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NEW MATERIALS FOR FINISHING OF ANCIENT MONUMENTS AND PROCESS OF OBTAINING AND APPLYING

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Abstract

The work relates to a composition of an additive mortar with a volumetric weight below 250kg/mc, the thermal conductivity coefficient below 0,08kcal/m×h×°C, mechanical strengths more than 7daN/cm² with self-cleaning effect after commissioning. In order to obtain a self-cleaning effect over time by eliminating chromatic deviations, the composition of ZnO, TiO_2 *and the three colored ceramics mixture is reformulated by optimizing the content based on color adjustment, by using a specialized software and CIE L*a*b* colorimetry for pressed bulk powders, at the medium one given by the patina. The composition optimization is performed by modifying, as appropriate, the addition rate of eggshell powder by a reformulated percentage related to the three fine colored ceramic powders. The freshly prepared mortar is applied to the restoration of the historical monument's facades through physical-structural and chromatic reintegration interventions. Depending on the conservation state of the apparent structures, two stages with differentiated specific operations are used: for surfaces without gaps, but chromatically degraded and with deposits of embedded dirt, it is spread with a trowel in the form of thin plasters on fiberglass mesh and in case of damage with deep lacunars areas the consolidation of the mobile structures will be first executed and grouting with a simple mortar based on river sand, expanded perlite, Portland cement and water in gravimetric ratio sand:perlite:cement:water = 2:1:2:5. After strengthen the same thin plasters will be applied on the fiberglass mesh. The new mortar allows the accomplishing of a series of advantages both in the processes of paste obtaining, as well as during commissioning and after, respectively within the period of integration in the tourist circuit.*

***Keywords**: Historical monument; Thin plasters; Additive mortar; Photocatalysis; Self-cleaning of exterior trim; Restoration and preservation.*

Introduction

In the current practice of restoring the finishes of ancient monuments, additive mortars are used, which in addition to the self-cleaning effect of the external parietal surfaces, must have a volumetric weight below 250kg/m^3, a thermal conductivity coefficient below 0.08Kcal/m×h×°C, a mechanical strength more than 7daN/cm² and allowing a good

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compatibility with the operating support, and by in mass staining before application, do not to affect the patina [1].

In this respect there are known a lot of pre-dosed dry mortars commercially delivered in bags which are mixed with the water before use, based on fine aggregates, mineral binders and polymeric additives in order to improve the chromatic, physical-structural and mechanical performances. Depending on applications (masonry mortars, plaster mortars, adhesive mortars for ceramic tiles, mortars for decorative plasters, mortars for external thermal insulation systems, mortars for repairs, etc.) the three major components (fine aggregates, inorganic or mineral binders and polymer binders) vary between large concentration limits [2-7]. These mortars have the disadvantage that neither the compatibility nor the synergy studies were involved in the formulation of the composition, and from rheological point of view the pastes obtained from pre-dosed dry powders do not allow an easy application.

Excepting the mineral binders and aggregates, the polymeric additives for plasters are redispersible powders from the polymers group or vinyl and acrylic copolymers, cellulose ethers, etc. [8], which allow, in addition of improving the permeability and adhesion to the substrate, an increase of plasters durability and an adjustment of workability to the desired level, and by controlling the water content contributes to modeling of cement hydration kinetics and wall breathing [9]. The polymeric systems used of mortars additivation, form during implementation the membrane systems that affect the respiration of the wall and do not allow the diffusion of volatile components or the segregation of electrolytes, leading to fluorescence and microbiological contamination. Thus, almost all polymeric binders give a good adhesion to the substrate and a low water permeability coefficient but have the disadvantage of poor drying characteristics (high permeability to water vapors) [10-12]. Also, there are known gypsum-based mortars [13], which have the disadvantage of higher specific weights, higher index of chemical activity, with tendencies to acid hydrolysis and rate of degradation to sudden variations in humidity and temperature, reducing the durability of plasters. In all these mortars, the role of additivation with photocatalytic materials, having the effect of dirt deposits self-cleaning on the external monument's surfaces, is little highlighted or not at all.

Starting from these patents, within our team, an additive mortar was elaborated used in the restoration interventions of the ancient monument's facades, strongly affected by patina and with dirty deposits, with or without lacunars areas (lack of material). In this context the most kindred mortar composition of those used in the monuments restoration was selected namely a thermal insulation mortar based on expanded perlite prepared from 180...220 parts of Portland cement, 90...120 parts of fly ash, 50...80 parts of quartz sand, 90...150 parts of expanded perlite, 12...15 parts of acrylic polymer emulsion, 6...12 parts of ethylene-vinyl acetate copolymer emulsion, 15...20 parts of polypropylene fibers and 10...20 parts of redispersible emulsion cellulose ether. This composition has the disadvantage of using a high number of components, which complicates the mixing and homogenization process of redispersible polymer and copolymer emulsions, with high production cost and toxicity for the applicant and which gives mortars high specific weights [14].

By corroboration with the literature in terms of obtaining, characterizing and applying of photocatalytic materials with self-cleaning effect of dirt deposits along with knowledge of the self-cleaning mechanism, the paper presents the formulation of a new additive mortar composition, its obtaining process and application technology. The composition was developed so as after its implementation at the restoration of historical monuments facades (structural-superficial and chromatic reintegration), to feel in time the self-cleaning effect of surface and respectively the harmonization (improvement) of chromatic deviation under the influence of environmental factors and pollutants including microbiology. This mortar allows the achieving of specific applications for hydro-, thermo- and sound-insulating plasters, with volumetric weights less than $250kg/m^3$, thermal conductivity coefficient below 0.08kcal/m×h×°C, mechanical strength over $7daN/cm^2$ and a good compatibility with the support, respectively a synergy in the application, without affecting the patina of time.

The problem solved by our invention [15] consist of use a light mortar with reinforcing aggregate expanded perlite and finely divided eggshell, both additivated with very fine powders of ZnO, TiO_2 and three burnt clay ceramics, differently colored in titan red, brown and black, and as a mineral binder was used Portland cement, fine powder of calcium oxide (dehydrated calcium lime), fly ash resulted from burning of sunflower husks and acrylic binder. Depending on the conservation state of the apparent structures, the mortar applying process on the historical monuments facade involves two stages, with differentiated specific operations: for surfaces without gaps, but chromatically degraded and with deposits of embedded dirt, when thin plasters on fiberglass mesh are achieved, or the case of damages with deep lacunars areas when the consolidation of the mobile structures will be first executed with a simple mortar based on river sand, expanded perlite, Portland cement and after strengthen the same thin plasters will be applied on the fiberglass mesh. This applying process leads to improving of permeability and adhesion to the substrate, an increase in the durability of the plasters and an adjustment of the workability in the intervention area, and by controlling the water content an improvement of the hydration kinetics of the mortar and an optimal respiration of the wall.

Theoretical part

The mechanism of photocatalytic processes for self-cleaning of old monuments facades

Since 1972, when Fujishima and Honda [16] studied the photocatalytic decomposition of water on a TiO_2 catalyst, special attention has been paid to heterogeneous photocalysis and the obtaining of photocatalytic materials, with applicability in the remediation or protection of the facades of ancient monuments [17-21]. Heterogeneous photocatalysis involves the use of phocatalysts made of semiconductor materials with carefully controlled properties (high sunlight absorption coefficient and increased conductivity for photogenerated load carriers), such as mixt oxides, hydroxo-oxides of Zn(II), Ti(IV), Zr(IV), etc., and solar energy, a natural and renewable source of energy [21, 22]. Therefore, the elaboration and formulation of the composition of semiconductor materials, which have a wide selective spectral response, with increased activity and stability, are key targets in optimizing the technologies for obtaining these materials and the compositions of the mortars, for an efficient use of solar energy in the field of self-cleaning mortars, which are intensively studied in recent years [17].

Therefore, heterogeneous photocatalysis uses as an energy source the solar radiation and semiconductor mesoporous nanomaterials with photosensitive properties. Their main feature is the energy of the forbidden band (Eg) which is defined as the difference between the lower limit of the conduction band (BC) and the upper limit of the valence band (BV). By exposing the photocatalyst to light radiation, part of the incident radiation (the one with energy higher than the energy of the forbidden band of the semiconductor, $h\nu \geq Eg$) will be absorbed by the material, and the electrons (e^-) will be promoted from the valence band (BV) to the conduction band (BC), leading to the formation of voids (h^+) in the BV.

This will result in pairs of electrons (e^-) and voids (h^+), chemical species with oxidizing and reducing properties, respectively. Electrons will interact with the oxygen leading to the formation of superoxide radicals ($O_2^-\bullet$), and voids interact with water molecules forming HO• radicals, reactive oxide species, which will degrade the organic molecules of superficial dirt deposits, until mineralization. It should be noted that for an effective photocatalytic degradation of organic deposits, the processes of oxygen reduction and oxidation of adherent dirt must occur simultaneously, in order to avoid the accumulation of electrons in the conduction band, thus reducing the recombination rate of electrons and voids [23-25].

Heterogeneous photocatalysis has a number of advantages related to the complete oxidation of organic deposits in reduced time (at most a few hours), the possibility of their photodegradation at very low concentrations (of the order of ppb), the availability of extremely active and inexpensive photocatalysts, easy to adapt to the mortars used in the finishing operations of the surface structures of old monuments.

The efficiency of heterogeneous photocatalysis processes increases if the recombination stage of hollow electrons is slowed down by using simple semiconductor photocatalysts, doped semiconductors or coupled (tandem) with another semiconductor(s). Also, the combined photocatalyst/electron acceptor system has proven to be very effective in the processes of photodegradation of organic deposits on the finishes realized with apparent mortar.

In general, the dirt films on the surface of the old monuments facades, resulting from the deposition in time of nanodispersions in the atmosphere, contain organic compounds, natural or synthetic, most of them resulting from the pyrolysis of fuels and fossil fuels, which also have the property of coloring the substrates (mortars, brick, ceramics or apparent stone). In general, the existence of color is given by the presence of double conjugated bonds in organic molecules or radicals.

The photocatalytic properties of semiconductors are most often related to the structure of energy bands and the type of electrical conduction. As it is known, the energy of the forbidden band (Eg) is an important feature of the semiconductor material. In addition, the composition of the crystal phases, the crystallinity, the morphology and the specific surface are also significant parameters that improve the photocatalytic activity of the semiconductor catalysts [17, 23].

Among semiconductor photocatalysts, simple or double metal oxides, as well as those chemically or physically doped, play an important role in the application of new photocatalytic technologies capable of eliminating dirt deposits and chromatic deviations of external parietal finishes. The value of the forbidden band energy and the morphologies corresponding to semiconductors based on metal oxides and sulphides are shown in Table 1.

Table 1. Characteristics of materials used to obtain mortars for autocatalytic facades

Material	Synthesis method	Morphology	Forbidden band energy, Eg [eV]	References
TiO_2 films	DC reactive magnetron spraying	Granular with distinct submicrometric formations	3.25 – 3.3	[27]
TiO_2 doped with ZnO	Sol-gel	Granular	3.07-3.15	[28]
TiO_2-CdO films	Doctor blade	Porous	2.97-3.2	[28]
ZnO nanoparticles	Precipitation Poliol reaction	Aggregates of various shapes	3.11 – 3.14	[29, 30]
ZnO film	Hidrothermal	Micro/nanostructures	3.2	[31, 32]

Functional characteristics of photosensitive materials with self-cleaning effect of superficial deposits

Among the semiconductor materials, which can function as photocatalysts with self-cleaning properties of facade mortars, the most studied are: TiO_2, as such and doped [25-28] and ZnO [29-33].

One of the most important parameters of these materials is the long-term sustainability and long-term cleanliness of the facade. It is known that plasters based on lime mortars contain nanopores, which absorb moisture and decrease the surface tension in the water drop. This water penetrates into the top layer of the plaster and, upon repeated vaporization, exerts pressure on the impurities captured on the plaster. It is also known that nanopores are active in engaging the optimal humidity regime not only in contact with rainwater, but also with the humidity in the air [25-33].

TiO_2 and ZnO-based photocatalyzers provide a very effective self-cleaning effect for a bright and lasting facade. Another very important aspect, it is related to the activity of bacteria, algae, fungi and other microbiological organisms, which over time form biofilms, and can degrade under the influence of photocatalysis.

Thin-layer plasters for the facade are special plasters based on lime, cement or gypsum, some of which can be applied to the restoration of old monuments both in the form of thin support and as decorative plaster. Unlike standardized plasters with a minimum thickness of 10 or 15mm, thin-layer plasters are applied with a thickness layer of 3 to 6mm. As a rule, thin-layer plasters are applied on flat supports at a thickness of about 4mm. The applicator must take into account that by using thin-layer plaster, the maximum flatness tolerances of 2 to 3mm can be compensated with the usual thickness of the plaster. In principle, higher dimensional mass tolerances should be applied to the base of the plasters. Evenness tolerances of 5mm between non-flat supports and finished surfaces of walls cannot be compensated by thin-layer plasters [21].

Obtaining photosensitive nanomaterials for self-cleaning mortars

Among the materials presented in the specialized literature used as photochemical catalysts for facade finishing mortars, involved in the restoration of old monuments, titanium dioxide (TiO_2) and zinc oxide (ZnO) were taken into consideration. TiO_2 samples doped with ZnO, obtained by the sol-gel method, contain the same crystalline phase (anatase), but have specific surfaces and different forbidden band values. Photocatalytic tests are performed mainly at a concentration of 20-50mg/L. These materials, like the systems with photocatalyst, are irradiated with UV light (6.5mW/cm^2 intensity) for 120min. The results showed that doping TiO_2 with ZnO has a positive effect on the photocatalytic activity, especially when the percentage of doping is less than 0.5% (% by mass). A higher percentage of doping in TiO_2 can induce the conglomeration of ZnO particles, which generate recombination centers of electron-void pairs. In contrast, zinc oxide (ZnO) obtained through the hydrothermal method, which was applied in a large number of scientific papers highlighting the study of photocatalytic properties, was prepared by two different methods: the method of precipitation in aqueous systems, using a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and NaOH, followed by a heat treatment of the powder obtained at 700°C and the polyol method, using the mixture $Zn(CH_3COO)_2 \cdot 2H_2O$ and 2-ethoxyethanol, followed by the same heat treatment [31].

The average size of ZnO crystalites obtained by the precipitation method is 34.54nm, while for ZnO obtained through the polyol method it is 26.22nm. This difference is due to the synergistic effect induced by the 2-ethoxyethanol solvent during the preparation process. The BET-specific area value is higher for ZnO obtained by precipitation (6.07m^2/g) compared to ZnO obtained by the polyol method (2.71m^2/g). As for the Eg value, it is not significantly influenced by the synthesis method, the reported values being 3,11eV for ZnO obtained by precipitation, respectively 3,14eV for ZnO prepared by the polyol method.

The photocatalytic experiments were performed on artificially patinated surfaces with soot film deposits, on which it was sequentially applied by brushing 5 layers of aqueous nanodispersions containing 1.5g/L ZnO, followed by drying (evaporation in the atmosphere). The samples were irradiated with UV light for 240 minutes. The results showed that the ZnO obtained by the precipitation method has a degradation efficiency of 87%, while the ZnO obtained through the polyol method has a degradation efficiency of 99.5% [31-35].

Experimental part

Materials, equipments, operations and work steps

The formulated composition and the obtaining and applying procedure of the new mortar remove the disadvantages of those presented in the critical analysis of the known stage by the fact that in order to obain thin plasters and beaumontage on the historical monuments facade affected by environmental factors, after the implementation its provide self-cleaning effect, while preserving the patina. It consist of 15 parts by weight of mineral binder in a mixture of fly ash resulted from the burning of sunflower husks, Portland cement and calcium oxide, ground to a fineness of 6...10% residue on a sieve of 4900meshes/cm^2, in gravimetric ratio ash:Portland cement:calcium oxide = 1:2:2 and 10 parts by weight of expanded perlite and fine eggshell powder, both with a grain size less than 0, 1mm dditives with ZnO and TiO_2.

For the patina effect in the last mixture is added fine powder obtained by grinding, in a mill with high alloy iron balls, and sieving, through a sieve of 4900meshes/cm², of three ceramics differently colored in titian red, brown and black. All these micropowders, obtained separately by grinding, are mixed in gravimetric ratio perlite:eggshell:ZnO:TiO_2:colored ceramics = 6.00:3.60:0.16:0.04:0.20. For this mixture, the content of ZnO, TiO_2 and the three colored ceramics is previously optimized in defined ratios to adjust the color of the mixture (bulk powders) according to an expected vintage effect, which after the application to approach of the average background shade given by the patina of time or ancienty [35-37]. In this purpose, by involving the CIE L*a*b* reflection colorimetry, the combination ratio of the fine ceramic powders (titian red, brown - burnt shade and black) was obtained by changing the addition rate in the mixture of perlite, eggshell, ZnO and TiO_2, with a percentage reformulated by using a specialized soft for fine powder mixtures. The whole mixture, consisting of the two powder systems, is homogenized by mixing with 25 parts by weight water, which contains dispersed acrylic binder (in gravimetric ratio water:binder = 2:8) [38]. The obtained paste is applied on the facade of historical monuments, depending on the conservation state of the apparent structures, using two distinct operations: (i) for surfaces without gaps, but chromatically degraded and with deposits of embedded dirt, thin plasters on fiberglass mesh, (ii) in the case of damages with deep lacunars areas the consolidation of the mobile structures will be first executed with a simple mortar based on river sand, expanded perlite, Portland cement and water in gravimetric ratio sand:perlite:cement:water = 2:1:2:5 and after strengthen the same thin plasters will be applied on the fiberglass mesh.

Results and discussions

Mortar's obtaining and commissioning

There is presented only one example of mortar accomplishment, the one often used to restore the facades of historical monuments, with poor conservation status, which require absolutely necessary or urgent interventions.

At the beginning it is ground separately the eggshell, the fly ash resulted from the burning of the sunflower husks, the powders of the three ceramics, colored differently in titian red, brown (burnt shade) and black, respectively that of calcium oxide or dehydrated lime (with an active lime content of at least 85%) up to a fineness of 6 ... 10% residue on a 4900mesh/cm^2 sieve. After that, is homogenized separately the mixture of fly ash resulted from the burning of sunflower husks, Portland cement and calcium oxide in gravimetric ratio ash:Portland cement:calcium oxide = 1:2:2 and respectively the mixture of expanded perlite, the eggshell powder, calciumoxide, ZnO, TiO_2 and three burnt clay ceramics differently colored in titian red, brown and black, in gravity ratio perlite: eggshell:ZnO:TiO_2: colored ceramics = 6.00:3.60:0.16:0.04:0.20.

The color optimization in order to adjust the chromatic tonality to that of the time patina is realized involving a specialized software and the CIE L*a*b* reflection colorimetry. For this, the surfaces of the facades with unaffected patina by environmental factors are chosen and are colorimetricized in several points, and then the content in zinc oxide, titanium dioxide and the three differently colored ceramics is modified, to the detriment of the shell egg, up to a nuance equal to the average of the chromatic deviations (ΔE^*) determined on the facades, also involving the CIE L*a*b* reflection colorimetry, this time carried out on planimetrically pressed bulk powders [36-38]. After the two dry powder systems are mixed for 10-20 minutes, then homogenized by sieving, using a 0.063mm mesh sieve, the acrylic binder is dispersed in the water, in gravimetric ratio 2: 8.

Finally, the mortar is obtained from 15 parts by weight of the mixture consisting of fly ash, Portland cement and calcium oxide, with 10 parts by weight mixture of expanded perlite, eggshell, calcium oxide, zinc oxide, titanium dioxide and the three colored ceramics and 25 parts by weight water with acrylic resin.

The obtained mortar paste is applied on the historical monuments facades depending on the conservation state of apparent structures, using two steps with different specific operations:

for surfaces without gaps, which are finely fragile (with microcracks or ancient cracks), chromatically degraded and with deposits of embedded dirt [39, 40], it is spreads with a trowel in the form of thin plasters over a fiberglass mesh, previously deposited on a very thin plaster of the same mortar, and in the case of damages with deep lacunars areas (detached cracks, deep cracks and crevices), the grouting will be first executed with a simple mortar based on river sand, expanded perlite, Portland cement and water in gravimetric ratio sand:perlite:cement:water = 2:1:2:5 and after strengthen the thin plaster will be applied by using the light mortar, with self-cleaning properties, initially applied in the form of a very thin plaster on the grouted area, on which the fiberglass mesh is fixed by pressing, over which it is then spread manually with spatula or mechanically a thin layer of plaster.

The advantages of the new mortar

The advantages of the new additivated mortar for self-cleaning of the historical monument's facades, which require restoration interventions, are structured on the three levels of execution, namely:

a) Mortar obtaning

- involves the use of ecological raw materials, easy to procure and economically efficient;
- grinding, sieving, dosing and mixing operations are easy to perform, using simple machines and reduced workmanship;
- allows to obtain fresh mortar pastes, because the two systems of fine powders binder and the one for matrix insertion, can be kept in paper bags lined inside with hydrophobic polymer foil, separately or in a homogenized bulk mixture;
- have a conservation period of at least 30 days, after which, before application, they are mixed with water until an optimal paste is obtained, depending on the requirements.

b. Mortar commissioning

- allows a proper structuring of the uniform and homogeneous thin layer and a grouting in the intervention area;
- does not present micro cracks to contraction;
- adheres well to the operating support;
- offers a good workability;
- it is economical and can be applied to both exterior and interior walls;
- the composition can be applied to any type of plaster, ad for spreading it in a thin and uniform layer, the workability of the paste is achieved by changing the content of water added for wetting in ratio with the redispersible solid powder;
- can be applied manually or mechanically on any type of facade with chromatic deviation, chemical degradation (efflorescence, segregation, etc.) and physical-structural and mechanical damage (dynamic cracks, lack of material, etc.).

c. Afer the mortar commissioning

- achieves an efficient consolidation and a compatible restoration through structural and chromatic integration of the intervention area;
- does not generate the appearance of inflorescences and microbiotic attack;
- has a self-cleaning effect over time;
- does not produce chromatic deviations and other alterations or microstructural destructions of the surface and interior; provides superior thermal insulation to many similar materials;
- it is a light and durable material;
- has good hydro-, thermo- and sound-insulating capacity;
- allows the breathing of the interior masonry and shapes the water balances in the volume phase of the wall.

Conclusions

The composition of additive mortar with self-cleaning effect for finishing of ancient monuments is a light material with a volumetric weight below 250kg/m^3, with a thermal conductivity coefficient below 0,08 Kcal/m×h×°C and a mechanical strength more than 7 daN/cm². This is constituted by: 15 parts by weight of mineral binder in a mixture of fly ash resulted from the burning of sunflower husks, Portland cement and calcium oxide, ground to a fineness of 6...10% residue on a sieve of 4900meshes/cm², (in gravimetric ratio ash: Portland cement: calcium oxide = 1:2:2) and 10 parts by weight of expanded perlite and fine eggshell powder, additived with ZnO, TiO_2 and three burnt clay ceramics differently colored in titian red, brown and black, (in gravity ratio perlite: eggshell: ZnO: TiO_2: colored ceramics = 6.00: 3.60: 0.16: 0.04: 0.20), both with a grain size of less than 0.06mm.

In order to achieve a homogeneous composition with synergistic effect and high compatibility of the components, through preliminary studies, it was allowed to obtain pastes with efficient rheology at commisioning, which offers high resistance to environmental factors.

The new mortar also allows, after commisioning, the reduction of chromatic deviations by self-cleaning. It can be used to restore the facades of historical monuments without damage by material loss, but with superficial degradation of finishes, with the modification of the patina by visible chromatic deviations. In thi case the added mortar is spread with a trowel in the form of thin plasters on fiberglass mesh. Additionaly, can be used to restore the facades of historical monuments with lacunar areas (material losses on large surfaces), when first the consolidation of mobile structures (cracked or alveolar) is achieved by using classic mortars, then the additivated mortar is spread with a trowel in the form of thin plasters on fiberglass mesh.

This mortar allows the accomplishing of a series of advantages both in the processes of paste obtaining, as well as during commissioning and after, respectively within the period of integration in the tourist circuit.

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References

[1] G.S. Sîrbe, S.V. Panaite, I. Sandu, D.M. Copcea, A.V. Sandu, O.L. Sîrbe, I.G. Sandu, O. Pop, *Predosed mortar composition,* **Patent RO134834** (A2) — 2021-03-30.

[2] A. Moanta, C.R. Fierascu, I. Petre, et al., *Mortar composition used for protecting historical buildings and/or monuments, comprises Portland cement, river sand, and hydroxyapatite-type antimicrobial agent, in which calcium is partially replaced with silver, and has preset density,* **Patent RO133614-A2/2019**.

[3] H. Yang, Y. Che, *Patching material for use in repairing historical monuments, comprises sticky rice, lime, brown granulated sugar, fine aggregate, complex mineral admixture, reinforcing agent and mineral pigment,* **Patent CN104119055-B/2015**.

[4] I. Mohanu, D. Mohanu, M. Georgescu, et al., *Mortar for Treatment of Gaps Within Plastering and Support of Mural Paintings in Historical Monument,* **Patent RO128208-B1/2013.**

[5] I. Mohanu, D. Mohanu, I. Gomoiu, et al., *Mortar for Treatment of Gaps Within Plastering and Support of Mural Paintings in Historical Monuments,* **Patent RO128207-B1/2013.**

[6] I. Azkarate Mendibe, J.M. Dominguez Montalban, J.A. Ibanez Gomez, et al., *Lime mortar for restoration of historical artistic patrimony, comprises dry solid composition and water, where solid composition has sand limestone, hydrate lime, natural zeolites and additives,* **Patent ES2304872-B1/2008.**

[7] Consejo Superior Investigaciones Cientif, *Lime mortar for use in buildings and historical monuments-contains slaked lime, scrap and copper salts plus sand and volcanic ash*, **Patent ES2097697-B1/1997.**
[8] R. Bayer, H. Lutz, **Dry mortars – from Ullmann`s Encyclopedia of Industrial Chemistry**, 2003.
[9] J. Pourchez, P. Grosseau, B. Rout, *Changes in C_3S hydratation in the presence of cellulose ethers*, **Cement and Concrete Research**, **40**, 2010, p. 179.
[10] G. Klimburg, *Mortar – Contg expanded perlite, white cement, air-entraining-agents and opt celulose derivs,* **Patent FR2173293(A1)1973-10-05.**
[11] J. Yang, *Interior wall perlite heat-insulating decorating plate for buildings and manufacturing method thereof,* **Patent CN105113743(A)-2015-12-02.**
[12] Q. Wang, Y. Guo, *Modified Expanded perlite thermal – insulation mortar and preparation method thereof,* **Patent CN108863233 (A)**-2018-11-23.
[13] M. Maier, *Mortar pump for pumping aerosol and perlite* – based insulation plaster, **Patent EP2886868(A1) 2015-06-24.**
[14] Q. Wang, Y. Guo, *Expanded perlite thermal – insulation mortar and preparation method thereof*, **Patent CN108911630 (A)**-2018-11-30.
[15] I. Sandu, G. Deak, I.C.A. Sandu, M.-A. Moncea, I.G. Sandu, F.D. Dumitru, A.V. Sandu, M. Matei, S. Panaite, M.D. Boboc, *Additivated mortar composition for finishing works in old monuments and process for preparing and applying the same,* **Patent RO135116 (A0) — 2021-07-30.**
[16] A. Fujishima, K. Honda, *Electrochemical photolysis of water at a semiconductor electrode*, **Nature, 238**, 1972, pp. 37-38.
[17] D. Ayodhya, G. Veerabhadram, *A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sulfide nanostructures for environmental protection,* **Materials Today Energy, 9**, 2018, pp. 83-113.
[18] K. Yang, X. Li, C. Yu, D. Zeng, F. Chen, K. Zhang, W. Huang, H. *Ji, Review on heterophase/homophase junctions for efficient photocatalysis: The case of phase transition construction*, **Chinese Journal of Catalysis 40,** 2019, pp. 796–818
[19] A.A. Muresan, S. Attia, *Energy efficiency in the Romanian residential building stock: A literature review,* **Renewable and Sustainable Energy Reviews, 74,** 2017, pp. 349–363.
[20] I. Visa, M.D. Moldovan, M. Comsit, M. Neagoe, A. Duta, *Facades integrated solar-thermal collectors - challenges and solutions,* **Energy Procedia, 112,** 2017, pp. 176–185.
[21] I. Sandu, C.T. Iurcovschi, I.G. Sandu, V. Vasilache, I.C. Negru, M. Brebu, P.S. Ursu, V Pelin, *Multianalytical Study for Establishing the Historical Contexts of the Church of the Holy Archangels from Cicau, Alba County, Romania, for its Promotion as a World Heritage Good I. Assessing the preservation-restoration works from the 18th century,* **Revista de Chimie, 70**(7), 2019, pp. 2538-2544.
[22] C. Byrnea, G. Subramanian, S.C. Pillai, *Recent advances in photocatalysis for environmental applications,* **Journal of Environmental Chemical Engineering, 6**(3), 2018, pp. 3531-3555.
[23] D. Spasiano, R. Marotta, S. Malato, P. Fernandez-Ibanez, I. Di Somma, *Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach,* **Applied Catalysis B: Environmental, 170-171,** 2015, pp. 90–123.
[24] I. Sandu, I. Popescu-Ciocirlie, I. Gruia, O. Calancia, D.G. Cosma, I.G. Sandu, D.G. Cozma, *Production and characterization of the oxide enriched materials for ceramic varistors II. Synthesis, chemical and physico-structural analysis, conductive grains doping influence upon the current-voltage characteristics,* **Revista de Chimie, 49**(11), 1998, pp. 756-768.
[25] I.Sandu, I. Popescu-Ciocirlie, I. Gruia, O. Calancia, G. Limisca, I.G. Sandu, *Production and characterization of the oxide enriched materials for ceramic varistors.* 1. *General aspects regarding the production, structure and characteristics of the ceramic varistors,* **Revista de Chimie, 49**(10), 1998, pp. 673-681.

[26] E. Jimenez-Relinque, M. Castellote, *Hydroxyl radical and free and shallowly trapped electron generation and electron/hole recombination rates in TiO2 photocatalysis using different combinations of anatase and rutile*, **Applied Catalysis A, General 565**, 2018, pp. 20–25.
[27] S. Tuckute, S. Varnagiris, M. Urbonavicius, M. Lelis, S. Sakalauskaite, *Tailoring of TiO2 film crystal texture for higher photocatalysis efficiency*, **Applied Surface Science, 489,** 2019, pp. 576–583.
[28] I. Zad, W. Zhang, W. Zheng, Y. Zhu, Z. Zhang, J. Zhang, M. Imtiaz, W. Abbas, D. Zhang, *The highly efficient photocatalytic and light harvesting property of Ag-TiO2 with negative nano-holes structure inspired from cicada wings,* **Scientific Reports, 7**, 2017, Article Number: 17277.
[29] V.E. Copcia, C.M. Hristodor, S. Dunca, R. Iordanova, A. Bachvarova-Nedelcheva, N.C. Forna, I. Sandu, *Synthesis and antibacterial properties of ZnO/clinoptilolite and $TiO_2/ZnTiO_3$/clinoptilolite powders,* **Revista de Chimie, 64**(9), 2013, pp. 978 – 981.
[30] M. Suchea, I.V. Tudose, S. Ionita, I. Sandu, F. Iacomi, E. Koudoumas, *ZnO Nanostructures for Potential Applications in Organic Solar Cells,* **Revista de Chimie, 66**(12), 2015, pp. 2044-2046.
[31] R. Taourati, M. Khaddor, A. El Kasmi, *Stable ZnO nanocatalysts with high photocatalytic activity for textile dye treatment*, ***Nano-Structures & Nano-Objects*, 18,** 2019, Article Number: 100303.
[32] W. Chen, Q. Liu, S. Tian, X. Zhao, *Exposed facet dependent stability ZnO micro/nano crystals as a photocatalyst,* **Applied Surface Science, 470,** 2019, pp. 807–816.
[33] Y. Zhou, L. Xu, Z. Wu, P. Li, J. He, *Optical and photocatalytic properties of nanocrystalline ZnO powders synthesized by a low-temperature hydrothermal method*, **Optik, 130,** 2017, pp. 673–680.
[34] G. Byzynski, A. Prado Pereira, D.P. Volanti, P. Ribeiro, E. Longo, *High-performance ultraviolet-visible driven ZnO morphologies photocatalyst obtained by microwave-assisted hydrothermal method*, **Journal of Photochemistry and Photobiology A: Chemistry, 353,** 2018, pp. 358–367.
[35] M.S. Azmina, R.Md. Nor, H.A. Rafaie, N.S.A. Razak, S.F.A. Sani, Z. Osman, *Enhanced photocatalytic activity of ZnO nanoparticles grown on porous silica microparticles*, **Applied Nanoscience**, **7,** 2017, pp. 885-892.
[36] I. Sandu, C. Luca, I.C.A. Sandu, A. Ciocan, N. Suliteanu, *A study on the compatibility of the old, traditional artistical techniques with the new materials and methods used in the restauration, preservation processes. II - A chromatic analysis,* **Revista de Chimie, 52**(9), 2001, pp. 485-490 .
[37] A.M. Saviuc-Paval, I. Sandu, I.M. Popa, I.C.A. Sandu, V. Vasilache, I.G. Sandu, *Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements II. Microscopic and colorimetric analysis,* **Revista de Chimie, 63**(2), 2012, pp. 170-178.
[38] A.M. Saviuc-Paval, A.V. Sandu, I.M. Popa, I.C.A. Sandu,A.P. Bertea, I. Sandu, *Colorimetric and microscopic study of the thermal behavior of new ceramic pigments,* **Microscopy Research and Technique, 76**(6), 2013, pp. 564-571.
[39] P. Spiridon, I. Sandu, L. Stratulat, *The Conscious Deterioration and Degradation of the Cultural Heritage,* **International Journal of Conservation Science, 8**(1), 2017, pp. 81-88.
[40] A.A.T. Traistaru, I.C.A. Sandu, M.C. Timar, G.L. Dumitrescu, I. Sandu, *SEM-EDX, water absorption, and wetting capability studies on evaluation of the influence of nano-zinc oxide as additive to paraloid B72 solutions used for wooden artifacts consolidation,* **Microscopy Research and Technique, 76**(2), 2013, pp. 209-218. DOI: 10.1002/jemt.22155.

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