CHAPTER 4.1 DEVELOPMENT OF GREEN HYGIENIC COATING BASED ON ESSENTIAL OIL MICROCAPSULES

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ABSTRACT

The challenges for developing new materials are accomplishing more functionality with less material due to the increasing efficiencies of the smart approaches. In this sense, the coating technology based on the incorporation of microcapsules has emerged recently as a strategy in the advance of protective and functional materials, promising an environmentally friendly approach. Microbial colonization of painted surfaces is a major concern because it shortened the useful life of the coating by discoloration and degradation. Besides there is a great concern about the indoor microbial colonization especially in places that should have high standards of environmental hygiene as in the food industry and those related to human health-care. The aim of this work is to develop a novel green antifungal water-borne paint formulated with melamine-formaldehyde (MF) microcapsules containing essentials oil as biocide agent. The microcapsules were synthesized by interfacial polymerization. Melamine-formaldehyde resin was used for the microcapsule shell wall, and two different essential oils (EOs) as core materials. The EOs studied were Tea Tree and Lavandin Abrialis. Microcapsule morphology was examined by Field-Emission Scanning Electron Microscopy (FE-SEM), while their size distributions were determined by light diffraction (LD). Microcapsule composition (shell and core) was analyzed by FTIR-ATR spectroscopy. Preparation of acrylic water-borne paint was done in a high speed disperser. The microcapsules (MF-Tea tree and MF-Lavandin) were incorporated into the original paint just before used, at 6% by weight of the total paint composition. As negative control a paint without biocide was used. The effectiveness of these microcapsules on paint film was evaluated by plaque inhibition assay. Commercial gypsum boards were used as substrate. Each painted panel was inoculated with 100 µl of the spore suspension of *Aspergillus sp*. and kept in a culture chamber at 86% relative humidity for 4 weeks. The fungal growth was estimated as a percentage of coverage onto the surface and scored according to ASTM D5590 standard specification. The results obtained in antifungal assay on paint film were promising. According to ASTM D5590, the score obtained by MF-lavandin paint was 1, which indicate just a trace growth onto the painted surface (<10%). On the other hand, the control and MF-Tea tree paints obtained the same score: 4 points, the highest qualification (fungal growth >70%). Comparing those results, it can be seen that

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Aspergillus sp. growth reduction was significant when MF-lavandin paint was used, suggesting that those microcapsules had an inhibitive activity on the dry film whereas MF-Tea tree had not such activity.

Keywords: antifungal paint; essential oil; Lavandin Abrialis; microencapsulation

INTRODUCTION

Microbial colonization of painted surfaces is a mayor concern because it shortened the useful life of the coating by discoloration and degradation. Besides there is a great concern about the indoor microbial colonization especially in places that should have high standards of environmental hygiene, as in the food industry and those related to human health-care. Among the most deleterious organisms are fungi, a very large and diverse group which is found in practically every ecological niche. The genera most frequently isolated inside buildings are *Penicillium*, *Aspergillus*, *Cladosporium* and *Alternaria*[1-4].

The antimicrobial coatings can supply an extra line of defense for maintaining hygiene standards. The most important property of hygienic coatings is its antimicrobial activity (against bacteria, viruses, fungi and spores) but they also need to be non-toxic and non-allergic to humans while, at same time, they must be non odorous, durable and cost effective [5]. The water-borne paints are complex mixtures of polymers, pigments and functional additives. In these paints the vehicles is an emulsion of resin in water, and have been created as alternative to solvent borne paint because of the volatile organic compound (VOC) content in these paints is significantly lower, thereby reducing VOC emissions. Waterborne paints dry by evaporation of the water. The coalescing solvents allow the resin particles to fuse together (coalesce) as the water evaporates to form a continuous coating. The disadvantage of these paints is the high content of additives required for its formulation, all susceptible to biodeterioration[6-8].

Conventional additives used as biocides in paints and coatings are often toxic, causing environmental pollution and health problems [9,10]. An eco-friendly alternative for replacement could be the use of natural products, such as essential oils.

Essential oils (EOs) are known for their antiseptic, i.e. bactericidal, and fungicidal, and medicinal properties so; they are commonly used in pharmaceutical, cosmetic and food industries. Generally, EOs are volatile substances sensitive to oxygen, light, moisture, and heat, characterized by a strong odour. They are formed by aromatic plants as secondary metabolites[11,12]. These reported special characteristics could impair their applicability.

The coating technology based on the incorporation of microcapsules has emerged recently as a strategy in the advance of protective and functional materials, promising an environmentally friendly approach. The challenges for developing new materials are to accomplish more functionality with less material due to the increasing efficiencies of the smart approaches

Microencapsulation provides many benefits for coatings containing biocides. The microcapsule protects the biocide from degradation and allows the proper control of the release process, prolonging thereby the duration of the biocidal effect and reducing the waste of biocides. In this sense, essential oils had been reported more effective when they are microencapsulated, thus improving their long-term function and durability [13]. There are several chemical methods for the microencapsulation of essential oils such as in situ polymerization, coacervation, and interfacial polymerization [14]. The in situ polymerization relies on prepolymers formed in a continuous phase. Urea and melamine, along with formaldehyde, have usually been used for the synthesis, and the characteristics of microcapsules, such as morphology and particle size distribution, rely on the preparation conditions including the rate of shear, the shearing period, the kind of emulsifier used, and the viscosity of the core material.

The aim of this work is to develop a novel green antifungal water-borne paint formulated with melamine-formaldehyde (MF) microcapsules containing essentials oil as biocide agent.

MATERIALS AND METHODS

Materials. Poly (ethylene-alt-maleic anhydride) (Poly (E-MA)), formic acid and Tea Tree (*Melaleuca alternifolia*) oil were purchased from Sigma Aldrich (Argentina). The commercial melamine-formaldehyde (MF) prepolymer Beetle® PT312 (73% solids content and 0.2% to 0.3% free formaldehyde) was purchased from BIP Limited (Oldbury, UK). The essential oil Lavandin (*Lavandula hybrid var. Abrialis)* was purchased from Indukern (Brazil). Agar-agar was supplied by Parafarm (Argentina) and proteose peptone was purchased from Oxoid (Tecnolab, Argentina). All materials were used as received without further purification.

Preparation of the MF microcapsules by in situ polymerization. The MF microcapsules were prepared using a modified *in situ* polymerization procedure[15]. MF resin was used for the microcapsule shell wall and two essential oils (EO) as core materials. The biocide agents studied were the essential oil of Tea Tree (TTO) and Lavandin (LVO). Experimentally, 2.55 g of MF resin was first dissolved (in a 250 mL beaker) in 30 g of water containing the surfactant Poly (E-MA) (3.3% w/w) and sodium hydroxide (1.4% w/w). Then, 17 g of essential oil was added slowly to the aqueous continuous phase under stirring to form the emulsion. The resulting mixture was stirred at 1000 rpm for 1 hour. After this time, the pH of the reaction mixture was adjusted to 5 using formic acid, and the temperature of the reaction was raised up to 70 ºC and maintained for 3 hours under stirring. After 3 hours, the synthesized MF microcapsules were cooled down to room temperature, cleaned with methanol/water and resuspended in water.

Characterization of the microcapsules

Scanning electron microscope (SEM). The morphology of MF-Essential oil microcapsules was examined by Field-Emission Scanning Electron Microscopy (FE-SEM) on a FEI Quanta 650 microscope using aluminium tape as support. Before imagining, the samples were coated by Au-Pd.

Particle size distribution. The average diameter of the MF-Essential oil microcapsule and its size distributions were determined by light diffraction (LD) on a Mastersizer 2000 (Malvern Instruments). The particle size was expressed as the equivalent volume diameter and three replicates were performed for each batch of microcapsules, in order to reduce error, an average curve was calculated and analyzed. Microcapsules were dispersed in water in a sonicator before testing.

Fourier transform infrared (FT-IR) spectroscopy. The infrared spectra of the MF-Essential oil microcapsules and that of paint film containing MF-EO microcapsules, as KBr pellets, were obtained by a FT-IR (Spectrum, Perkin Elmer, USA) spectrometer according to diamond ATR method, in order to identify their chemical structure. The FT-IR spectra were recorded in the 4000 to 400 cm^{-1} range and scanned with background correction at 60 scans with 4 cm^{-1} resolutions.

Fungal strain and culture. *Aspergillus sp*, isolated from contaminated interior paints, was used in the study. The main reasons for choosing *Aspergillus* was that this fungus is a primary colonizer of building materials because its low water activity request, fast growth, easy viewing and major resistance to biocides[1,16].

The fungus was cultured in agarized media (MCA: 1.5g agar-agar, 1.0g dextrose, 0.5 g protease peptone, 0.1g KH_2PO_4, 0.05g $MgSO_4$ and distilled water up to 100 mL) and incubated at 28º C for 7 days. The spore suspension was prepared from a MCA culture and incubated in the conditions before mentioned. The spores were removed from the plate and placed in a test-tube with 5 mL of NaCl 0.85% (w/v) and 0.005% (w/v) of Tween-20. The spore concentration was adjusted to 10^6 spores /mL employing a Neubauer chamber.

Paint formulation. Acrylic water-borne paint was formulated without any kind of biocide; the composition is shown in **Table 1**. Paint preparation was done in a high speed disperser. In the first step water was mixed with dispersing, antifoaming and thickener additives. Then, the pigments (titanium dioxide, calcium carbonate) were added and finally the resin (an acrylic styrene) together with the co-solvents. After preparation, the paint was filtered and kept in a closed jar under laboratory conditions until use.

The microcapsules (MF-Tea tree and MF-Lavandin) were incorporated into the original paint just before used, at 6% (w/w) by weight of the total paint composition. As negative control, paint without biocide was used.

TABLE 1. Paint composition

Component	% (w/w)
Water	25.20
Antifoaming	0.30
Cellulose Thickener	0.50
Dispering agent	0.45
Wetting agent	0.15
Pigments	64.3
Resin	7.20
Mineral spirit	1.30
Butylglycol	0.60

Antifungal assay on paint film. Commercial gypsum boards, cut into test pieces (2.5 cm x 2.5 cm) and sterilized at 121 ºC for 20 min, were used as substrate. The panels were painted with two coats of the formulated paints and were kept under laboratory conditions for 15 days to cure the paint. Afterward, the panels were irradiated with U.V-light for 20 minutes, for providing a superficial sterilization and, then, placed into Petri dishes containing filter paper moistened with 1 mL of sterile water. Each panel was inoculated with 100 µL of the spore suspension of *Aspergillus* and kept in a culture chamber at 86% RH for 4 weeks. Four replicates were used for each paint. The fungal growth was estimated as a percentage of surface coverage. The panels were scored according to ASTM D5590 standard specification (**Table 2**)[17]. Additionally, observations by scanning electron microscopy (SEM) were made. The selected samples for further studies were those that presented better result and the control. The panels were prepared as follows: small sections of the panels surfaces were cut and fixed in 2.5% v/v gluteraldehyde (24h) and dehydrated in graded series of ethanol solution from 20% v/v at 100% v/v. Finally, they were dried with the critical point and coated with gold. The coated samples were examined by Scanning Electron Microscopy (FE-SEM) on a FEI, Quanta 200 microscope at high vacuum.

TABLE 2. Fungal growth qualification over the surface (ASTM D 5590)

Growth observation	Qualification
None	0
Trace of growth (<10%)	1
Light growth (10-30%)	2
Moderate growth (30-70%)	3
Heavy growth (>70%)	4

RESULTS AND DISCUSSION

Characterization. SEM photographs of microcapsules morphologies obtained by the *in situ* polymerization method, containing the essential oils, are shown in **Figure 1A and 1B**. As can be seen, microcapsules have spherical shape and a smooth surface. The melamine-formaldehyde microcapsules revealed sizes of around 15 µm for the Lavandin oil (**Figure 1A**) and sizes of more than 20 µm for the Tea Tree oil, (**Figure 1B**). The average size of these microcapsules was subsequently confirmed by laser diffraction measurements (**Figure 2**).

The graphical distribution of the mean diameters for the different microcapsules is indicated in **Figure 2A and 2B**. Both microcapsules had narrow particle size distribution. The mean particle sizes showed changes depending on the essential oil employed. The average particle size diameter was 15 µm in the case of Lavandin microcapsules while those Tea Tree size microcapsules reached 22 µm. Thus, the prepared microcapsules in this study seemed to be adequate for incorporation in a paint, due to them monodisperse size distribution. In addition, the greatest mean particle sizes of MF- Tea tree can be attributed to the viscosity of the core material used for microencapsulation, which is an important factor affecting the particle size of the MF microcapsules [14].

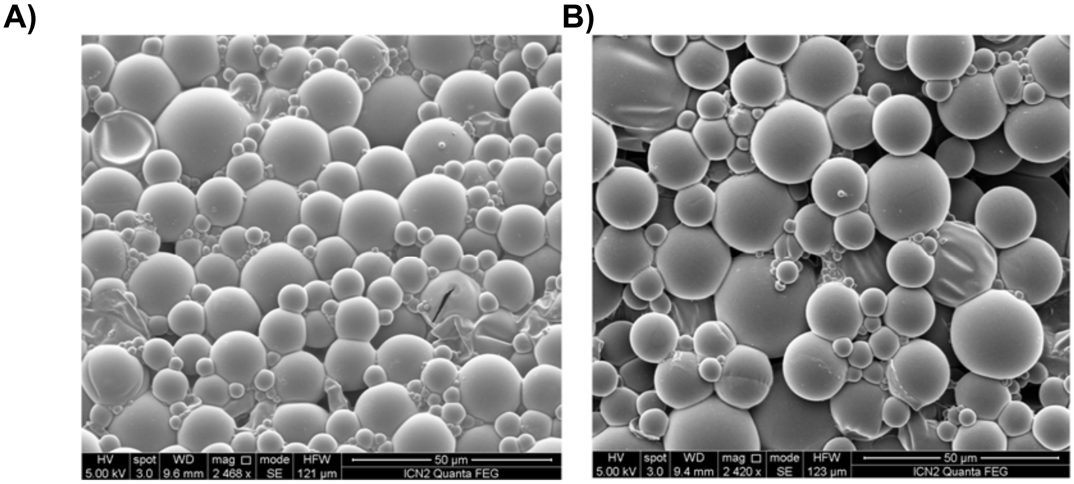

FIGURE 1. SEM micrographs of melamine-formaldehyde microcapsules containing A) Lavandin oil and B) Tea Tree oil, at 2400x magnifications

FTIR studies were conducted to confirm whether the EO-microcapsules were prepared successfully or not. **Figure 3A** and **3B** depict chemical components of microcapsules containing LVO or TTO as core material and melamine-formaldehyde as the wall respectively.

First of all, melamine-formaldehyde resin can be assumed to constitute in the capsule walls because the secondary amine group N-H stretching vibration was observed at 3393 cm^{-1} and 3349 cm^{-1} in the respective spectrum **(Figure 3 A-b** and **3B-b**). This result is supported by a previous investigation[18] of melamine-formaldehyde prepolymer prior to encapsulate core material which showed N-H vibration at 3300 cm^{-1}. The C-N stretching vibration was shown at 1339 -1336 cm^{-1}. These findings partially matched those reported in a previous study [18,19] dealing with melamine formaldehyde as wall material of microcapsule. In addition, strong adsorption peaks located at 2967-2963 cm^{-1} are associated with the C-H stretching vibration which was frequently encountered in organic compounds like natural essential oil.

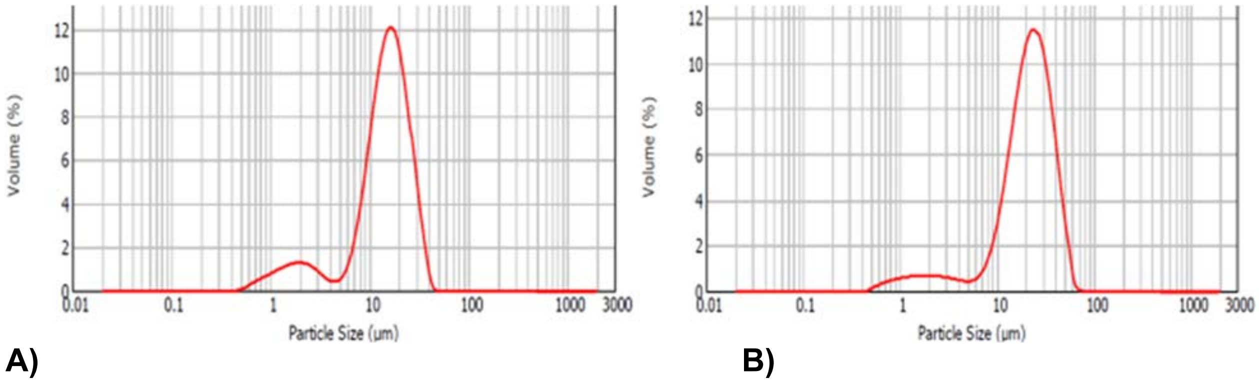

FIGURE 2. Particle-size distribution for A) the MF-Lavandin microcapsules and B) the MF-Tea Tree microcapsules, as measured by laser diffraction

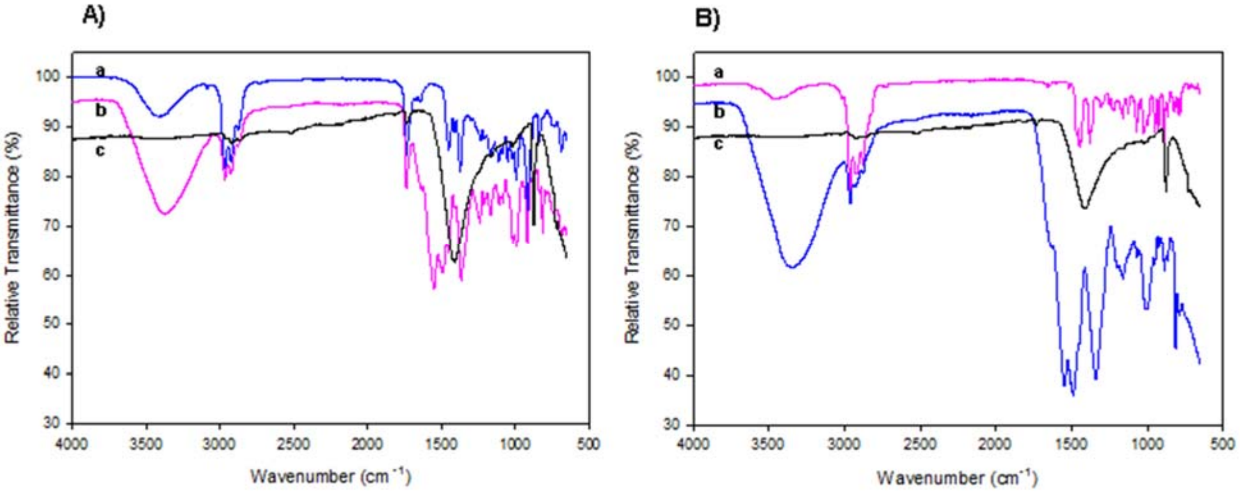

FIGURE 3. FT-IR spectra: (A) a) Lavandin oil, b) MF-Lavandin microcapsules and c) paint film containing MF-Lavandin microcapsules. (B) a) Tea tree oil, b) MF-Tea tree microcapsules and c) paint film containing MF-Tea tree microcapsules.

Figure 3A-a shows FTIR spectra corresponding to Lavandin oil. The basic components of the LVO are linalool, linalyl acetate, lavandulol, and citronellol [20]. These components have characteristic molecule groups such as –COOR and C=O. In **Figure 3A-a** the strong absorption peak of the LVO due to carbonyl was found at 1741 cm^{-1}. Besides, other notable peaks appeared at 2970 cm^{-1}, 1460 cm^{-1}, 1371 cm^{-1}, and 1000 cm^{-1}, which are due to C–H stretching vibration, CH_2 asymmetric deformation, CH_2 symmetric deformation [21].

Figure 3B-a shows FTIR spectra corresponding to Tea Tree oil. The TTO spectrum shows characteristic bands corresponding to its major components such as 1-terpinen-4-ol, γ-terpinene, 1,8-cineole and α-terpinene, among others, in published reports [22]. It shows characteristic peaks corresponding to the vibrations OH around 3400 cm^{-1}, alkyl C-H stretching vibration between 2960 and 2854 cm^{-1}. The band corresponds to C=O vibration bond was found at 1744 cm^{-1}. Between 1464 and 1385 cm^{-1} the C-H bending vibration was observed. Characteristic absorption band of vibration C-O-C aromatic rings appeared at 881 cm^{-1}.

In summary, FT-IR spectroscopic data showed that essential oils were successfully encapsulated by melamine-formaldehyde as wall.

In order to chemically characterize the paints film with MF-essential oil were performed spectra FTIR, **Figure 3A-c and 3B-c**. The spectra show the bands due to $CaCO_3$ (1726 cm^{-1}, 1415 cm^{-1}) and talc (1015 cm^{-1}) as well as the typical one for the acrylic resin at 1720 cm^{-1}. $CaCO_3$ and talc are one of the pigments used in latex paints. These results are consistent with studies reported [23]. The bands due to the MF-essential oil did not appear, showing the optimal encapsulation of essential oil in the microcapsules.

Antifungal assay on paint film. Figure 4 shows in detail the antifungal effects of microcapsules in paint by quadruplicate, compared with the respective control (paint without microcapsules) after 4 weeks.

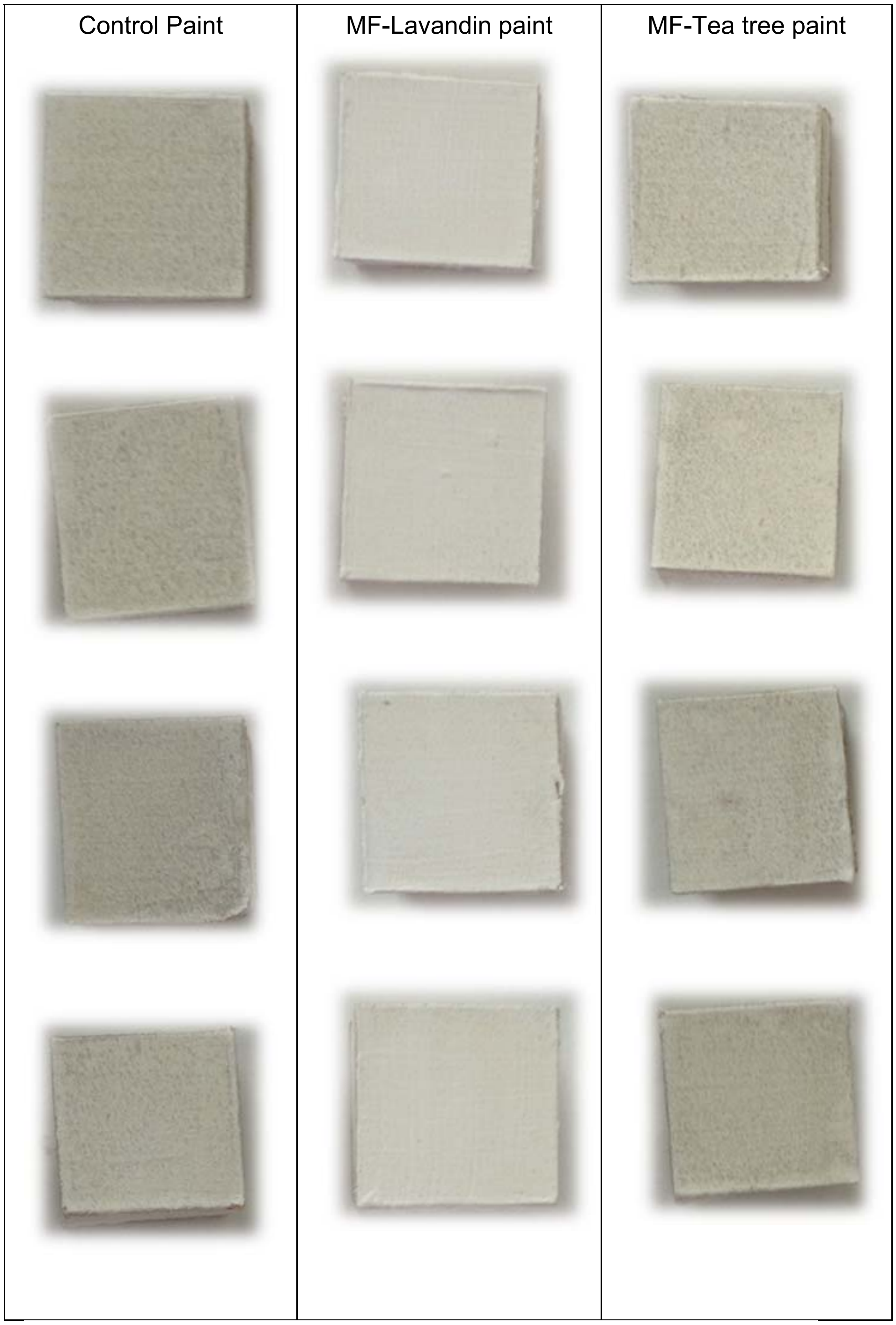

FIGURE 4. Antifungal assay on paint film containing MF-EO exposed to *Aspergillus sp.* after 4 weeks (quadruplicate)

Evaluation of the fungi growth degree on paints by ASTM D5590 (4th week) is shown in **Table 3**.

TABLE 3. Fungal growth qualification over the paint surface

Paint	Qualification
Control	4
MF-Lavandin	1
MF-Tea tree	4

According to standard specification, the score obtained by MF-lavandin paint was 1, which indicate just a trace growth onto the painted surface to naked eye (<10%). On the other hand, the control and MF-Tea tree paints obtained the same score: 4 points, the highest qualification. This score corresponds to degree of coverage by the fungal growth higher than 70%. Comparing the results, it can be seen that *Aspergillus sp*. growth reduction was significant when MF-Lavandin paint was employed, suggesting that these microcapsules has fungal growth inhibition activity on the dry film whereas MF-Tea tree did not affect the growth.

Observation of paint film by scanning electron microscope (SEM). Macroscopic observation was confirmed by SEM. The **Figure 5** shows the micrographs of the fungal film of the control paint and paint with MF-Lavandin microcapsules.

As shown in **Figure 5A**, the fungal colonization is abundant, with a wide mycelial development covering all control paint surface together with many spores. The spores are dark pigmented and lead to an aesthetic damage in the paint. Moreover, it is well documented that spores are the principal source of fungal bioaerosol that cause irritative disorders (i.e. allergy and asthma) [4,24]. On the other hand, in **Figure 5B** it can be seen a poor mycelial development and a few spores, also it is possible to distinguish the microcapsules immersed into the paint.

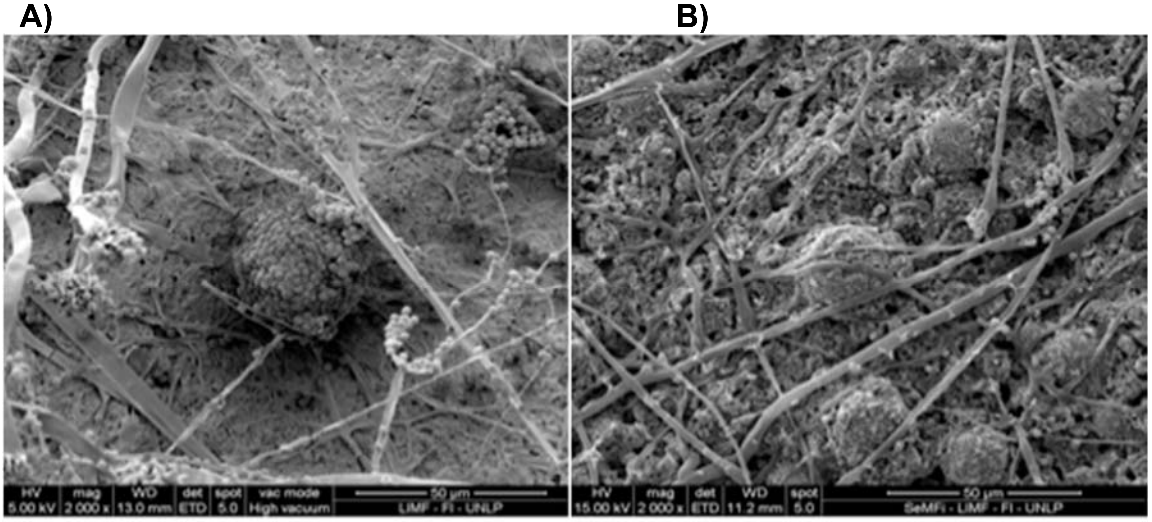

FIGURE 5. SEM micrographs: a) control paint and b) MF-Lavandin paint, exposed to *Aspergillus sp.* after 4 weeks, at 2000x magnifications.

CONCLUSION

This work has proposed the use of melamine-formaldehyde resin microcapsules containing two different essential oils as a natural biocide, for the development of a green hygienic coating. The microcapsules containing LVO and TTO, obtained by in situ polymerization, were evaluated with regard to their morphologies, size distribution, and chemical structure. The formation of MF-EO microcapsules has evidenced smooth surface morphologies and the mean particle sizes have reached values around 15 and 22 µm. These microcapsules resulted adequate to be incorporated in a paint, due to them monodisperse size distribution. FTIR studies have demonstrated that the essential oils were successfully encapsulated by melamine-formaldehyde as wall and the microcapsules were effectively incorporated in the paint.

It is important to keep in mind that a paint is a complex system and, at the same time, essential oil is a volatile compound. For this reason, it is important to achieve a good system of encapsulation to reduce the loss of essential oil and decrease the possible interaction with others paint components, thus, the oil will be available exclusively as biocide. In this sense, the results obtained in the antifungal assay on paint film were promising. It can see that the growth reduction against *Aspergillus sp* was significant when MF-Lavandin were incorporated in the paint, suggesting that these microcapsules have fungal growth inhibition activity on the dry film.

This kind of coatings has a good potential, given that the essential oil is a natural resource, renewable and eco-friendly. An inconvenience, in this time, is the cost of raw materials. When the process is considered for mass production, cost can be high, but may be acceptable if they are considered for special applications, those cases where conventional technology fails or when restrictions to traditional biocides would be implemented. Further experimental investigations are needed and work together with companies to make feasible the selection of ideas, technologies and eco-friendly compounds for the generation of commercial products.

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