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SCIENTIFIC PAPER

PHOTOCATALYTIC AND SUPERHYDROPHILIC PHENOMENA OF TiO₂ COATED CLAY ROOFING TILES

The coating procedure of clay roofing tiles was obtained using a simple spraying technique of a laboratory made TiO₂ suspension. This was followed by a thermal treatment at 120/150 °C ($\tau = 30$ min). The defined mass % of TiO₂, grain size value of TiO₂ and its crystal form were the main characteristics of the designed suspensions. The tile samples were studied in their progressive ageing with exposure to visible light and water rinsing procedure. The photocatalytic activity of the coatings was determined after visible irradiation (sun and artificial light) of the defined intensity ($I = 80$ W/m²) through the measurements of the absorption values of the rhodamine B, while the results of the superhydrophilic property were obtained based on the measurements of the water contact angle. Considering the energy consumption, it was shown that the tile products based on the new designed suspension could be produced in already existing industrial dryers using the existing waste heat in the industrial line.

Key words: clay roofing tiles; titania; photocatalytic activity; superhydrophilicity.

Built environment is very sensitive to the contamination by organic, inorganic and microbiological deposits, which change both their esthetic and durability characteristics. New technologies of self cleaning building materials based on a heterogeneous photocatalytic effect is a promising approach in creation sustainable construction materials, which are also active in air remediation [1].

Building materials with photocatalytic active TiO₂ coating show positive affection to degradation of organic [2] and microbiological contaminants [3]. Although there are a large number of investigations of TiO₂ coating application, there are only few scientific works that deal with the complexity related with the manufacturing of clay roofing tiles with TiO₂ active layer [9].

Clay roofing tiles are ceramic materials with high percentage of porosity (up to 23 %) and with a surface that supports the proliferation of microorganisms [6] which could cause mechanical and chemical damage [7]. The relatively high surface configurations of

these materials, as well as their roughness characteristics, cause many difficulties considering the setting up of the procedure of a TiO₂ suspension (coating method, thermal treatment and greater consumption of suspensions than for nonporous substrate). Other different factors, related to titania suspensions, seem to affect the coating efficiency: TiO₂ crystallite size and level of crystallinity, dopants as well as production methods [8]. Mixed titania coatings, with a high density of interfacial sites, could promote a charge separation and an enhance photocatalytic activity [4,5]. The design of the TiO₂ suspension is important for the overall activity and other relevant properties of the new self cleaning tile product.

The aim of this work was the design a new TiO₂ suspension based on a commercial suspension A-visible light sensitive and a laboratory made one, suspension B-UV sensitive. The idea was to build up a TiO₂ coating material for clay roofing tiles with self-cleaning properties and significant photocatalytic activity by using waste energy in the thermal treatment.

EXPERIMENTAL

Material and procedure

Clay roofing tiles. The clay roofing tiles were manufactured in A.D. Polet, the clay roofing tile com-

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Paper received: 14 December, 2009

Paper revised: 13 January, 2010

Paper accepted: 15 January, 2010

pany, a member of the Nexe group, Novi Becej, Serbia. The raw material was based on a mixture of clayey material, quartz, mica and carbonates (dolomite, calcite). From these tiles, plates of 6 cm×6 cm×2 cm dimensions were sampled as substrates for coating procedures.

TiO₂ suspensions. Two kinds of TiO₂ suspensions (A and B) were used in order to design a new TiO₂ coating of a satisfactory photocatalytic activity and high self-cleaning surface properties (coating M). The main characteristics of the suspension A were: 0.94 mass % of TiO₂, transparent sol, grain size less than 30 nm (anatase crystal form of TiO₂), while in the case of the suspension B the characteristics were: 2.5 mass % of TiO₂ (aqueous - deionised water, colloidal dispersion - VP Disp.W 2730 X, Degussa, Frankfurt, Germany, grain size less than 100 nm, dominate anatase crystal form of TiO₂) and 0.208 mass % of poly (ethylene glycol) (PEG) (Baker, Germany).

Tile samples coated with TiO₂ suspensions. The main characteristics of the coatings obtained from the suspension A were: low temperature of the thermal treatment (30 °C/30 min), good adherence to the tile surface but a small value of the photocatalytic activity (6% solution of rhodamine B). The coating characteristics obtained with the B suspension were: higher temperature treatment (290 °C/30 min) than in the case of the previous suspension A but weaker adherence to the tile surface with a significant photocatalytic activity (30%-test reaction rhodamine B) in comparison with the coating obtained by the suspension A.

New designed suspension M (volume ratio: A/B = 1/3) had the following characteristics: transparent sol, grain size 14 nm (anatase crystal form of TiO₂).

Tile samples without TiO₂ film. These samples were named R (referent) while the tile samples coated with the commercial TiO₂ suspension A (1, 3 and 5 layers) dried at 30 °C were named A1, A3 and A5 respectively. The samples coating based on the mixture M with 1, 3 and 5 layers and dried at 120 °C/150 °C ($\tau = 30$ min), were named M1201, M1203, M1205; M1501, M1503, M1505, respectively. As a coating method, a simple spray technique was used ($p = 8$ bar).

Characterization

Thermal characteristics of the basic TiO₂ suspensions A and B were determined with a differential scanning calorimeter (DSC - Q 20 TA Instruments).

Morphological characterization of the dried drops of the M suspension on the glass surface after the thermal treatments at 120 °C/150 °C was performed by stereo microscopy (OMANO OMXTL/V7, articulated boom microscope).

Photocatalytic activity of the coatings A and M were evaluated in the liquid phase by monitoring the degradation of the water solution of rhodamine B (RB) under visible light irradiation of the defined intensity at room temperature. The initial concentration of the rhodamine B solution in the preadsorption test was 2×10^{-5} mol l⁻¹. The preadsorption test of the tiles in Rhodamine B solution was done to prevent the tiles from adsorption process during the test of the photocatalytic activity. The adsorption of the RB (20 µmol/l) by the tile sample was proceeded in the dark for 12 h. The procedure was continued in the dark with the test solutions of RB (10 µmol/l) for the interval of 24 to 36 h (until the adsorption of the dye was completed). The adsorption was considered complete if the differences in the concentration of RB measured after 30, 60, 120 and 150 min were less than 5%. The concentration of the rhodamine B solution during the photocatalytic test was 10^{-5} mol l⁻¹. The light source was "Osram Vitalux" lamp ($t = 25$ °C, $I = 80$ W/m², visible light). The irradiation intensity were measured by radiometer (Solar Light PMA 2100, UV-A detector PMA 2110, Photopic detector PMA 2130 H for visible light, Solar Light co., INC Glenside, PA 19038). The evaluation of the RB concentration was analyzed by measuring the absorbance/concentration with the spectrophotometer (Evolution 600 spectrophotometer) at wavelength 554 nm. The extent of the RB photocatalytic degradation is evaluated as:

$$Act(\%) = \frac{c_0 - c}{c_0} \times \frac{c_1}{c_0} \times 100 \quad (1)$$

where c_0 is the concentration of the test solution of RB before preadsorption, c_1 is the concentration of the dye after the pre-adsorption test (before irradiation) and c is the concentration of RB after the irradiation. The total irradiation time of the experiments was 3.5 h.

The photocatalytic activity of the coated tiles was examined before and after the samples rinsing procedure with water (flow rate was 0.136 l s⁻¹ during 30 min under 45° angle).

Degradation of model organic component - iso-propanol in gas medium - was carried out in the reactor system. The main parts of equipment were: 1) air-tight cylindrical reactor made of stainless steel (approximately 1.4 l in volume) covered by a quartz glass, 2) 300 W xenon lamp, 3) humidity control part with molecular sieves, 4) diaphragm pump and 5) FTIR spectrometer (Perkin Elmer Spectrum BX, US). All parts were connected by Teflon tubes. Valves were built at appropriate places.

The sample was placed in the reactor in the position where the light intensity of Xe lamp was 30 W/m² in the UV range ($\lambda = 300-400$ nm). The system was hermetically sealed and the diaphragm pump was used to ensure the constant air flow through the system.

Before the start of the experiment the relative humidity at 23 °C in the system was kept in the range of 25-30 % by drying air through molecular sieves. This was done to prevent the influence of high relative humidity on the rate of the degradation of pollutants [10]. The relative humidity and temperature were controlled by thermo and hygrometer put into the reactor.

Each experiment was performed injecting 3 μ l of iso-propanol (≈ 800 ppm in gas phase for the described reactor system) through a septum in the reacting system. After that, acetone oxidizes to CO₂ and water (Figure 1).

The lamp was turned on approximately 1-6 h from iso-propanol injection, when constant readings of iso-propanol were achieved, which occurred when the adsorption of iso-propanol onto the samples was

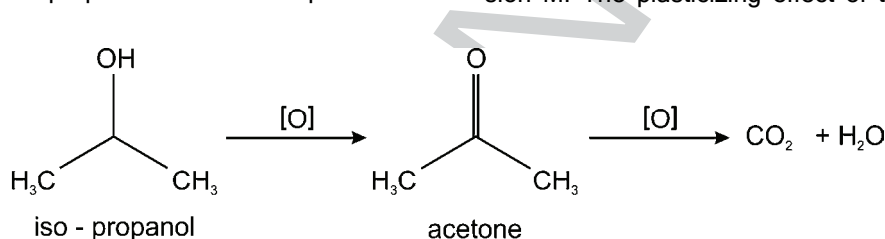


Figure 1. Reaction of decomposition of iso-propanol into acetone and further into CO₂ and H₂O.

accomplished. The infrared part of the spectrum was blocked by an adequate filter.

The monitoring of the oxidation of iso-propanol into acetone and the subsequent degradation of acetone was followed by calculation of the area of the peaks characteristics for iso-propanol and acetone, at 951 and 1207 cm⁻¹ respectively, measured by a FTIR spectrometer and analysed by software. The working time was set up for approximately 24 h.

Hydrophilic characteristics were determined by the contact angle measurements (Surface Energy Evolution System, Advex Instruments). The change of water contact angle before and after irradiation by Osram Vitalux lamps (the same laboratory conditions as for the photocatalytic activity examinations, $\tau = 3.50$ h) were registered. In this way the photocatalytic effect could be correlated with the water contact angle values. The results are calculated as average values of at least 10 measurements of the water contact angle in ambient air. The water droplet had a volume of ~ 10 μ l.

RESULTS AND DISCUSSION

Thermal characteristics of the basic suspensions A and B

The new suspension M was designed based on the mixture procedure of the suspensions A and B (volume ratios: 1/3, 1/1, 3/1). The temperatures for the thermal treatments of the new suspension were determined based on the results of the DSC measurements in a sealed pan (Figure 2). The endothermic peaks for the suspension A (Figure 2a) indicate the decomposition of the organic compounds. Figure 2b indicates an intensive peak corresponding to water evaporation covering the peaks of the suspension B which correspond to other processes. After the drying procedure it was possible to locate the temperature interval of the decomposition of the PEG material in the suspension B (Figure 2c). The incorporation of the PEG in the suspension A could be the cause of a slight reduction in the temperature transformation of the organic compounds of the new designed suspension M. The plasticizing effect of this additive (PEG

material) could be explained by the reduction of the attractive forces among the present polymer chains.

Based on the results of the DSC measurements, the temperatures 120 and 150 °C were identified as adequate for the thermal treatment of the new suspension M. The already existing industrial dryers in the production of clay roofing tiles could be used for the possible industrial application of the suspension M, which is a very important fact considering the energy consumption at the industrial level.

Morphological characteristics of M films

Morphological characterization of the dried drops of the M suspension on the glass surface (Figures 3 and 4) presented a preliminary investigation considering the coating surface porosity after the thermal treatments at 120/150 °C. The highest porosity with an optimal pores distribution was identified in the case of the mixture M with the volume ratio A/B = 1/3. This surface porosity could be the most promising parameter for the photocatalytic efficiency of the new

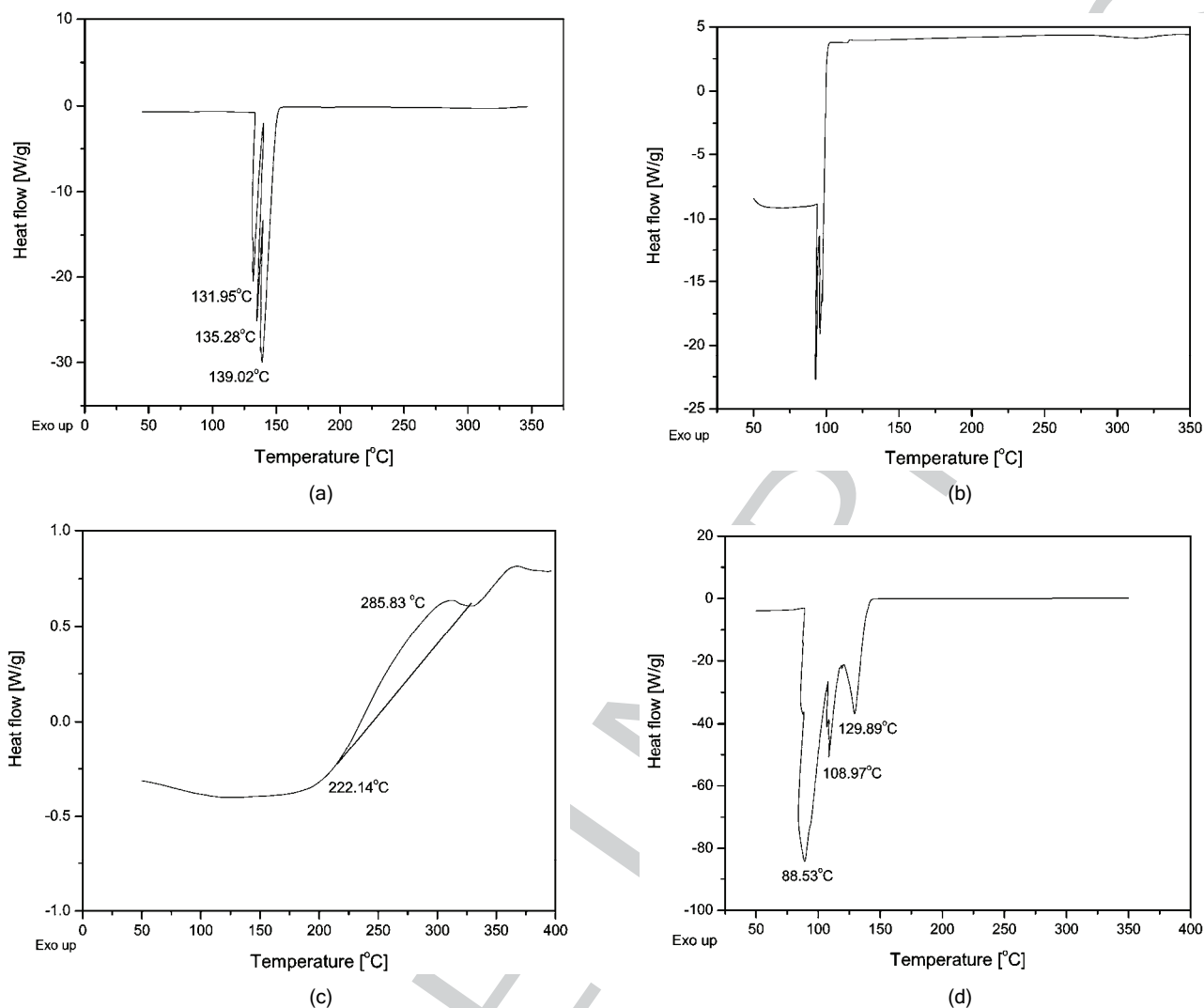


Figure 2. DSC curves of TiO₂ suspensions (a), suspension A (b), suspension B (c), suspension B dried at 105 °C (d) and new designed suspension M (1A:3B).

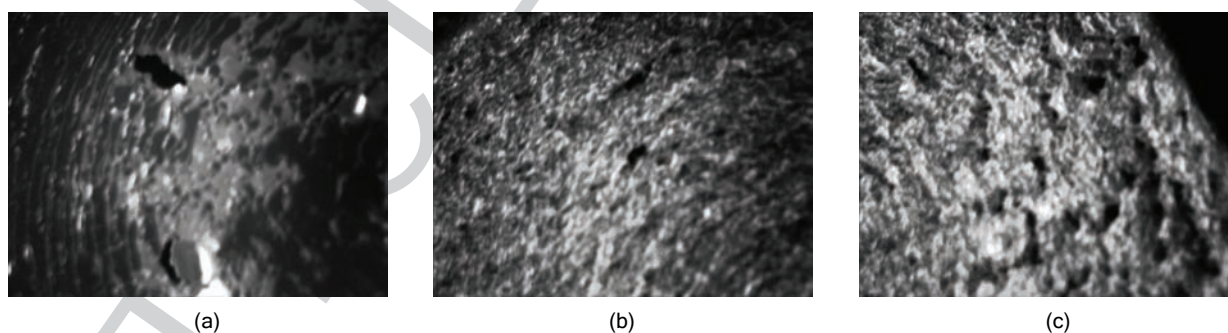


Figure 3. Drops of mixture M deposited on the glass surface and dried at 120 °C for 30 min, volume ratio 3A:1B (a), 1A:1B (b) and 1A:3B (c); stereo microscope images, 75 \times .

designed coating M as the diffusion towards and from the surface is an important step in catalysis.

Activity of the tiles coated with A suspension

The photocatalytic activities of the tiles coated with A suspension, determined in a natural condition

(sun as light source), were not high. The best result was achieved in the case of the tile coated with A3 suspension (Figure 5).

The activity determined under artificial light (Figure 6) points out the following correlation among the

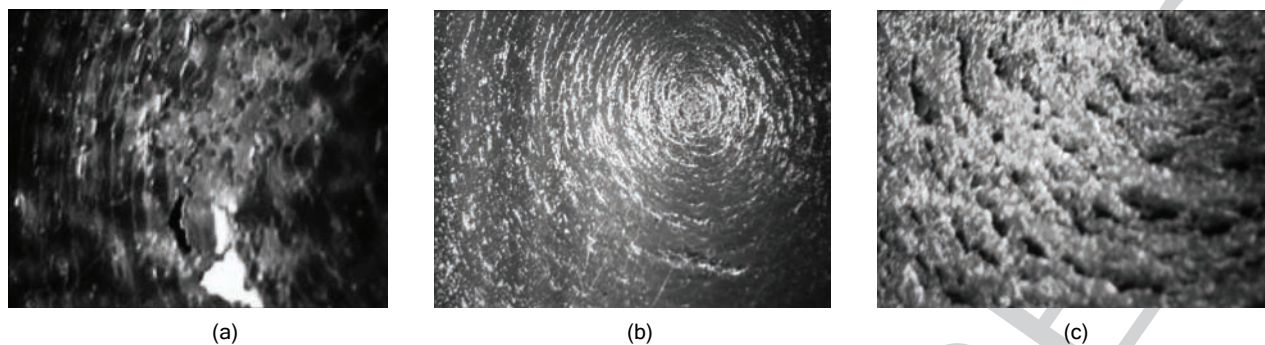


Figure 4. Drops of mixture M (volume ratio 1:3, 1:1 and 3:1) deposited on the glass surface dried at 150 °C for 30 min, volume ratio 3A:1B (a), 1A:1B (b) and 1A:3B (c); stereo microscope images, 75x.

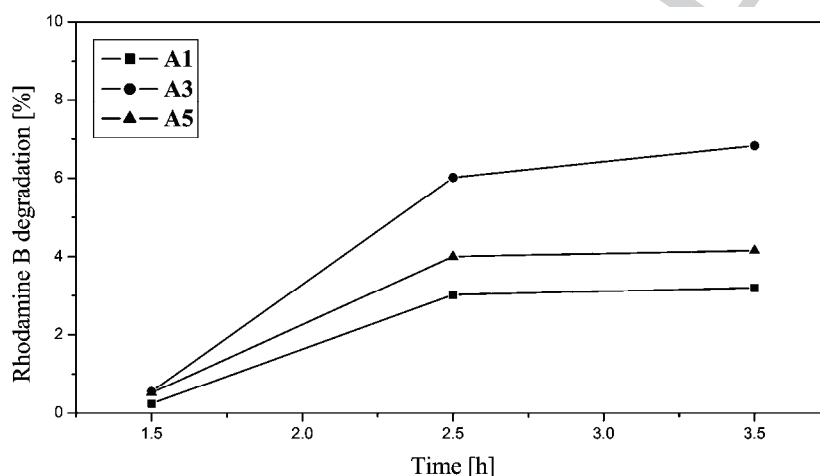


Figure 5. Photocatalytic activity of the tiles coated with A1, A3 and A5 films - sun as light source.

tiles, namely, the A5 sample has the highest activity before the rinsing test, while A1 and A3 have the highest activity after the rinsing procedure.

Activity of the samples coated with M suspension

The tile samples with M coating have a higher photocatalytic activity than samples with the coating A. The possible explanation could be found in the higher temperature of the thermal treatments (120 and 150 °C), higher mass % of TiO₂ in the suspension M than in the commercial suspension A. Figure 7a shows that samples with smaller layer numbers possess higher photocatalytic activity than samples with larger layer numbers. It was also noticed that there is no difference between the samples before and after the water rinsing procedure.

The durability of the coating M on the rinsing procedure is significant (Figure 7b). The highest photocatalytic activity is noticed in the case of the samples coated with 3 layers (both thermal treatments: 120/150 °C).

Degradation of model organic component in gas medium by FTIR - gas/solid interface

The photocatalytic activity of the samples was evaluated as the velocity of the initial acetone formation because the photocatalytic oxidation of iso-propanol into acetone is rapid at room temperature, but subsequent oxidation of acetone to CO₂ and H₂O is slower. For a very short time, the slope of the curve for acetone formation gives an evaluation of the formation velocity as a constant value [11] (Figure 8). The velocity of the acetone formation is expressed as volume per time (ppm/h) in the gas phase (Table 1). In addition, being the first intermediate of iso-propanol degradation, acetone formation is a characteristic and distinguishing feature of iso-propanol photo-oxidation. The conversion of iso-propanol over acetone to CO₂ and H₂O is shown in Figure 8 ($c_{initial}$ is the threshold concentration of iso-propanol in the gas phase; c_0 is the constant concentration of the iso-propanol in the system after required absorption time ($t_{absorption}$)).

As the model systems for the above test, the tiles coated with 3 and 5 M layers, fired at 150 °C, and

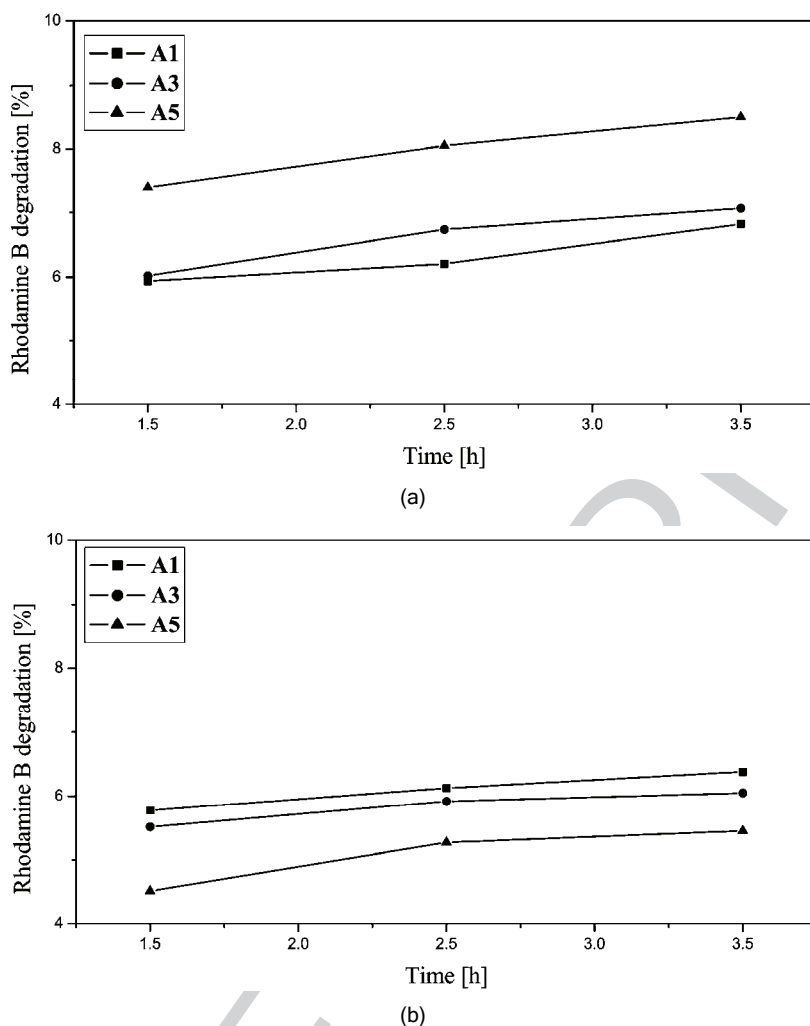


Figure 6. Photocatalytic activity of the tiles coated with A1, A3 and A5 films-before (a) and after (b) water rinsing procedure - Osram Vitalux as the light source.

the tiles coated with 3 A layers fired at 30 °C were chosen. This choice was done based on the previous photocatalytic measurements (Figure 7). The greatest value of iso-propanol decomposition rate (182 ppm/h) is obtained in the case of the tile sample coated with 3 M layers (Table 1). A great difference between this value (182 ppm/h) and the tile coated with A suspension per 3 layers (112 ppm/h) was noticed.

Topography of the coated samples and water contact angle

Surface properties, more exactly hydrophilicity and hydrophobicity, are important characteristics of clay roofing tiles coated with photocatalytic films. By a surface absorbing water process, a direct contact between water molecules and the coated surface is obtained.

The OH[•] and O₂[•] forms are created which is very important for the photocatalytic processes on the tile surface. In this way the photocatalytic effect could be

correlated with the water contact angle values. The obtained results of the contact angle measurements are shown in Tables 2 and 3 for the samples of A and M series.

After the light irradiation procedure, a reduction of water contact angle value was noticed for all samples (Tables 2 and 3). It was caused by a reasonable photon energy quantity absorption by the TiO₂ coated surface. A quantity of Ti³⁺ was formed [12], which is responsible for the photocatalytic activity and superhydrophilicity of the coated tiles. Table 2 indicates that samples with A coating have a slightly hydrophilic surfaces which is confirmed by higher values of the contact angle. The highest hydrophilicity for the samples A was noticed in the case of the A3 sample before, as well as after the irradiation procedure (Table 2, Figure 9). The contact angle values for the M series samples (Table 3) are much lower than for the A series. Obviously, the hydrophilicity of these tiles is higher in com-

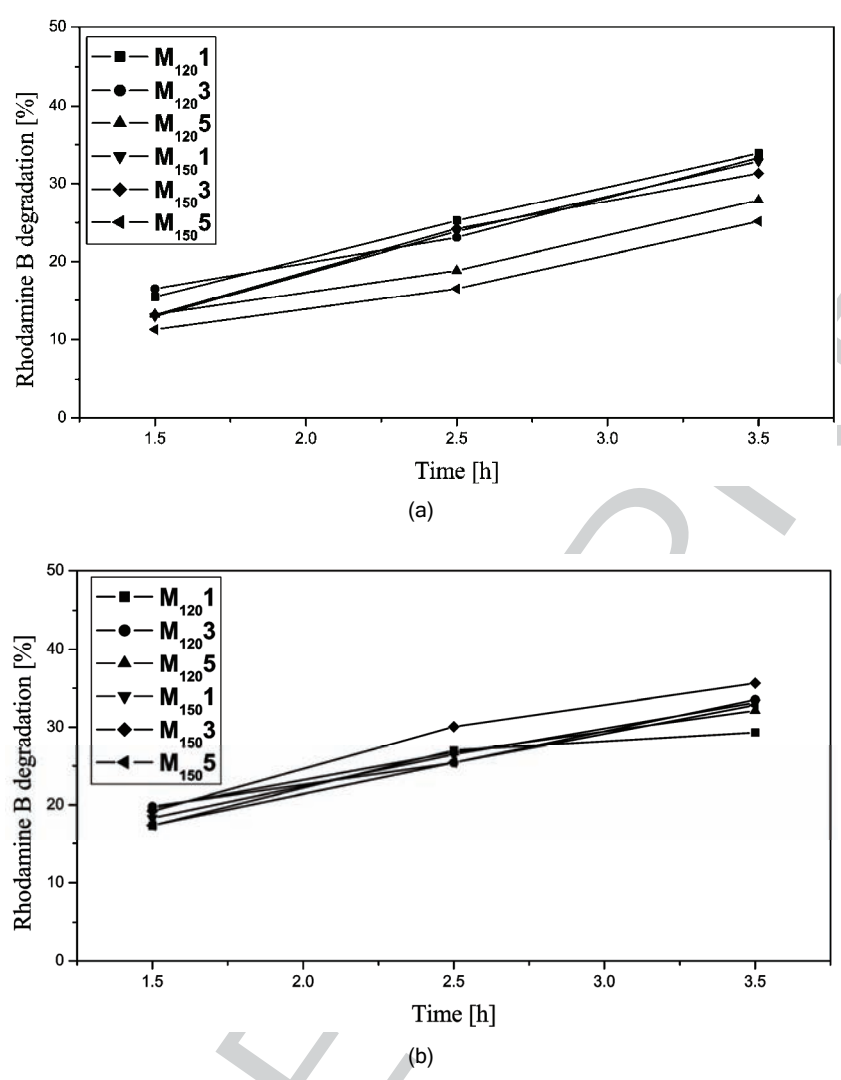


Figure 7. Photocatalytic activity of the tiles coated with M coating before (a) and after (b) water rinsing procedure.

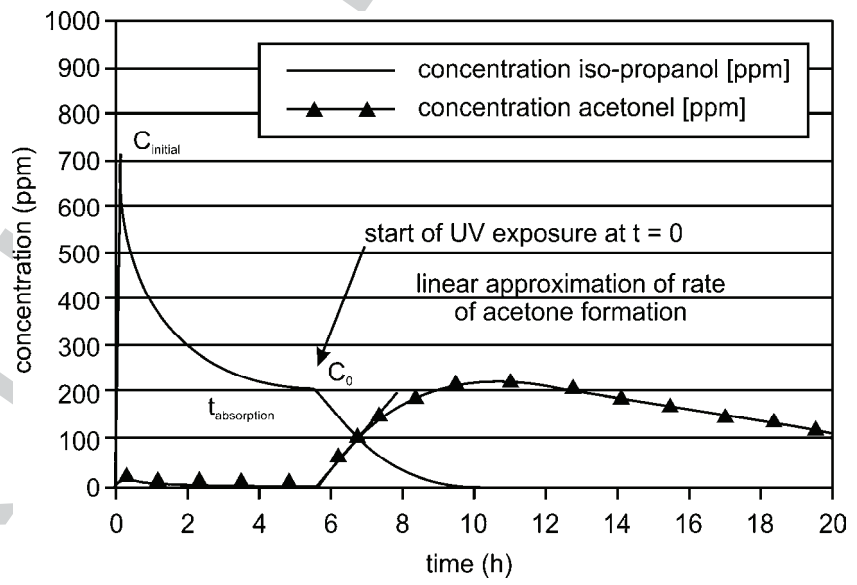


Figure 8. The course of the photocatalytic degradation of iso-propanol is demonstrated.

parison to the ones coated with the commercial suspension A, contributing in that way to better self cleaning properties. It is also necessary to notice that the samples coated with 3 M layers and dried at 120 °C (Table 3) showed higher values of self-cleaning activity, Figure 10.

Table 1. Velocity of the acetone formation

Tile sample	Velocity of acetone formation, ppm/h
A3	112.0
M ₁₅₀ 3	181.6
M ₁₅₀ 5	119.2

Table 2. Values of the contact angle measurements before and after irradiation - Osram Vitalux lamp

Sample	Contact angle, θ_c / °, before/after irradiation	Tile surface state
R Tile	63/64	Hydrophilic
A1	88/74	Hydrophilic
A3	85/72	Hydrophilic
A5	96/73	Hydrophobic/hydrophilic

Table 3. Values of the contact angle measurements before and after irradiation - Osram Vitalux lamp; tiles coated with M suspension

Sample	Contact angle, θ_c before/after irradiation ^a	Tile surface state
R Tile	63	Hydrophilic
M ₁₂₀ 1	28	Very hydrophilic
M ₁₂₀ 3	23	Very hydrophilic
M ₁₂₀ 5	25	Very hydrophilic
M ₁₅₀ 1	30	Hydrophilic
M ₁₅₀ 3	28	Very hydrophilic
M ₁₅₀ 5	31	Hydrophilic

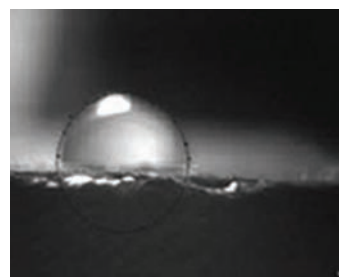
^aAfter light irradiation, the values of the contact angle were <10°

The topography of the analyzed tiles was additionally characterized according to the roughness characteristics (Tables 4 and 5).

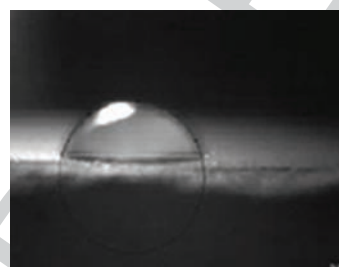
The roughness values of the coated tiles are lower than in the case of the referent tile (R).

Regarding the nature of the films, the suspension M formed a coating with lower Ra value (arithmetic mean of the absolute departures of the roughness profile) in comparison with the suspension A. With the increase of the layer number the roughness of this value is lower.

The greater difference between the samples, considering the value *Ra*, is noticed in the case of the systems designed with one layer (M1201/M1501). Considering the influence of the temperature, it is evident that *t* = 150 °C resulted as the temperature which influenced the lowest roughness value of the tiles.



(a)

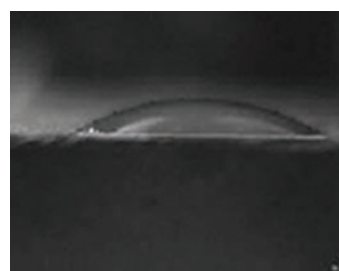


(b)

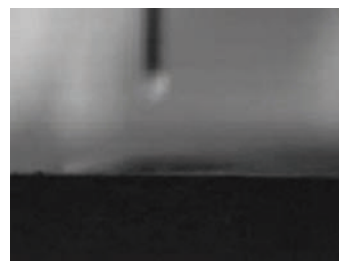
Figure 9. Contact angle measurements for tiles coated with A3 before (a) and after (b) irradiation.



(a)



(b)



(c)

Figure 10. Contact angle measurements for tiles coated with M3120 (a) and M3150 (b) before irradiation and M3150 (c) after irradiation.

Table 4. Roughness values of the tiles coted with A coatings

Sample	Ra^a	Rz^b	Rf^c
R Tile	2.96	17.87	28.63
A1	2.91	16.8	26.23
A3	2.89	16.87	23.6
A5	2.78	16	20.63

^aArithmetic mean of the absolute departures of the roughness profile;

^bmaximum peak to valley height of the profile within a sampling length;

^ctotal height of the profile

Table 5. Roughness values of the tiles coted with M coatings

Sample	Ra^a	Rz^b	Rf^c
R Tile	2.96	17.87	28.63
M ₁₂₀ 1	2.81	16.63	23.86
M ₁₂₀ 3	2.51	13.23	20.03
M ₁₂₀ 5	2.41	13.13	19.63
M ₁₅₀ 1	2.59	14.23	18.46
M ₁₅₀ 3	2.45	13.17	19.5
M ₁₅₀ 5	2.50	13.63	18.77

^aArithmetic mean of the absolute departures of the roughness profile;

^bmaximum peak to valley height of the profile within a sampling length;

^ctotal height of the profile

CONCLUSIONS

- The new design TiO₂ suspension (M) based on the balanced ratio of two initial suspensions (commercial A and laboratory B) showed a synergy effect avoiding the drawbacks of the parent suspensions.

- It was shown that photocatalytic activity is not proportional to the content of TiO₂, the number of layers applied to the matrix being the crucial factor for the optimal properties. In the case of the suspension M, the best photocatalytic activity is obtained for the samples with three layers.

- Samples with new designed coating M show better self-cleaning properties (lower water contact angle values, higher activity-rhodamin B test and FTIR test) in comparison to the commercial coating A.

- Samples with M coating show high resistance to water rinsing procedure which was manifested with small or negligible decrease of the photocatalytic activity.

- The roughness of the tiles coated with M suspension was lower than the roughness of the ones coated with the suspension A.

- Considering the energy consumption in the industrial line, it was shown that the tile products based on the new designed suspension M could be produced in already existing industrial dryers using the existing waste heat in the industrial line.

Acknowledgements

This work was supported by the Ministry of Sciences and Technological development, project TR 19005.

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