Permanent Non-Leaching Multi-functional Organoclays for Improvement of Durability of Biocide-free Wood Coating Systems

Solvita Kostjukova, Llc. ALINA, Julija Karasa, University of Latvia, Matiss Pals, University of Latvia, Juris Kostjukovs, Llc. ALINA, Karlis Kostjukovs, Riga Technical University, Latvia

Abstract

The developed multi-functional organoclays are used for trendy transparent and semi-transparent exterior wood coatings to improve durability of the coating products by protecting from degradation processes as abrasive influence, UV radiation, moisture and microbial influence. The organoclay characterise large surface area, non-toxicity and excellent adsorption ability.

The field tests that are carried out in aggressive environments confirm the improvement of the durability (less abrasive degradation and bleaching by UV radiation) and aesthetic look of finished exterior objects when organoclay additive was added to coatings matrix.

Reports on organoclay leaching tests proved zero-leaching of organoclays and activating agents used for clay modification. To determine leaching was used spectrophtometrical method and high-performance liquid chromatography time of flight masspectrometry. The analytical methods were validated following industry standards.

Obtained organoclays is non-toxic additive that can be effectively dispersed into different solvent and binder systems. Organoclays can be used as alternative additives in coatings matrix to prolong whole lifecycle of the treated objects with potential applications in the building finishing industry.

Introduction

Naturally occurring clay minerals (especially bentonite, smectite or montmorillonite) have been extensively used to manufacture organoclays because of the montmorillonite minerals excellent properties, such as high cation exchange capacity, swelling behaviour, adsorption properties, large surface area, chemical inertness and low or zero toxicity [1].

The manufacturing process of organoclays are based on modifying the raw dioctahedral expandable clays with the cationic surfactants (mainly alkylammonium salts) or other organic compounds (organophilisation) [2].

Intensively analysing the interaction between clay minerals and organic compounds have provided knowledge to be used for organoclay applications – the most common applications are as rheological control agents e.g. drilling muds, as sorbents of various organic pollutants, as components in the synthesis of clay-based polymer nanocomposites, etc. For described properties the organoclays are known and widely used in the paint and coating industry as rheological additives. In the paint and coating industry the concentrated organoclays are used solely in solvent-borne coatings as their hydrophobic properties make it very difficult to disperse them in water-borne coating systems [3].

The knowledge of wide applications served as basis for novel multi-functional organoclays development for interior and exterior architectural paint and coating producers to reduce the use of hazardous chemicals and heavy metals, so called biocides, in readymade products. [5]

The novel multi-functional organoclays is an Eco-alternative for hazardous chemicals used for in-can and film preservation that are strictly regulated by ECHA as well as Nano-materials that have been shown to be dangerous for the human health. Currently paint and coating manufacturers use hazardous chemicals (biocides), this is perceived as market standard. 75 % of manufactured architectural paint is treated with an in-can Biocide (11,718 tons or 33,3 € million annually) and 7 % of manufactured paint is treated with a film biocide, (6,076 tons or 47 € million annually). Globally biocide consumption in architectural paints only is 57K tons, 257M € market value, EU market size is 17,7K tons, 80M€ market value. [4].

In this study the development, functionality and properties of novel multi-functional organoclays (Patent publication No: WO/2018/130880) are considered to respond to demanding standards of paint and coating manufacturers for trendy transparent and semi-transparent exterior wood coatings to improve durability of the coating products by protecting from degradation processes as abrasive influence, UV radiation, moisture and microbial influence.

Development of Multi-functional Organoclay

The development of the clay organophilisation process was started with the European's deposits raw materials containing only about 40% of the smectite-type (montorillonite) clay and currently more than 60% saturated smectite clays from Germany and Spain are used for the manufacturing of the multi-functional organoclays. The increment of the active ingredient in raw material allows increasing the loading of the organic species, thereby decreasing the amount of the addable organoclay in the finished matrix (paints and coatings), as a result the initial properties of the treated matrix stay unchanged. The proposed multi-functional organoclay is produced by one step method that differs from the usually used cation exchange procedure. Applied methodology does not demand the usage of any hazardous organic solvents. It is fast, energy saving, and zero waste technology compared with other alternatives. The process can be defined as introduction of the selected guest organic compound into the smectite interlayer spacing by solid-state intercalation.

The X-ray powder diffraction (PXRD) analyses are employed for the characterisation of the finished multi-functional organoclay. The interlayer spacing of the smectite increases after the selected cationic surfactant is successfully introduced into dioctaedrical clay mineral. Non-destructive PXRD technique allows proving the formation of the organoclay by evaluating the changes of the interlayer spacing of the raw and finished materials. PXRD patterns usually are obtained for air-dried and crushed into fine powder samples of raw material and produced organoclays.

Obtained PXRD data for raw smectite clays (content of smectite / montmorillonite is 40-60%) and obtained organoclays samples confirms the organophilisation carried out by technique described in EP2690067 (A1). Characteristic reflection of montmorillonite corresponding to interlayer distance of mineral d = 12.5 Å shifted to smaller 2θ angles for obtained multi-functional organoclay. Increment of the basal spacing of the clay mineral from 12.5 Å to 41 Å indicates on the intercalation of the selected cationic surfactant into the clay structure. All measurements are performed on Bruker D8 Advanced diffractometer, CuKα radiation in 3 – 40 ° 2θ interval with step 0.5°.

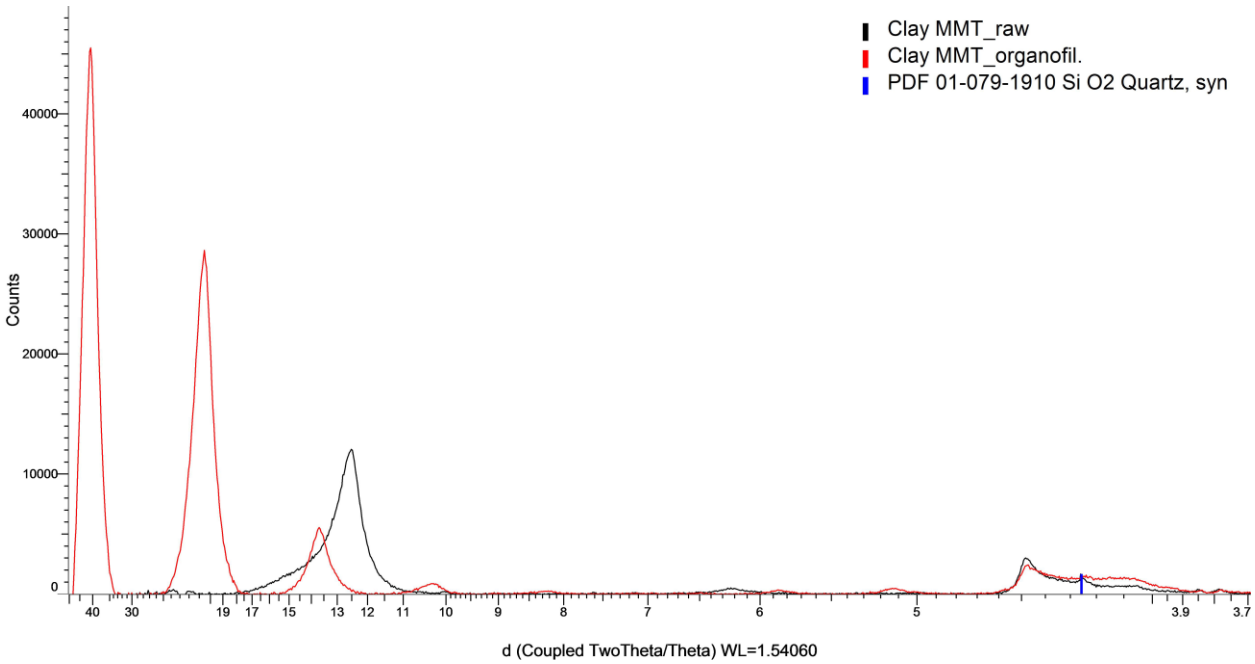

Figure 1. PXRD pattern of raw montmorillonite and obtained multi-functional organoclay sample (MMT - montmorillonite)

Functionality and Properties of Multi-functional Organoclay

The considered organoclays must meet following paint and coating industry requirements (the requirements were obtained by interviewing sixteen manufacturers in Germany, Denmark, Finland and Latvia): high dispersibility in different standard formulations; industry standard particle size, no-influence on white base DIY segment paint colour, compatibility in different pH level and different standard formulations.

In terms to improve the dispersibility of the multi-functional organoclay as additive into finished matrix, the manufacturing method was improved; as a result, the multi-functional organoclay water or natural oil slurry is obtained. The slurry form has increased dispersibility properties that helps to integrate easily organoclays into different water-borne and natural oil-borne paint and coating formulations and minimize the risks for agglomerates as well as polymerisation processes. Most common multi-functional organoclay saturation of the water or oil is at least 50%. Such approach eliminates additional energy intensive post-processing – organoclay drying and grinding.

In terms to meet the paint and coating pigment particle size standards and to improve the multi-functional organoclay efficacy into the volume of the paint and coating formulations, the particle mineral base size of the organoclays was decreased from 150 microns to 15 microns. In the Figure 2 you can see the smooth organoclay particle distribution into the volume on natural oil base primer in 10000 times increase. It is possible to see that even the mineral base particle size and agglomerates are smaller than 1-5 microns in average.

The decreased particle size and improved dispersibility properties led to decreased adding proportion of the multifunctional organoclay in the paint and coating formulations that allowed to meet the industry requirement - to reach the multifunctional organoclay efficacy below 1% proportion of the dry matters. The decreasing the addable proportion led to less or no-influence on the white base paint colour in DIY segment. The testing was carried out using standard test procedure – CIELAB that demonstrated the multifunctional organoclay influence on the dry formulation in calculated error limits.

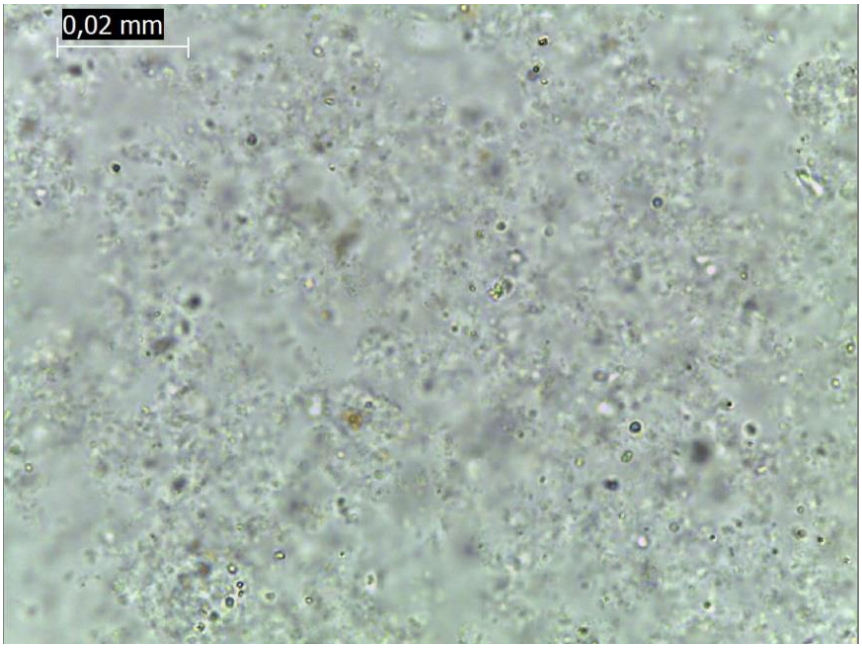

Figure 2. Multifunctional organoclay particle dispersion in natural oil base primer picture in 10000:1 resolution.

To demonstrate the multifunctional organoclay durability and safety was used validated quantitative analytical methods to tests if the organoclay has leaching of used organic compounds.

One of the methods – HPLC – analytical procedure for the assay of Trimethyloctadecylammonium chloride (ODTMA) in organoclay washing solution using high performance liquid chromatography time of flight masspectrometry (HPLC-TOF-MS) was developed by co-authors [6].

For the validation, the following parameters were evaluated during the study in accordance with the International Conference on Harmonization Q2B guideline “Validation of Analytical Procedures: Methodology” and US Food and Drug Administration “Guidance for Industry Bioanalytical Method Validation”: specificity; linearity and working concentration range; precision (repeatability and intermediate precision); accuracy and stability. The validation provides linear and reproducible results. A high percentage recovery showed that the method can be successfully used on a routine basis. In precision study the effect of external parameters (different analysis days) were studied and method was found to gives reproducible results. Conclusion was made that the HPLC method is precise.

Additionally, the different washing-out solvents were used to model and analyse durability, compatibility and possible leaching depending on different formulations. In this study was analysed four different organoclay samples. 1 gram of sample was taken and suspended in either 10 mL deionized water, acidic water (Formic acid, pH=2), basic water (Ammonium hydroxide, pH = 11) and highly ionic water (NaCl, γ = 3 mg/mL) to simulate possible natural conditions. Samples were vortexed for 30 min and then filtered through 0,45 µm syringe filter. Samples were directly analysed using HPLC-ToF-MS. The samples shown no leaching of active compound - Trimethyloctadecylammonium chloride (ODTMA) regardless of used washing solution. Concentration of active compound was under limit of detection for these samples (< mg/mL), therefore conclusion was made that multifunctional organoclays are durable and the leaching is under detection level.

The other method – spectrophotometry – was developed by co-authors for quantitative quality assessment of the multifunctional organoclay manufacturing in industrial level as the HPLC requires specific equipment

and is time and resource consuming. The task of this study was to develop the analytical procedure for the assay of ODTMA in organoclay washing solution using spectrophotometrical determination.

The analytical procedure was developed, and the following parameters were evaluated during the study in accordance with the International Conference on Harmonization Q2B guideline “Validation of Analytical Procedures: Methodology” and US Food and Drug Administration “Guidance for Industry Bioanalytical Method Validation”: linearity and working concentration range; precision (repeatability and intermediate precision) and accuracy. Method was based on bromphenol blue reaction with quaternary ammonium compound. The validation procedure shoved linear and reproducible results. A high percentage recovery showed that the method can be successfully used on a routine basis. In precision study the effect of external parameters was studied, and method is found to gives reproducible results. Conclusion was made that the spectrophtometrical is precise.

In terms of determination of the UV protective properties was carried out weathering QUV-testing and CIELAB test procedure. For weathering QUV-testing prepared wood panels were covered with standard decking oil. The QUV-testing was done accordingly to ASTM G145 standard. The samples are evaluated after 500 h and 1000 h. The appearance is evaluated for gloss loss and opacity.

The multifunctional organoclay demonstrate UV protection. Theoretically the effect of such functionality is based on property to absorb or reflect UV radiation. The UV protection of the multifunctional organoclay is provided by smectite, illite, hematite and silica presence in the composition. The smectite part is described with UV absorption ability and illite, hematite and silica with UV reflection ability.

The field tests that are carried out in aggressive environments confirmed the improvement of the paint and coating durability (less abrasive degradation and bleaching by UV radiation) and aesthetic look of finished exterior objects when organoclay additive was added to coatings matrix.

The trendy transparent, semi-transparent and white paint and coating outdoor exposure testing results was chosen to demonstrate the improvement of the paint and coating durability when multifunctional organoclays are added. The transparent, semi-transparent and light colour paint and coating are preferred in modern trends of exterior wood coatings.

While proceeding the field test preparation phase, the intensive study was dedicated to the multifunctional organoclay compatibility properties with different paint and coating formulation systems. There was reported high compatibility with chosen formulations, including water-borne PU/Acrylic binder systems, different natural oil and resin binders, bio-base binders and other conventional industry standard binders. There was reported influence on viscosity that was concluded being insignificant. The long-term compatibility studies are continued to evaluate long-term viscosity changes.

The multifunctional organoclay additive was added to transparent linseed oil-based primers, decking oils and paints in terms to prolong the shelf-life of the finished wood objects, according real field tests were carried out. Commonly such coated wood surfaces degrade within one to three seasons, especially it is a crucial factor for annual temperature and humidity variations of Eastern Europe. So real finished objects (wooden decks, garden furniture and other samples) were exposed in outdoor conditions (field tests) for several months.

Field tests (outdoor exposure) of the treated wood objects showed that multifunctional organoclay added to the linseed oil-based primer, linseed oil-based paint, decking or exterior oil improved the durability of the coating, significantly improving the aesthetic look and decreasing cracking of the coated surfaces of finished objects (Figure 3, 4 and 5).

Figure 3. Material: Exterior Oil (to be used outdoor for basic treatment and maintenance of new and previously oiled wood surfaces such as decks, garden furniture) in the picture: to the left – with 2% of the multifunctional organoclay; to the right – without the multifunctional onal organoclay additive. Test description: previously oiled garden furniture 4 years old, oiled with/without 2% additive, 16-month outdoor exposure, Latvia

Figure 4. Material: standard decking oil in the picture: to the left – without the multifunctional organoclay; to the right – with 4% of the multifunctional additive. Test description: 7-month outdoor exposure, test method close to standard EN927-3, Denmark –West

Figure 5. Material: White linseed oil paint in the picture: to the left – with 2% of the multifunctional organoclay additive; in the middle – without the multifunctional organoclay additive; to the right – with the 1% of the biocide PREVENTOL MP700. Test description: 12-month outdoor exposure, test method close to standard EN927-3, Latvia

Additionally, in the Figure 5 it is demonstrated that the multifunctional organoclays are comparable to conventional biocides for the sustainable preservation purposes, even more – the multifunctional properties improve the durability, the aesthetic look and decreasing cracking at the same time not polluting the environment and do not cause the harm to human health. in human and environmentally healthy way.

Conclusion

The production method improvement, controlled multifunctional organoclay particle size and the water and oil-base slurry form of multifunctional organoclays allow even dispersions in different water-borne, solvent-borne and oil base formulations and improve efficacy of multifunctional organoclay in paint and coating matrixes.

Various field tests carried out in aggressive environment confirm the improvement of the durability (less abrasive degradation and bleaching by UV radiation) and aesthetic look of finished exterior objects when the multifunctional organoclay are added to the paint and coating formulations.

The multifunctional organoclays are alternative for paint and coating whole lifecycle sustainable protection. The organoclay are zero leaching, non-hazardous, non-allergic and low CO2 material.

With increasing awareness of how climate change affects the degradation of materials, the manufacturer standards for the sustainable protection alternatives are demanding. The conclusion is that the multifunctional organoclay additives fulfil the manufactures requirements towards sustainable preservation additives including high dispersibility in different standard formulations; industry standard particle size, no-influence on white base DIY segment paint colour, compatibility in different pH level and different standard formulations at the same time meeting EU regulations, that limits use of hazardous chemicals , satisfying sustainable building and product certification standards and helping entering the green building finishing market.

Acclowledgement

In accordance with the contract No. 1.2.1.1/16/A/005 between "Competence center of smart materials and technologies" Ltd. and the Central Finance and Contracting Agency, concluded on 26th of September, 2016, the study is conducted by “ALINA” Llc. with support from the European Regional Development Fund (ERDF) within the framework of the project "Competence center of smart materials and technologies".

References

[1] Park Y., Ayoko G. A., Frost R. L., Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media, Journal of Colloid Interface Science, vol. 354, 2011, pp. 292-305

[2] Bergaya F., Lagaly G., Surface modification of clay minerals, Applied Clay Science, vol. 19, 2001, pp 1-3

[3] Bodo Müller, Understanding Additives, European Coating Tech Files, Vincentz Network, Germany, 2010, pp. 74-77

[4] Report Biocides in Paints – 2017, www.biocide-information.com

[5] Kostjukova S., Karasa J., Kostjukovs K., Kostjukovs J., Stebelis D., Eco-shield for paints, European Coating Journal, vol 9, Vincentz Network, 2017, pp. 48-53

[6] Pals M., Putna-Nimane I., Kostjukovs J., Karasa J., Kostjukova S., Nakurte I., Determination and Toxicology Studies of Quaternary Ammonium Salts in Solution after Organoclay Processing, Key Engineering Materials, vol. 762, 2018, pp. 368-372