements were carried out in the range from 200 to 800 cm-1, with a speed of 240nm/min and opening width of 1.00 nm.

Atomic force microscopy (AFM)

To evaluate the films' surfaces, a Multimode AFM (Digital Instruments VEECO Methodology Group, USA) with a NanoScope IIIa controller was used, equipped with a J-type scanner (max. scan size of 150x150x6 mm). The topography of samples was studied in the tapping mode. The cantilever (Olympus Tapping Mode etched silicon probes, Veeco Methodology group) has a spring constant of ~42 N/m and a radius of 5-10 nm to ensure good imaging resolution and nanometer-scale indents. Images were obtained using probe excitation frequencies of 300 kHz. All the images were captured at a scan rate of 0.5-1 Hz. A set point to the

free amplitude ratio (Rsp) of 0.75, corresponding to a 25% attenuation of the amplitude of vibration, was used for all the images.

Results and Discussion

After examination of the paint film biocides treated specimens' by optical microscopy, the most significant changes observed can be summarized in: the eventual appearance of spots associated to both biocides, displaying of biocides deposits over the surface forming a translucent thin layer in the specimens treated and the brightness alteration of the paint film surfaces in the samples treated with Preventol RI80® (fig.1).

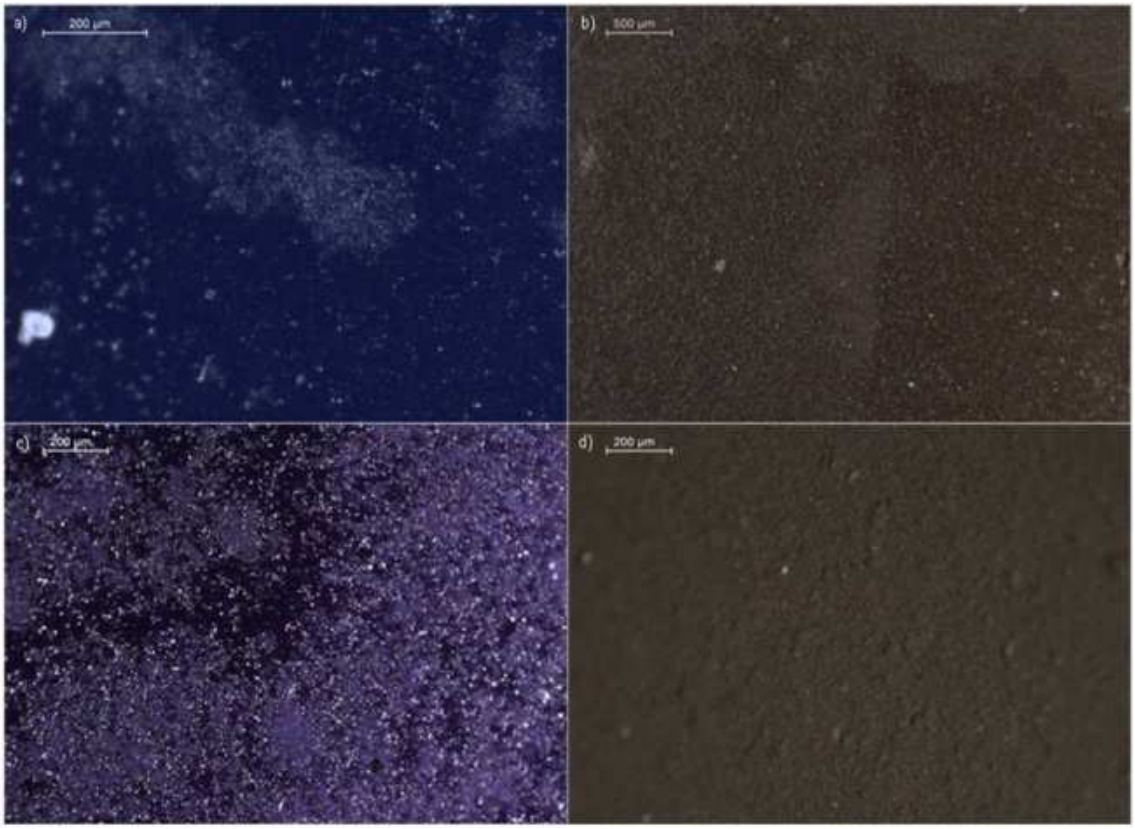

Fig.1 – Optical microscope images for the samples: a) Liquitex ® PB15 treated with Preventol RI80®; b) Liquitex® PBr7 treated with Preventol RI80®; c) Flashe® PB15 treated with Preventol RI80®; d) Flashe® PBr7 treated with Biotin T®.

The alterations observed by Light Microscopy were confirmed by examination of the specimens with SEM-EDX. Furthermore, the observation by SEM allowed identification of dirt particles adhered to the acrylic surface. The X-ray microanalysis demonstrates the presence of calcium carbonate ($CaCO_3$) added by the manufacturer as inert charge. Also, copper was identified, associated with the phthalocianine blue color and sulfur that is associated to the anionic type surfactants (sulfonate). In the specimens treated with Biotin T® was clearly observed a thin organic layer covering the surface, associated to the biocide deposits as micro-droplets that explain the uneven color alteration (fig. 2).

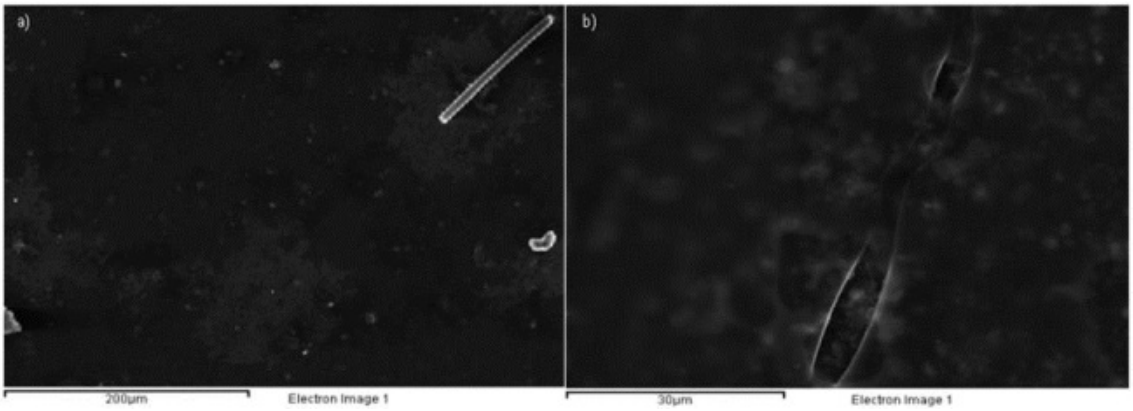

Fig. 2 – Scanning electron microscopy for the samples: a) Liquitex® PB15 treated with Preventol RI80®; b) Secondary electron microphotograph of Liquitex® PBr7 treated with Biotin T®.

The Flashe® umber specimens treated with Biotin T® had a thin layer of organic nature with abundant micro-crackle on the surface (fig.3), which is associated with deposits of biocides and to migration of additives from the bulk to the film surface, caused by the treatment. The SEM-EDS analysis revealed the presence of chlorine associated with the biocide (quaternary ammonium salt) deposited on the surface, as well as sodium and magnesium.

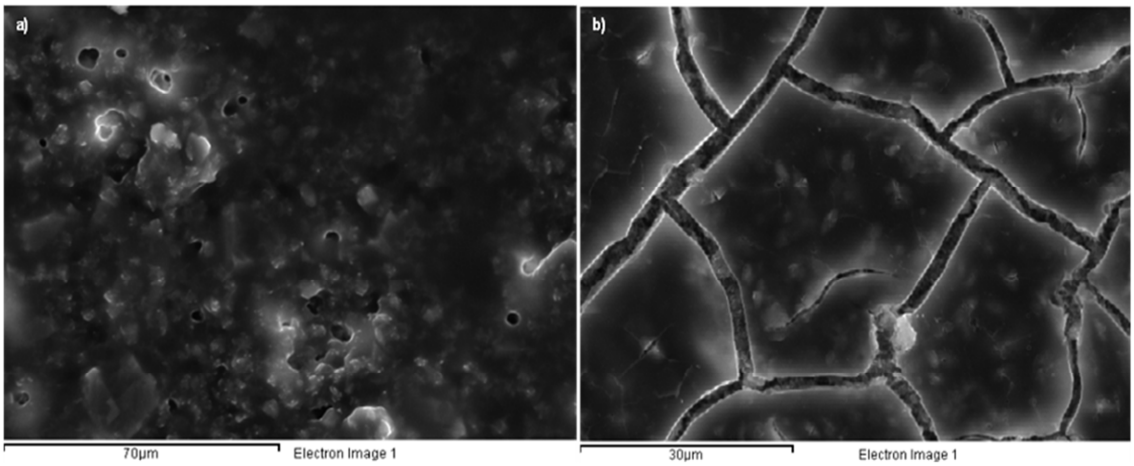

Fig. 3 – Scanning electron microscopy images for the samples: a) Flashe® PB15 treated with Preventol RI80®; b) Secondary electron microphotograph of Flashe® PBr7 treated with Biotin T®.

The chemical composition changes were evaluated by comparing the IR absorption spectra obtained before and after the biocide nebulization treatment. Tab. 1 summaries the main IR absorption bands of analytical interest identified in the studied Liquitex® paint films series. The paint films under study exhibited IR absorption spectra dominated by the IR band of binding medium's (acrylic, PVAc) bands ascribed to the pigment's (organic and inorganic), bands of calcium carbonated included by the manufacturer as an extender and bands ascribed to a non-ionic surfactant PEO (PEG) type. The IR spectra obtained after biocide treatment with Biotin T® were dominated by the IR absorption bands corresponding to the PEG-type surfactant.

Liquitex® HB		
IR absorption band (cm^{-1})	**Functional group assigment**	**Compound assignment**
3400	OH stretching vibrations	Water of hydration, diversified hydroxylic structures
2955, 2932	CH_3 and CH_2 antisymmetric stretching vibrations	Acrylic medium
2924	CH_3 and CH_2 antisymmetric stretching vibrations	Acrylic medium
2884	CH_3 symmetric stretching vibrations	Polyethylene glycol surfactant (PEG)
2872	CH_3 symmetric stretching vibrations	Acrylic medium
1726	C=O stretching vibrations associated to acrylated and methacrylate groups	Acrylic medium
1611	C=C- stretching vibrations, aromatic ring (ring breathing)	Phtalo blue, octylphenol polyethoxylate surfactant
1556	COO- asymmetric stretching vibrations associated to carboxylate groups	Metal-acrylates and/or methacrylates complex (only in burnt umber)
1509	C=C- stretching vibrations, aromatic ring (ring	Phtalo blue pigment, sodium octylphenol ethoxylate
1468(s)	CH_2 symmetric bending vibration	Acrylic medium
1449	CH_3 asymmetric bending vibration	Acrylic medium
1385	CH3 symmetric bending vibration	Acrylic medium
1340	Bending vibration CH_2 group	Acrylic medium, PEG
1146	Stretching vibration of C-O, C-C and Si-O groups	Acrylic medium, silicates associated to burnt umber pigment (max. 1110 cm-1), PEG (1060 cm-1)
750	Aromatic ring rocking vibration	Phtalocianine blue pigment

Tab. 1 – The IR absorption bands of analytical interest identified in the studied Liquitex® HB paint film series before and after biocide treatment.

The main IR absorption bands of analytical interest identified in the studied Flashe® paint films treated with biocide are summarized in tab. 2. Flashe® paint films exhibited IR absorption spectra dominated by the IR bands of the PVAc-VeoVa polymer and calcium carbonate (CaCO3). This pigment was included by the manufacturer as an extender in the commercial formulation of paints. These results suggest that the aquoues medium used for the nebulization of the biocide prompts the surfactant to migrate from bulk to the film surface. No significant changes were observed for those probes treated with Preventol RI80®, with the exception of the IR bands associated to the biocide.

Flashe®		
IR absorption band (cm^{-1})	Functional group assigment	Compound assignment
3100	OH stretching vibrations	Water of hydration, diversified hydroxylic structures
2955, 2926	CH_3 and CH_2 antisymmetric stretching vibrations	PVAc-VeoVa
2871, 2857	CH_3 symmetric stretching vibrations	PVAc-VeoVa
1736	C=O stretching vibrations associated to acetate groups	PVAc
1611, 1509	Stretching vibrations, aromatic ring (ring breathing)	Phtalo blue pigment
1556-39	COO- asymmetric stretching vibrations associated to carboxylate groups	Calcium-carboxylate complex
1423	Stretching vibration of carbonate group	CaCO3
1370	CH_3 symmetric bending vibration	PVAc-VeoVa, PVAOH
1115	Stretching vibration associated to C-C groups	PVAc-VeoVa, Preventol®
1012	Silicate stretching vibrations	Silicates, Burnt sienna pigment
945	Stretching vibration associated to C-C groups	PVAc-VeoVa
870	Stretching vibration of carbonate group	Calcium carbonate extender
750	Aromatic ring rocking vibration	Phtalocianine blue pigment
712	Stretching vibration of carbonate group	Calcium carbonate extender
600	Stretching vibration of Fe-O groups	Fe-O pigment

Tab. 2 – The IR absorption bands of analytical interest identified in the studied Flashe ® paint film series before and after biocide treatment.

The reflectance spectrum obtained on the surface of the Liquitex® paint films treated with both biocides shows a noticeable displacement of the reflectance bands characteristic of the pigments (phtalocianine blue, 450 nm and 580 nm; burnt sienna 390 nm and 800 nm) to a greater wave length values (fig.4). This result suggests that the treatment with the biocides caused an alteration in the color of the paint turning in to the green-orange. Being that the tested biocides shows, itself, reflectance spectrum with bands in the yellow-orange region. These products applied as a thin layer on the surface of the paint film would act as a yellow filter which produces, first, a shift of the reflectance bands characteristics of the pigments and secondly, a reduction in the reflectance value (% R) of the paint film. This confirms the results obtained by SEM and FTIR. Similar results to those obtained in the Liquitex® specimens were obtained in Flashe® specimens.

The AFM micrographs obtained on the film-substrate surface of some of the studied paint films shows a typical honeycomb- type latex structure (fig.4). This morphology evidences that the coalescence phase in the core of these acrylic paints' films was still incomplete after one year.

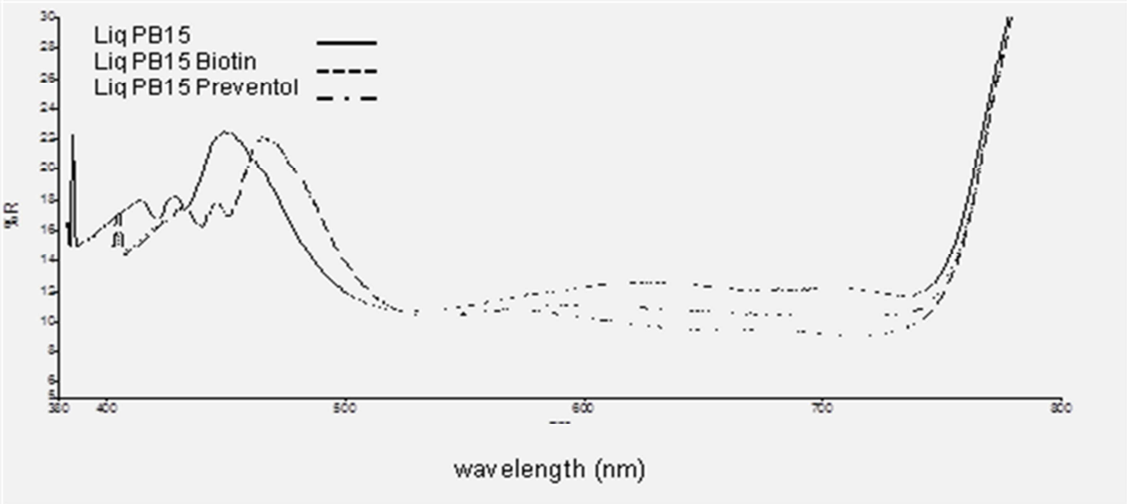

Fig. 4 – Reflectance spectrum of the Liquitex® phtalocyanine blue paint film before and after biocide treatment.

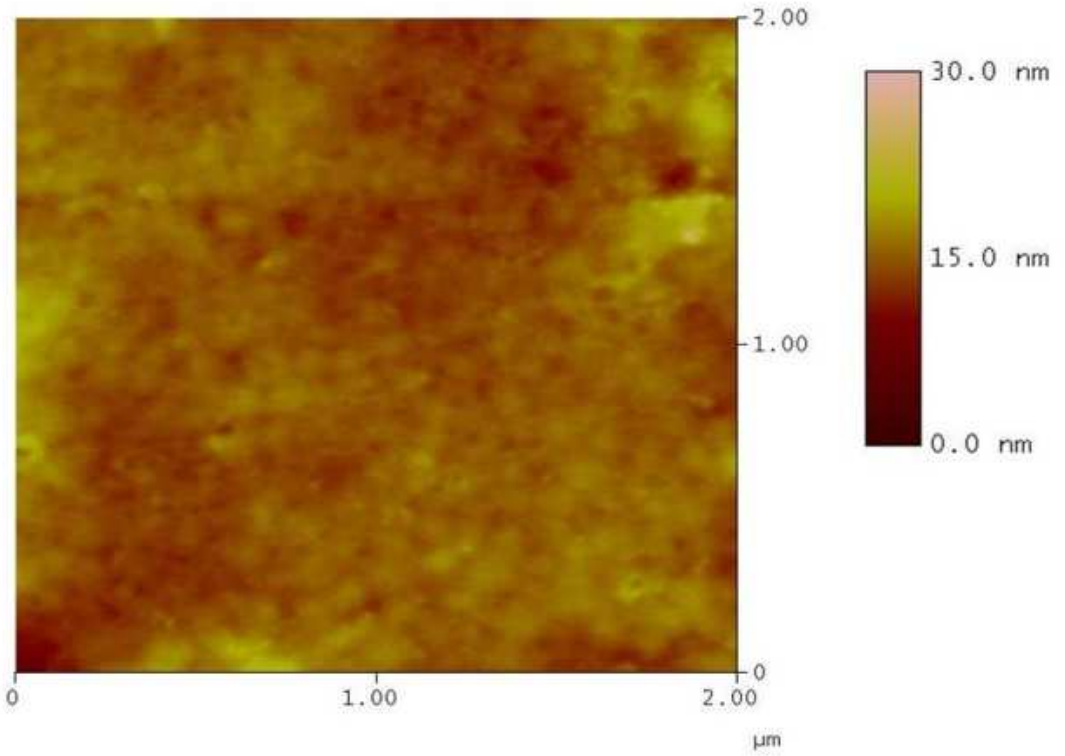

Fig. 5 – Atomic force micrograph showing substrate- film surface of the Liquitex® PB15 paint film.

Conclusions

Some of the most significant changes observed by microscopy were: appearance of spots and alteration of the brightness of the paint film, as well as, deposits of biocide. A notable delay in the coalescence phase of drying of the acrylic polymer used as binding media was recognized by means of AFM. Spectroscopic analysis results suggest that the application of the biocide causes a significant migration of additives to the surface from the *core* film.

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