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Research article

Evaluation of the preventive characteristic of commercial anti-foam products on the proliferation of micro-organisms on the surface of fired clay roofing tiles

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Abstract

The Centre Technique de Matériaux Naturels de Construction (CTMNC) is regularly asked about the roofing tiles treatment and maintaining techniques and about properties and efficiency of the different commercial anti-foam products. So, in order to best respond to them, the CTMNC suggested to realize a study to verify what the manufacturers claim about their products and their efficacy. The aim of this study is to present the main results about the efficacy of anti-foam products against micro-organisms.

Physico-chemical characteristics such as pH, water miscibility, density and the molar concentration of the active molecule of 27 products have been studied and compared to the manufacturer data. Moreover, with the use of a water streaming test, it has been possible to compare the efficacy of the different studied products on the proliferation speed of microorganisms on the roofing tiles surfaces.

Key words: Roofing tiles, greening, water-streaming test, anti-foam product

1. Introduction

The roof is the architectural element which covers the superior part of a building. It allows principally protecting its interior against bad weather and humidity. However, the action of time and of bad weather can sometime degrade the roof and its components. This study is specially consecrated to the fired clay roofing tiles. Fired clay roofing tiles are ceramic porous materials obtained by the firing at high temperature of a clayey mixing. Due to it porosity, it degradation is possible. In fact, the porosity favors [Barberousse 2006, Fassier 2009, Van de Voorde 2012] :

- The penetration of water in the material by capillarity which can cause mechanical damage of the fired clay roofing tile and its shattering during the cycles of frost and de-frost,
- The hanging and the proliferation of micro-organisms which cause the esthetical and chemical degradations of the material and weaken the surface of the product (micro-organisms will be developed thanks to the minerals contained in the fired clay roofing tile). This colonization can also cause cracks in the material increasing the humidity rate in the product and develop a bigger sensibility to the cycles of frost and de-frost.

In order to avoid these degradations, several types of commercial treatments based on the use of chemical products have been developed. In fact, there are a lot of request of customers about these techniques of treatment and about the efficacy of different commercial products. So, in order to answer to these questions, this study has been managed to verify the claims of the manufacturers about their products and also their efficacy.

This paragraph presents the different products allowing treating the roof tiles and shows an inventory of commercial products used in this study.

The different types of micro-organisms

Five types of living organisms can be responsible of the colonization of façades and roofing tiles: bacteria, algae and cyanobacteria, mushrooms, lichens and foams.

Bacteria are unicellular micro-organisms from 0.5 to 1.5 µm, heat-resistant and present initially and naturally on all types of supports and in all the environments. They are pioneers on the process of colonization. These bacteria product acids which degrade the material and can provoke a loss of cohesion of the material that indeed sometimes cracks.

Algae and cyanobacteria are organisms from 0.5 to 1 mm which are autotrophic that is to say able to create their own organic matter from mineral elements using the photosynthesis. They have a fast development and a green, blue, brown or red coloration. They secrete a mucilaginous envelope which is viscous substance very hygroscopic holding water and mineral particles which can cause the bursting of roofing tiles during the cycles of frost and de-frost.

Mushrooms are heterotrophic organisms which need a high humidity to grow. Such as bacteria, they secrete organic acids which will have similar effects on roofing tiles.

Lichens result of the symbiosis between algae or cyanobacteria and mushrooms. Mushrooms protect algae against their predators, supply them in water and feed substances that algae secrete. Lichens can be easily sticked on the support or penetrate in the material of several millimeters due to its erosion caused by the acid secretions of lichens.

Foams are the forms of dirt the most evolved. They are chlorophyllous plants as spongy carpet and protruding bushings. They are harmful because they promote the development of organisms previously presented.

The different techniques of treatment

There are two types of techniques allowing fighting against these phenomena damaging the roofing tiles: the curative treatment which aims to eliminate micro-organisms presented on the surface of the roofing tiles and the preventive treatment which allows limiting the appearance and the development of these organisms before colonization.

There are different types of anti-foams products such as anti-foams products, damp-proof products and waterproofing products.

Anti-foams products are biocide products which have a curative action and sometimes a preventive one on the development of algae, foams and lichens. It is difficult to estimate the efficacy of these products because their evaluation is not managed by standards.

Damp-proof product is a product which preserves and protects a material against water and humidity. It aims to increase the hydrophobic characteristic of the surface of the material in order to warn the penetration of the runoff water. There are film and no-film damp-proof products. Film damp-proof products create a film on the surface of the material which warn the penetration of the water in the support and also limit the transfers of vapor. It is like a glaze. No-film damp-proof products reduce the penetrations of liquid water but it must not modify the penetration of vapor.

At the end, waterproofing products are products, when they are deposited on the surface of the material that prevent liquid water to penetrate in the material and vapor to cross it. It is a film damp-proof product.

This study has been realized in order to evaluate the efficacy of commercial anti-foams products on the development and the proliferation of micro-organisms on the surface of fired clay roofing tiles.

2. Experimental

2.1 Klebsormidium flaccidum

Klebsormidium flaccidum is a filamentous alga hard-wearing to area strongly dehydrated even if it grows, most of the time, in areas which have a high humidity.

This alga is composed of cells to barred-shaped, forming long filaments slightly constricted at cross-walls, one parietal and cup-shaped chloroplast, covering about 2/3 of the cells, with one clearly visible pyrenoid (L = 5-25 µm, w = 4-12 µm) [Shirakawa 2011, Steward 1978]

The culture of Klebsormidium Flaccidum is realized on a modified Bold's basal medium composed of three mother solutions individually pressure-sealed, after their preparation, at 120°C for 20 minutes. 1 liter of liquid culture medium is composed of 10 mL of solution A, 10 mL of solution B and 1 mL of solution trace introduced in 1 liter of ultra-pure water. The medium is adjusted at pH 7 and then pressure-sealed before the introduction of the strain of algae [Bold 1964].

Each Erlenmeyer flask is put on magnetic agitator, to oxygenate again the medium to have a better reproduction and to homogenize the suspension, in an air-conditioned culture room at 20±0.5°C where light intensity is controlled (white light) and the photoperiod is 16h/8h (light/darkness).

The dosage of algae contained in the 2 liters Erlenmeyer flasks is determined by the measurement of the dry mass of the algae. A known volume of algae suspension is filtered on membranes in microfibers of glass which have a porosity of 1.2 µm (Whatman GF/C). These membranes are dried at 105°C for 3 hours. Then, the dry algae mass is determined and attributed to the filtered volume.

2.2 Analysis

pH measurement

The measurement of the pH of a solution or a suspension consists in the measurement of its acidity or its basicity. It is defined such as the negative logarithm of the concentration of hydronium ions and varies between 0 and 14 in water.

pH = hydrogen potential = - log $[H_3O^+]$

In fact, the pH measurement is based on the redox couple which involves the protons and the hydrogen:

Hydrogen/proton: $H_2 \leftrightarrow 2H^+ + 2e^-$ which potential is : $E_2 = - 59{,}1*10^{-3}*pH$

The reacting species are $Pt/H_{2(gaz)}/H^+_{(aq)}$ and, that is why, the potential taken by an electrode immersed in a flux of hydrogen at atmospheric pressure is proportional to the opposite of the pH value of the solution.

The determination of the pH value of a solution or a suspension can be made using a pH paper or with a pHmeter.

The use of the pH paper consists in an easy and fast method but it is not very accurate. pH paper strips are immersed of several colour indicators which have a coloration which varies in function of pH.

The accurate measurement of the pH of a solution needs to use a pHmeter. It is an electronic millivoltmeter which measured a difference of potential between two electrodes: an electrode of reference which potential is constant and independent of the pH of the solution (at constant temperature) and an electrode of measurement which potential is function of the pH of the solution. The device shows the results in millivolts or, after conversion, in pH units.

Before pH measurement, all the products are shaken with a magnetic agitator. This measurement has been realized with a pHmeter Cyberscan pH 1100 (Eutech instruments).

Density

The determination of the absolut density with a helium pycnometer takes place in the following steps. The device measures very precisely the variation of gaseous volumedue to the introduction of the sample in a calibrated compound; the volume is calculated from the change of pressure observed when the gas passes from one cell containing the sample (pressure P_2) to the reference cell (pressure P_1). This method is based on the Mariotte lay.

$$Vech = Vcell - \frac{V\exp}{\frac{P1}{P2} - 1}$$

The volume of the cell, V_{cell}, and the volume of expansion, V_{exp}, are constants given by the manufacturer. The maximum precision is about ±0.1% on the volume and about 0.001g on the weighing.

So, the absolut density is given by the following relation:

$$\rho = \frac{m}{V}$$

where m is the mass of the sample and V, the volume of the sample.

The density of the different products studied is obtained dividing the mass weighed by the volume studied. The mass is determined with a balance and the volume with a volumetric flask of 50 mL. The product is introduced dropwise to the mark of the flask with a pipette.

This measurement has been realized with a helium pycnometer which reference is ACCUPYC 1330 (Micromeritics).

Determination of the concentration of chloride ions

In order to verify the concentration of active ingredient indicated by the manufacturers for each product, a conductivity dosage with silver nitrate, allowing determining the concentration in quaternary ammonium compounds, has been realized [Site internet]. In fact, most of the products studied during this study contain this chemical compounds. The experimental device is described Figure 1. In the first step, the silver nitrate has been put in solution in ultra-pure water. To obtain a concentrated solution of silver nitrate at 0.025 $mol.L^{-1}$.

To realize this dosage, a beaker with 5 mL of product to dose and 200 mL of ultra-pure water has been deposited, under magnetic agitation, under a volumetric flask containing the solution of silver nitrate. This solution is put milliliter per milliliter in the beaker until the solution is trouble and that a white precipitate appears. At the end of the dosage, a curve representing the voltage in mV in function of the amount of silver nitrate introduced, in mL, in the beaker, is drawn. An example of a curve obtained is presented on the Figure 2.

The amount of chloride ions and also in quaternary ammonium present in the products tested is determined graphically: it corresponds to the amount of silver nitrate needed to equalize the concentration in quaternary ammonium and provoke the appearance of a white precipitate. This amount is indicated by the intersection of two lines corresponding to the brutal increase of the voltage.

The equation below shows the calculus allowing determining the concentration in chloride ions from the measured data.

$C_{Cl-} \times V_{product=} C_{Ag} \times V_{equivalent}$ that is to say $C_{Cl-} = \frac{C_{Ag} \times V_{equivalent}}{V_{product}}$.

Miscibility

During this study, the miscibility in water of different commercial products has been studied. The miscibility is the disposition which have two liquids to mix. For this, two equal amounts in water and in product have been put in a tube test. Then this tube has been shaked and after left one hour to decant.

The water-streaming test

To evaluate the behavior of commercial anti-foams products facing with the presence of micro-organisms, an experimental device has been developed. This device simulates speeding up the colonization, by algae, on the exposed surface of materials.

The principle of the water-streaming test consists in the dampening of the surface of the material by water streaming which is comparable to the rain flow on facades or roof tiles of buildings.

This device, developed by Boulon and Dubosc, is composed of a closed box where the humidity is relatively high, favorable to the development of micro-organisms [Dubosc 2001]. In this box, the samples are put back to back on two supports in stainless steel at an angle of 45° to increase the colonization process. At regular time intervals, the samples are sprayed by the *Klebsormidium Flaccidum* culture, kept at a constant temperature by a thermo-regulator, presented in the bottom of the box. This spraying is realized by a ramp pierced by holes which have a constant diameter at equal distance each other. Moreover, the box is installed in a room where the temperature and the relative humidity are controlled and have two footlights composed of two neon tubes which have a known intensity (1500 lux, 30W) and according to a photoperiod controlled (12h/12h).

At regular time intervals, the biological development is evaluated by pictures analysis. The kinetic of colonization on the surface of materials is evaluated by pictures analysis. The surface of the samples installed in the water-streaming test is digitized at regular time intervals with an office scanner. Then, the digitized pictures are treated to digitize the signal as on the Figure 3.

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Then, the digitized pictures are treated with a pictures analysis program to establish a histogram (Figure 4) representing the number of pixels in function of their intensity.

In this treatment, the intensity 0 is attributed to the black pixels and the white pixels correspond to the intensity 255. At the end, to make the area corresponding to the colonization of the micro-organisms more detectable, a threshold is realized for the maximal intensity of the peaks of the histogram. So, the micro-organisms seem to be white on the black support. Then, the percentage of colonization on the sample is obtained making the ratio between the pixels corresponding to the micro-organisms and the total number of pixels. To the end, a graph showing the evolution of the growing of micro-organisms in function of the exposure time in the water-streaming test is drawn for each sample series.

3. Materials

3.1 Inventory of the commercial anti-foams products

The first step of this study consists in making an inventory of the different products able to treat the roofing tiles, in fired clay products, available on the market. The aim of the part of this study is to list, analysis and study the efficacy of the commercial anti-foams products that a customer can easily buy for a reasonable price. This study will allow verifying the claims of the manufacturers concerning their products and so be able to answer correctly to the frequent customer’s requests against these products.

In order to realize this inventory, the web sites of the DIY shops and specialized manufacturers in the development of these products have been consulted. For each product, the recommendations of use, the active ingredient, the aims of the manufacturers and the safety data have been listed. This inventory allows noting that for roofing tiles, this is a large panel of anti-foams and equally of manufacturers and providers. The inventory elaborated during this study is not comprehensive but groups products which a customer can easily find on internet or in a shop. During this study, 27 anti-foams products have been studied. In most of them, the active ingredient is the benzalkonium chloride, excepted for one of them in which nonanoic acid is present. Moreover, this product is claimed eco-friendly.

3.2 The fired clay product used as reference

During this study, the roofing tiles used as samples have been made by extrusion. The clayey mixing used to elaborate the paste results of an industrial mixing used to make roofing tiles. The mixing is performed during 25 to 30 minutes with 18%$_{mass}$ of water to obtain a plastic paste which could be extruded. After extrusion, the roofing tiles obtained are cut at the desired size then dried on a plaster board during one day at ambiance temperature. Then, a second drying in a dryer is realized during two days (one day at 45°C and one day at 110°C). To finish, the roofing tiles have been fired following the thermal cycle presented Figure 5 during 36 hours.

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After firing, the different products have been deposited on the samples which measure 200x40 mm, following the instructions of the manufacturer. Thus, for this study, some products have been deposited with a brush, a roll or a spray. The amount deposited at the surface of the samples is about 4 mL.

The fired clayey mixing is composed of silica, micas and feldspars. Its chemical composition in $\%_{mass}$ is the following: 63% of silica, 15% of alumina, 3% of potassium oxide, 4% of iron oxide, 2% of titanium oxide, 1% of calcium oxide, 1% of magnesium oxide and 1% of sodium oxide. The specific surface area of the powder of the roofing tiles id about $1.5 m^2 g^{-1}$ and its density is about 2.69 g cm^{-3}. The size repartition of this powder is bimodal and the peaks are centered at 58.04 and 362.15 µm. The characteristic diameters are the following: d(0.1) is about 9.23 µm, d(0.5) about 76.96 µm and d(0.9) about 698.81 µm. The pH of this powder put in aqueous suspension is about 6.7.

Concerning the solid samples, its density is about 2.1g cm^{-3} and its porosity is about 21%. The average roughness of the surface of the samples is 2.4 µm with a standard deviation of 0.01. To finish, the static contact angle of a drop of water deposited on the surface of the samples is about 59°.

It is important to know the porosity of roofing tiles when the rate of colonization is studied. In fact, more the roofing tiles are porous, more the colonization will be possible and fast. However, this porosity is essential because it allows evacuating the vapor presented in the loft, avoiding the mold of the framework and also having a moist indoor air.

4. Results and discussions

4.1 Physical and chemical characterization of the commercial products

The commercial products listed previously have been characterized in order to verify the characteristics given by the manufacturers such as pH, density, miscibility in water and the concentration in active ingredient (chloride ions).

First the pH value of each commercial product has been determined with a pHmeter. The results are presented in Table 1.

For most of these commercial anti-foams products, the pH value seems to be neutral and between 6.25 and 8.2. Except, the product Q, which contains nonaic acid, shows an acid pH value of 1.63.

So, the customer must use personal protective equipment suitable to the pH value but also take in consideration the fact that fired clay products are composed of mineral material that could be attacked by a product which has an acid pH value. On the contrary, the basic pH values could attack the organic material and also the micro-organisms presented on the surfaces.

Concerning the measurement of the density of these products, the results obtained are visible in Table 2.

For most of the products, their density is about 1. So, these values obtained in laboratory are in agreement with these indicated by the manufacturers in the safety data.

Concerning the miscibility of these products in water, the results have shown that most of the products are miscible in water. It is important to notice that for one of the products, the manufacturer indicates on the safety data that its product is not miscible in water but in laboratory, it seems that this product is really miscible in water. It is important because the products which are not miscible are most of the time damp-proof products. These products can be diluted and the tolls to deposit the product can be cleaned with water and will be cleaned with special products such as white spirit or alcohol.

After, the concentration in chloride ions in each product has been determined. The results of the assays obtained for each product containing chloride ions are gathered in Table 3.

The assays realized in laboratory give an important range of concentration in quaternary ammonium from 0.018 to 1.203 $mol.L^{-1}$. The products M, T and L with respectively 0.381 to 1.203 $mol.L^{-1}$ are products which the solution is concentrated, it is necessary to dilute them before using on the roofing tiles. The dilution of these products tends to obtain a concentration equal to 0.095 $mol.L^{-1}$ for the product M, 0.033 $mol.L^{-1}$ for the product T and 0.057 $mol.L^{-1}$ for the product L. so, these results give a range of concentration of the products deposited from 0.018 to 0.130 $mol.L^{-1}$.

It is important to notice that the values obtained by this assay are slightly inferior that these indicated by the manufacturers (between 0.021 and 1.060 $mol.L^{-1}$) except for the product L'. That is to say that the indications indicated by the manufacturers could be not very accurate concerning the concentration of quaternary ammonium or about its introduced amount. In fact, the average difference between the value given by the manufacturers and the value measured is about -0.02 $mol.L^{-1}$.

Thereafter, it is important to associate these values of concentration with the speeds of colonization of roofing tiles by the micro-organisms to determine if the concentration in active ingredient can delay and/or slow down the greening of the roofing tiles and so, validate or not the preventive character of the products.

At last, for the product I, in the end of the assay, the color of the solution has turned to orange, which can signify that, the product I contained chromate ions.

4.2 Results obtained with the water-streaming test : validation of the preventive character

Concerning the reference samples, three identical samples have been put in the water-streaming test to submit them to the runoff of algae on their surfaces. The average results obtained for the reference samples are recapitulated on the Figure 6.

First, it is important to notice that for these samples, the reproducibility of the results and of the behaviors facing the greening can be considered valid.

For the reference sample, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the first 14 days, the development of micro-organisms at the surface of the samples starts and is relatively high and important. In fact, the rate of colonization reaches 4.56% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.33% per day. Thereafter, between the 14th and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 4.56 to 11.95% which leads to a speed of colonization, in this space time, of 0.53% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays relatively important and significant. At the end, after the 28th day of exposure, the speed of colonization and proliferation of algae at the surface of reference samples increases. So, the colonization becomes bigger and faster. In fact, the rate of colonization reaches 27.75% after 49 days of exposure which leads, on this period of test, to a speed of colonization of 0.75% per day.

Concerning the samples covered by different anti-foams products, three identical samples have been put in the water-streaming test to submit them to the runoff of algae on their surfaces. The average results obtained for the different samples are recapitulated on the Figure 7.

First, it is important to notice that for these samples, the reproducibility of the results and of the behaviors facing the greening can be considered valid. However, due to the important number of anti-foams products tested, it seems to be difficult to interpret the results in their overall. To do this, the results have been selected according to several categories.

Influence of the pH values of the anti-foams products

The results obtained for the different samples are recapitulated on the Figure 8.

For the sample which the pH value of the product is 1.6, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the first 14 days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.25% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.09% per day. Thereafter, between the 14th and the 21st day of exposure, the rate of colonization of the surface of the samples evolves from 1.25 to 4.89% which leads to a speed of colonization, in this space time, of 0.52% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. At the end, between the 21st and the 35th of exposure, the rate of colonization of the surface of samples evolves from 4.89 to 21.3% which leads to a speed of colonization, in this space time, of 1.17% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the pH value of the product is 7, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the first 14 days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.26% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.02% per day. Thereafter, between the 14th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 0.26 to 2.92% which leads to a speed of colonization, in this space time, of 0.13% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 35th and the 49th day of exposure, the rate of colonization of the surface of the samples evolves from 2.92 to 14.1% which leads to a speed of colonization, in this space time, of 0.80% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 49th and the 56th of exposure, the rate of colonization of the surface of samples evolves from 14.1 to 26.87% which leads to a speed of colonization, in this space time, of 1.82% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the pH value of the product is 8.2, the colonization of the surface by micro-organisms starts from the 14th day of exposure and becomes detectable, by picture analysis, after the 21st day in the water-streaming test. During the 28 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.52% after 28 days of exposure in the water-streaming test which leads to a speed of colonization of 0.02% per day. Thereafter, between the 28th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 0.53 to 3.62% which leads to a speed of colonization, in this space time, of 0.44% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 35th and the 42th day of exposure, the rate of colonization of the surface of the samples evolves from 3.62 to 10.43%, which leads to a speed of colonization, in this space time, of 0.97% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 42nd and the 49th of exposure, the rate of colonization of the surface of samples evolves from 10.43 to 23.21% which leads to a speed of colonization, in this space time, of 1.83% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

Following this individual analysis for each sample, it is possible to deduce a trend of behavior facing the colonization by micro-organisms for all the coatings of anti-foams products following their pH value.

Due to the results, it seems that the anti-foams products showing a pH value rather high (about 8) allow delaying the colonization by micro-organisms of the surfaces exposed. So, if the property searched is to delay the colonization of the surfaces by micro-organisms, it seems preferable to use basic anti-foams products.

On the other hand, for a same time of exposure, the coatings composed of anti-foams products which pH value is neutral (about 7) shows a speed of colonization of their surfaces by micro-organisms lower. In fact, such coatings need a time of exposure more important to reach the same rate of colonization of their surface.

Influence of the amount of anti-foam products deposited

The results obtained for the different samples are recapitulated on the Figure 9.

For the sample covered of 0.007L m^{-2} of anti-foams product, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the first 14 days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.15% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.08% per day. Thereafter, between the 14th and the 21st day of exposure, the rate of colonization of the surface of the samples evolves from 1.15 to 3.34% which leads to a speed of colonization, in this space time, of 0.31% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 3.34 to 10%, which leads to a speed of colonization, in this space time, of 0.95% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 28th and the 35th of exposure, the rate of colonization of the surface of samples evolves from 10 to 19.47% which leads to a speed of colonization, in this space time, of 1.35% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample covered of 0.35L m^{-2} of anti-foams product, the colonization of the surface by micro-organisms starts from the 14th day of exposure and becomes detectable, by picture analysis, after the 21st day in the water-streaming test. During the 28 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.71% after 28 days of exposure in the water-streaming test which leads to a speed of colonization of 0.06% per day. Thereafter, between the 28th and the 35st day of exposure, the rate of colonization of the surface of the samples evolves from 1.71 to 11.23% which leads to a speed of colonization, in this space time, of 1.36% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 35th and the 42nd day of exposure, the rate of colonization of the surface of the samples evolves from 11.23 to 32.3%, which leads to a speed of colonization, in this space time, of 3.01% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample covered of 5.25L m^{-2} of anti-foams product, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the 21 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 2.14% after 21 days of exposure in the water-streaming test which leads to a speed of colonization of 0.1% per day. Thereafter, between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 2.14 to 8.64% which leads to a speed of colonization, in this space time, of 0.93% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 28th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 8.64 to 22.06%, which leads to a speed of colonization, in this space time, of 1.92% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

Following this individual analysis for each sample, it is possible to deduce a trend of behavior facing the colonization by micro-organisms for all the coatings of anti-foams products following their amount deposited.

Due to the results, it seems that if the amount of the anti-foams deposited is about 0.35L m^{-2}(which is claimed on most of the labels of the anti-foams products), the colonization, of the surfaces exposed, by micro-organisms is delayed and slowed down. In fact, for a same time of exposure, these coatings show a speed of colonization of their surfaces by micro-organisms lower. In fact, such coatings need a time of exposure more important to reach the same rate of colonization of their surface.

Influence of the concentration in chloride ions of the anti-foams products

The results obtained for the different samples are recapitulated on the Figure 10.

For the sample which the concentration of chloride ions is 0.02mol L^{-1}, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the 14 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.5% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.11% per day. Thereafter, between the 14th and the 21st day of exposure, the rate of colonization of the surface of the samples evolves from 1.5 to 3.41% which leads to a speed of colonization, in this space time, of 0.27% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. At the end, between the 21st and the 28th of exposure, the rate of colonization of the surface of samples evolves from 3.41 to 19.9% which leads to a speed of colonization, in this space time, of 2.36% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the concentration of chloride ions is 0.06mol L^{-1}, the colonization of the surface by micro-organisms starts from the 14th day of exposure and becomes detectable, by picture analysis, after the 21st day in the water-streaming test. During the 21 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.25% after 21 days of exposure in the water-streaming test which leads to a speed of colonization of 0.01% per day. Thereafter, between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 0.25 to 1.78% which leads to a speed of colonization, in this space time, of 0.22% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 28th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 1.78 to 7.64% which leads to a speed of colonization, in this space time, of 0.84% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 35th and the 42th of exposure, the rate of colonization of the surface of samples evolves from 7.64 to 17.98% which leads to a speed of colonization, in this space time, of 1.48% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the concentration of chloride ions is 0.2mol L^{-1}, the colonization of the surface by micro-organisms starts from the 14^{th} day of exposure and becomes detectable, by picture analysis, after the 21^{st} day in the water-streaming test. During the 28 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 5.88% after 28 days of exposure in the water-streaming test which leads to a speed of colonization of 0.21% per day. At the end, between the 28^{th} and the 35^{th} of exposure, the rate of colonization of the surface of samples evolves from 5.88 to 29.12% which leads to a speed of colonization, in this space time, of 3.32% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the concentration of chloride ions is 1.2mol L^{-1}, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7^{th} day in the water-streaming test. During the 14 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.26% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.02% per day. Thereafter, between the 14^{th} and the 35^{th} day of exposure, the rate of colonization of the surface of the samples evolves from 0.26 to 2.92% which leads to a speed of colonization, in this space time, of 0.13% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 35^{th} and the 49^{th} day of exposure, the rate of colonization of the surface of the samples evolves from 2.92 to 14.1% which leads to a speed of colonization, in this space time, of 0.8% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 49^{th} and the 56^{th} of exposure, the rate of colonization of the surface of samples evolves from 14.1 to 26.87% which leads to a speed of colonization, in this space time, of 1.82% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

Following this individual analysis for each sample, it is possible to deduce a trend of behavior facing the colonization by micro-organisms for all the coatings of anti-foams products following their concentration of chloride ions.

Due to the results, it seems that the anti-foams products showing an average concentration of chloride ions between 0.06 and 0.2 mol L^{-1} allow delaying the colonization by micro-organisms of the surfaces exposed. So, if the property searched is to delay the colonization of the surfaces by micro-organisms, it seems preferable to use anti-foams products which have an average concentration in active ingredient such as the value above. It seems to be unnecessary to use, for this property, anti-foams products more concentrated.

On the other hand, for a same time of exposure, the coatings composed of anti-foams products whose concentration of chloride ions is the highest show a speed of colonization of their surfaces by micro-organisms lower. In fact, such coatings need a time of exposure more important to reach the same rate of colonization of their surface.

Influence of the price of the anti-foams products

The results obtained for the different samples are recapitulated on the Figure 11.

For the sample which the price of the product is about 0.5€ L^{-1}, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the 14 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.2% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.09% per day. Thereafter, between the 14th and the 21st day of exposure, the rate of colonization of the surface of the samples evolves from 1.2 to 3.62% which leads to a speed of colonization, in this space time, of 0.35% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Then, between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 3.62 to 11.49% which leads to a speed of colonization, in this space time, of 1.12% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 28th and the 35th of exposure, the rate of colonization of the surface of samples evolves from 11.49 to 25.4% which leads to a speed of colonization, in this space time, of 1.99% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the price of the product is about 5€ L^{-1}, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the 21 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 1.45% after 21 days of exposure in the water-streaming test which leads to a speed of colonization of 0.07% per day. Thereafter, between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 1.45 to 2.99% which leads to a speed of colonization, in this space time, of 0.22% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 28th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 2.99 to 8.18% which leads to a speed of colonization, in this space time, of 0.74% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 35th and the 42th of exposure, the rate of colonization of the surface of samples evolves from 8.18 to 21.16% which leads to a speed of colonization, in this space time, of 1.85% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the price of the product is about 15€ L^{-1}, the colonization of the surface by micro-organisms starts from the 14th day of exposure and becomes detectable, by picture analysis, after the 21st day in the water-streaming test. During the 21 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.25% after 21 days of exposure in the water-streaming test which leads to a speed of colonization of 0.01% per day. Thereafter, between the 21st and the 28th day of exposure, the rate of colonization of the surface of the samples evolves from 0.25 to 1.78% which leads to a speed of colonization, in this space time, of 0.22% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 28th and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 1.78 to 7.64%, which leads to a speed of colonization, in this space time, of 0.84% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 35th and the 42nd of exposure, the rate of colonization of the surface of samples evolves from 7.64 to 17.98% which leads to a speed of colonization, in this space time, of 1.48% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

For the sample which the price of the product is about 37€ L^{-1}, the colonization of the surface by micro-organisms starts from the first day of exposure and becomes detectable, by picture analysis, after the 7th day in the water-streaming test. During the 14 first days, the development of micro-organisms at the surface of the samples starts and is extremely low. In fact, the rate of colonization reaches 0.26% after 14 days of exposure in the water-streaming test which leads to a speed of colonization of 0.02% per day. Thereafter, between the 14st and the 35th day of exposure, the rate of colonization of the surface of the samples evolves from 0.26 to 2.92% which leads to a speed of colonization, in this space time, of 0.13% per day which shows an increase of the speed of colonization of the surface by micro-organisms. This speed of colonization stays however relatively low while significant. Between the 35th and the 49th day of exposure, the rate of colonization of the surface of the samples evolves from 2.92 to 14.1%, which leads to a speed of colonization, in this space time, of 0.8% per day which shows an increase of the speed of colonization of the surface by micro-organisms. At the end, between the 49th and the 56th of exposure, the rate of colonization of the surface of samples evolves from 14.1 to 26.87% which leads to a speed of colonization, in this space time, of 1.82% per day which shows an increase of the speed of colonization of the surface by micro-organisms.

Following this individual analysis for each sample, it is possible to deduce a trend of behavior facing the colonization by micro-organisms for all the coatings of anti-foams products following their price.

Due to the results, it seems that the anti-foams products showing an average price about 15€ L^{-1} allow delaying the colonization by micro-organisms of the surfaces exposed. So, if the property searched is to delay the colonization of the surfaces by micro-organisms, it seems preferable to use anti-foams products which have this kind of price. It seems to be unnecessary to use, for this property, anti-foams products more expensive.

On the other hand, for a same time of exposure, the coatings composed of anti-foams products which price is the highest shows a speed of colonization of their surfaces by micro-organisms lower. In fact, such coatings need a time of exposure more important to reach the same rate of colonization of their surface.

5. Conclusions

The aim of this study was to characterize and evaluate the efficacy, against the development and the proliferation of micro-organisms at the surface of roofing tiles, of anti-foams products.

The characterizations should verify the properties given by the manufacturers in the technical information and safety data. They have shown that it would be cautious about them. In fact, some pH values said to be basic have been revealed acid and some concentrations of chloride ions seem to be inferior to those claimed.

Water-streaming tests have been realized and they have shown that some anti-foams products are able to delay and/or slow down the colonization of their surfaces by micro-organisms following their pH value, their amount deposited at the surface of the roofing tiles, their concentration of chloride ions and their price.

Then, in order to try to understand how extrapolate the results obtained in the water-streaming test with a greening in natural conditions, several roofing tiles covered with some anti-foams products have been put in natural environment.

To finish, it will be interesting to make a test to estimate the permeability at the liquid water and at the vapor of these anti-foams products. This effect is important because if the vapor presented in the loft does not evacuate, loft will be too wet and mushrooms and moisissures could appear.

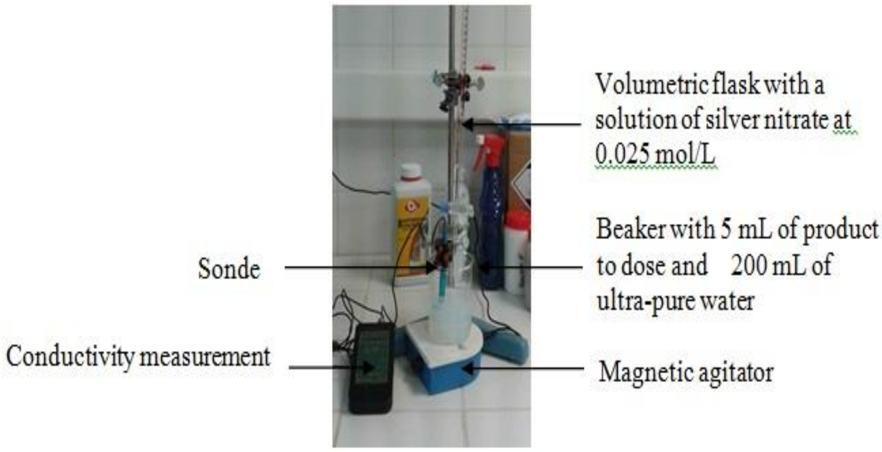

Figure 1: Experimental device used to quantify the concentration in chloride ions

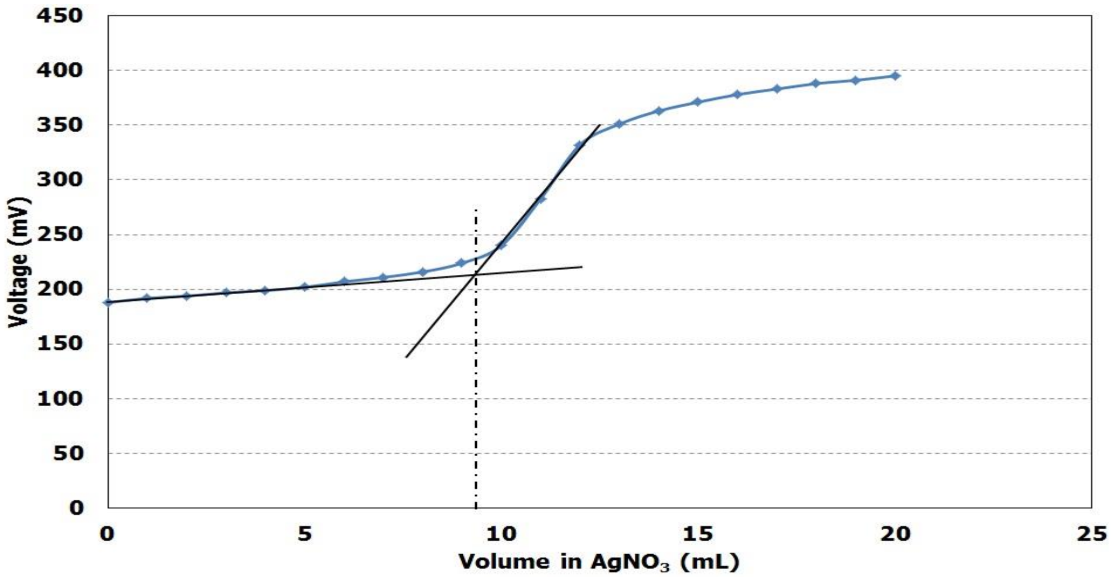

Figure 2: Example of conductivity curve obtained during the dosage in chloride ions of different product studied

Figure 3: Example of a digitized and converted into 256 grey levels roof tile

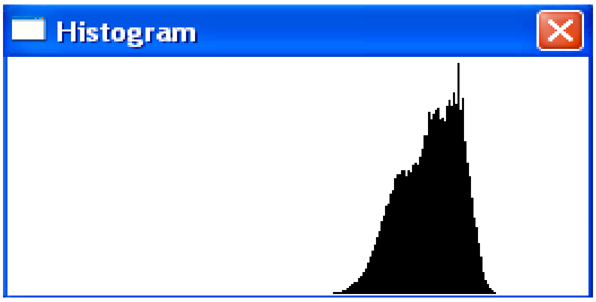

Figure 4: Histogram of the digitized picture representing the number of pixels in function of their intensity

Figure 5: Thermal cycle of firing of the roofing tiles

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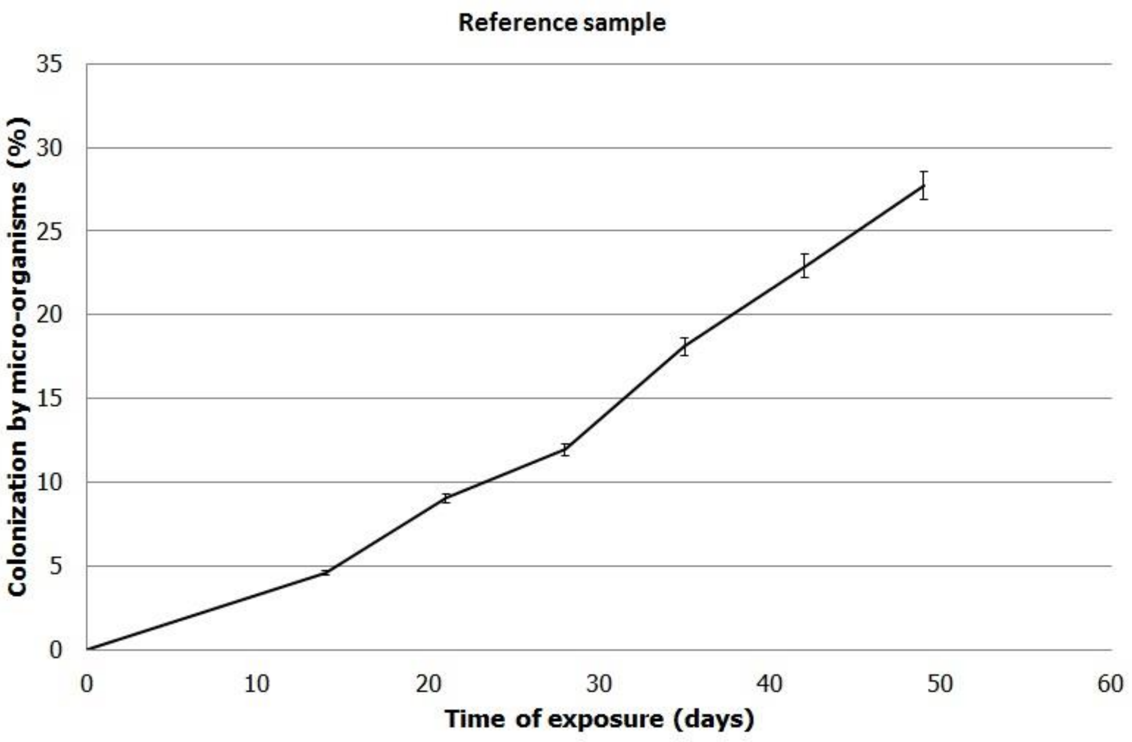

Figure 6: Kinetic of colonization and growth of micro-organisms at the surface of the reference samples

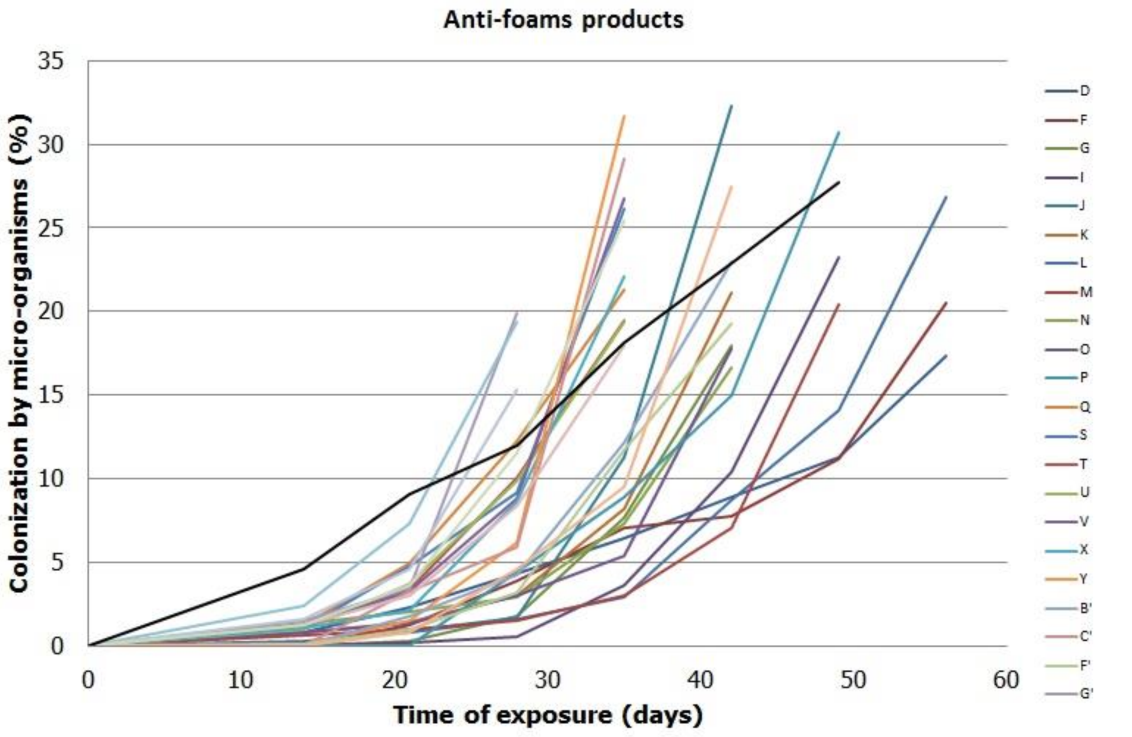

Figure 7: Kinetic of colonization and growth of micro-organisms at the surface of samples covered by anti-foams products

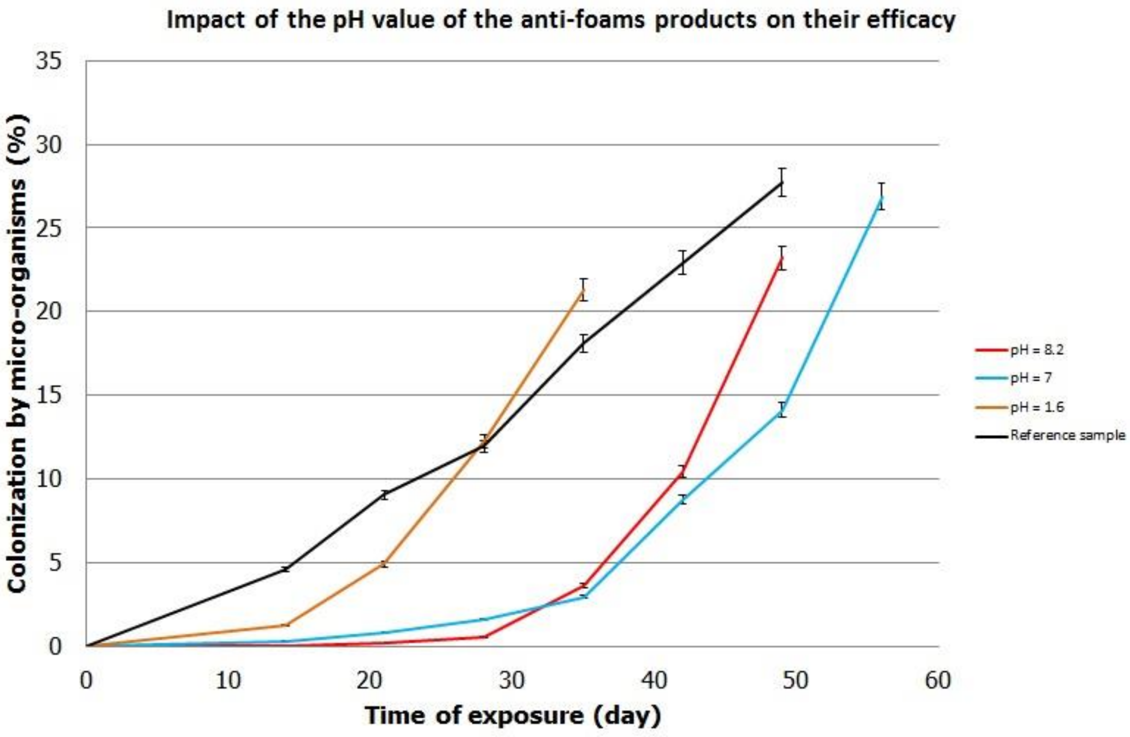

Figure 8: Kinetic of colonization and growth of micro-organisms at the surface of samples covered by anti-foams products following the pH value of the products

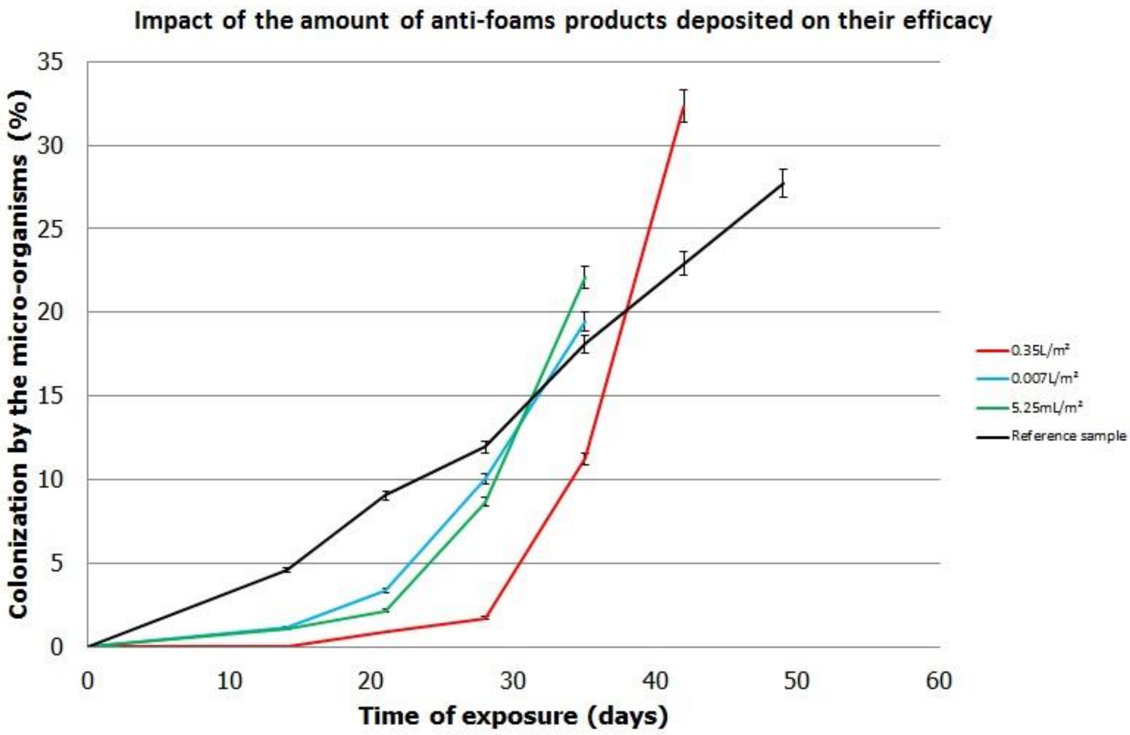

Figure 9: Kinetic of colonization and growth of micro-organisms at the surface of samples covered by anti-foams products following the amount of product deposited

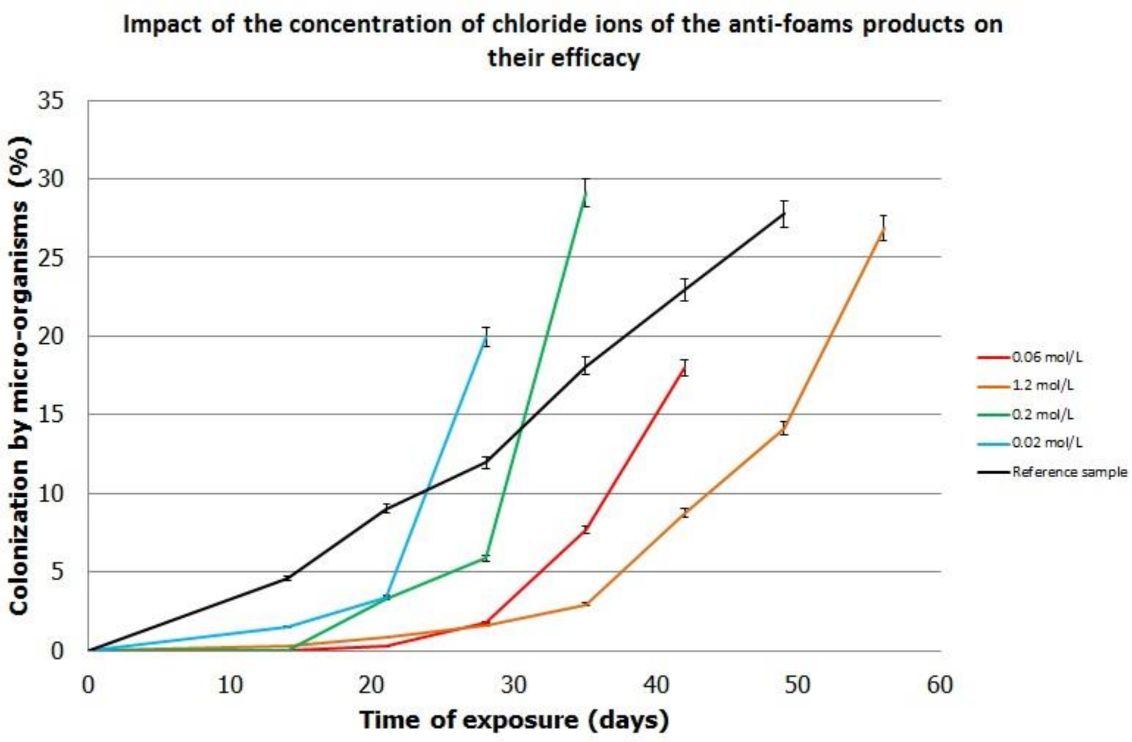

Figure 10: Kinetic of colonization and growth of micro-organisms at the surface of samples covered by anti-foams products following the concentration of chloride ions of the products

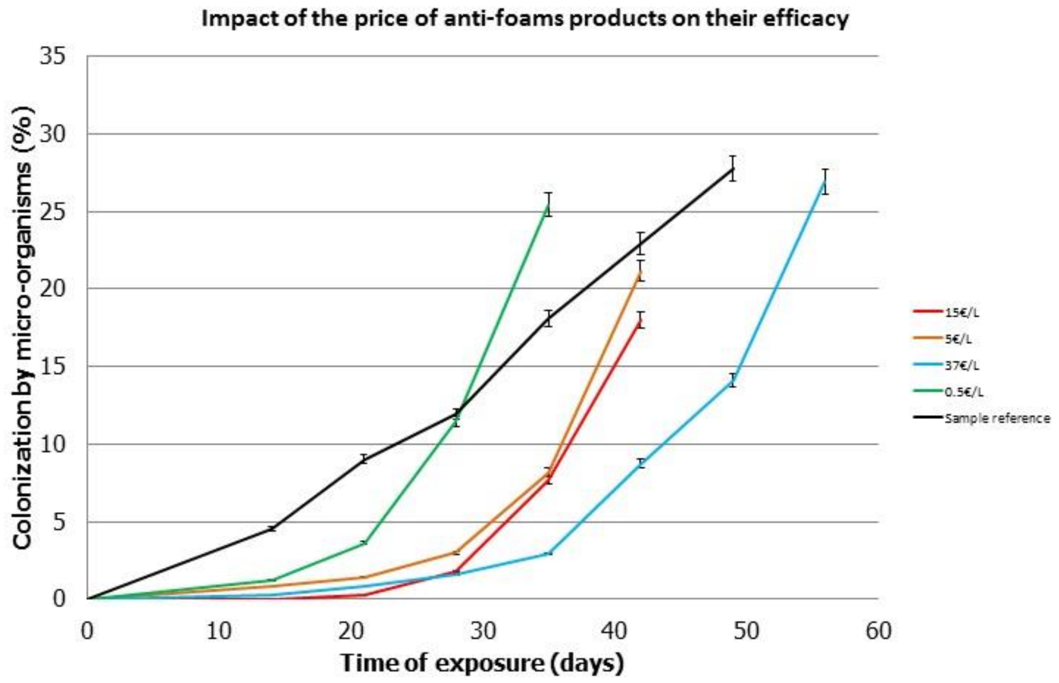

Figure 11: Kinetic of colonization and growth of micro-organisms at the surface of samples covered by anti-foams products following their price

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Product	pH at 21°C	Manufacturer indication
D	7	
F	7,75	7
G	7,25	6/8
I	8,2	
J	7,5	
K	7,3	8
L	7	7
M	7,25	7/8,5
N	6,8	8
O	6,74	8
P	7,3	7
Q	1,63	
S	6,67	7,3
T	6,31	7,5
U	6,25	
V	7,32	
X	7,9	6,7/8,2
Y	6,25	7
B'	7,29	
C'	6,72	6/8
F'	6,8	7
G'	7,65	
H'	7,97	
I'	6,26	
J'	6,84	8
K'	6,9	
L'	7,95	

Table 1: Results of pH measurements for each commercial product

Product	Density	Manufacturer indication
D	0,99	
F	1	1
G	0,99	1
I	1	
J	0,99	
K	0,99	1
L		<1
M	0,99	1
N	1	1
O	1	>1
P	0,99	<1
Q	0,99	1
S	0,99	1
T	0,99	1
U	1	1
V	0,99	
X	0,99	
Y	1	1
B'	0,99	
C'	0,99	<1
F'	1	1
G'	0,99	
H'	1	
I'	1	
J'	0,99	1
K'	0,99	
L'	1	

Table 2 : Results of the measurements of density for each product

Product	Concentration in chloride ions (mol/L)	Manufacturer indication
D	0,062	0,071
F	0,029	0,044
G	0,061	0,073
I	0,063	
J	0,048	0,07
K	0,048	0,056
L	1,203	
M	0,381	0,429
N	0,046	0,056
O	0,053	0,073
P	0,095	0,139
Q	0,068	0,088
S	0,043	0,056
T	0,988	1,06
U	0,056	0,086
V	0,091	0,115
X	0,067	0,087
Y	0,065	0,086
B'	0,084	
C'	0,115	0,132
G'	0,018	0,021
H'	0,024	0,028
I'	0,076	0,058
J'	0,047	0,057
K'	0,066	0,088
L'	0,046	0,028

Table 3: Results of the dosages in chloride ions for each product

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