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# ADVANCED RECOVERY OF CALCIUM CARBONATE WASTE AS A FILLER IN WATERBORNE PAINT

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## Abstract

The industry generates large quantities of waste, which must be capitalized and transformed in compounds with high added value. The objective of the present study is to obtain white waterborne paint using calcium carbonate as filler, a waste results from Romanian plant fertilizer manufacturing. The paints are used for protection of surfaces, with the focus on durability. Natural or synthetic calcium carbonate can be successful used as filler in paints, they have an alkaline pH-value and low oil absorption, very important technological properties. The calcium carbonate can significantly improve paint properties as sheen, opacity, viscosity, density and wear resistance.

This study is focused on the possibility to replace commercial filler with calcium carbonate waste and establishes the optimal content for obtaining waterborne paints with imposed properties. For obtaining white paint, the resin was mixed with 5- 30 g precipitated calcium carbonate /300 mL resin. The properties of paints obtained were determined and comparison with witness. Experimental data demonstrated that precipitated calcium carbonate (PCC) with particle diameters over 0.5 µm influenced negative opacity properties. For improved this property grinding for obtaining particles smaller than 0.5 µm is necessary. Using calcium carbonate waste, experimentally were obtained for waterborne paint properties close properties with witness. The PCC content can be increased to 30 g/300 mL resin, without affecting the paint properties, less the viscosity which is 14% above the required value.

*Key words:* calcium carbonate, filler, waste, waterborne paint

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## 1. Introduction

In the last decade waste capitalization represents a priority issue, for improving the environmental quality. The categories of wastes that contain recovery compounds is namely by-product, that shown necessity to keep achievement "zero waste" (Assi et al., 2020).

The paints are usually produced for protection and decorative aims of surfaces. Generally, there are two kinds of paints classified function of solvent type: water and organic solvent-based, but in the last years the water-based paints were recommended because they are environmentally friendly (Karakaş et al., 2015). The development of waterborne paints has an increasing interest, especially due to the more severe regulations regarding the emission of volatile organic compounds (COVs) in industrial coatings. Waterborne paints are mixtures of polymeric binder with fillers, different additives and pigments if they are coloured. A typical waterborne paint consists of 18-20% water, 30-32 % binder, 10-11% additives, and up to 38-40% fillers (Karakaş et al., 2015; Simion et al., 2015). As polymeric binders in waterborne paints

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are extensively used the acrylic latex polymers due to proper properties as elasticity, stability under UV, flexibility etc. Usually, different fillers are added to improve base material properties or reduce the cost. Mineral fillers are the most commonly used, from these, calcium carbonate is the most extensively used, as the limestone, dolomites or marble dust, precipitated carbonates, having imposed properties are also employed (Careddu et al., 2014; la Nasa et al., 2020). The calcium carbonate ($CaCO_3$) is one of the most widely used fillers in paint and coating industries (Ahmed et al., 2019). The properties of fillers are strongly influenced by surface properties, such as dispensability, oil adsorption capacity and suspension viscosity (Bouargane et al., 2020; Zheng et al., 2019).

Precipitated calcium carbonate (PCC) is recognized as filler for papermaking, plastics, rubber, paint etc. (Civancik-Uslu et al., 2018; Velts et al., 2011), but it can behave imposed properties, depending of the applications. The calcium carbonate application is determined by the greatest number of strictly defined parameters, such as morphology, structure, particle size, specific surface area, brightness, content of impurities, adsorption etc. (Jakob et al., 2018; Szep and Harja, 2007). The most important imposed proprieties are diameter and morphology of particles (Khanjani et al., 2020). Usually, calcium carbonate has three types of crystal polymorphs, which is generally classified as: rhombic (calcite), needle-like (aragonite) and spherical (vaterite), but in literature are reported a lot of other morphology, depending on the synthesis routes (Asadi et al., 2021; Gumfekar et al., 2011; Harja et al., 2010; Kumari et al., 2020). Among the different polymorphs of PCC, rhombic morphology is of great interest because of its wide use as filler (Harja and Ciocîntă, 2010).

Calcium carbonate can be obtained by direct grinding of raw materials, carbonation of lime and double exchange from calcium chloride and sodium carbonate (Harja et al., 2012; Harja et al., 2009; Ibrahim et al., 2014; Jimoh et al., 2018; Song et al., 2021). On the other hand, a large quantity of PCC results from different industries as waste, for example from nitrofosfor fertilizer. Calcium carbonate from the fertilizer industry (NPK) is a mono-constituent product and can be used in the paper and cardboard, paint industry, coatings, diluents, paint removal solutions, finishing and impregnation products, dyes, flocculation, precipitation and neutralization agents, soil amendment etc. (Harja and Tataru-Farmus, 2019).

The filler volume concentration (FVC) is one the important parameter in the formulated paints, which refers to the percentage of filler with respect to the total solid volume in a paint formulation. There is a critical filler volume concentration (CFVC), which depends of necessary binder to wet filler particles. The CFVC is determined for existing of coherent films, which is assured for concentration up to CFVC value. For determining CFVC there are different methods: optical (Elert et al., 2018), mechanical, gas permeability (Ferreira et al., 2010), and water permeability (Tressmann et al., 2020) etc. As demonstrated that polymer particle size and the polymer particle surface functionality will influence the CFVC (Karakaş et al., 2015).

The study of the interactions between the binder and the filler is essential to improve the properties of the coatings. In the process of film formation there exist a lot of interactions between fillers, different latex types and all types of additives from paint formulation (dispersants, rheology modifiers, tackifiers etc.), these interactions affect the quality of the film. The complex interactions appear in the all stages of film formation: wet, drying and dry state (Alvarez and Paulis, 2017; Heberling et al., 2014).

The challenge of this work has been to prepare waterborne paint-like blends using as filler calcium carbonate waste from fertilizer industry, and study of influence over waterborne paint properties. The waterborne paint properties were tested in industrial laboratory and the results are compared with the real acrylic waterborne paint.

## 2. Experimental part

### 2.1. *Characterization of PCC waste*

In this study it was used PCC waste from Romanian NPK industry. The PCC waste was collected in March-May 2019, and it was used without any processing. To establish the nature of the solid, XRD, EDAX, FT-IR spectrophotometry and chemical analysis were performed. The UV–Vis spectra were recorded using a Digilab Spectrofotometer FTS 2000; X-ray diffraction was recorded using X PANalytical X'Pert pro MRD X-ray diffractometer using copper target with nickel filter. The morphology was determined with electronic microscopy (SEM) using SEM Vega Tescan of 30 kV, samples being covered by an Ag layer. Particle sizes were determined with a diffractometer for particle size analysis type SALD-7001 laser equipped. The humidity was measured with thermo-balance KERN/MLS 50-3 HA160N METTELER TOLEDO HE73/01. To determine the white degree, the device WSB was used.

### *2.2. Paint formulations*

In this study it was used the resin Primal type™ CM-219 EF, with a solid content of 50% (https://www.rainers.rs/images/pdf/Primal-CM-219-EF-TDS.pdf). It is used for indoor and outdoor paints, primers etc., with applications on different mineral substrates: concrete, masonry, cement etc. The styrene/acrylic polymers do not reach the performance of pure acrylic polymers, while Primal™ CM-219 EF provides suitable properties. The resin characteristics are shown in Table 1.

The Primal™ CM-219 EF is recommended for different type of paints, especially for indoor applications, such as inner layers and wall paints. The most commonly used thickening agents in water-based paints are: Clays, Polysaccharides and Synthetics (polyurethanes and polyacrylics). Emulsified paints have the best ability to be stored at a pH between 8 and 9.5.

**Table 1.** The properties of resin Primal ™ CM-219 EF

| ***Properties*** | ***White liquid*** |
|---|---|
| Solids content | 49.5-50.5% |
| pH | 6.8-7.8 |
| Minimum film formation temperature | Approx. 19°C |
| Density | 1060 kg/m$^3$ (temp. 23°C) |

Water-based paints must contain wetting and dispersal agents due to their ability to reduce the surface tension of the system, the side effect of which is to retain the air absorbed by the product during the dispersion process. The colour and opacity of the paint are ensured by the pigment. According to the definition, however, the pigment must not be coloured and achieve the opacity of the film. As a paint preparation machine, a paint dispenser is used (Fig. 1).

**Fig. 1.** Paint disperser

Technical conditions of operation: peripheral rotor velocity above 20 m/s; the diameter of the rotor is 1/3 of the diameter of the vessel; the quantity entered once must be chosen in such a way that it is not greater than 2d and less than d/2. First it is added a quantity of binder to cover the rotor and then shake. Then, the pigments are added and the device is kept shaking until the desired dispersion is achieved. If thickening agents are added to the paint, they shall be added only after the dispersion has been completed.

For obtaining white paint, the resin was mixing (1200 rpm) with precipitated calcium carbonate. Dosages between 5-30 g/300 mL resin were used, maintaining the solid content in the range 45-50%. The experiments were conducted in producer's laboratory, after its formulation.

*2.3. Paint characterization*

The content of non-volatile substance was determined according to the standard (SR EN ISO 3251:2008) by applying the paint using a wand on an aluminium foil (10 cm x10 cm) and heating to 105°C for 10 min. Density was determined by the pycnometer method (SR EN ISO 2811-1:2016). For the determination of the contrast ratio (CR) and the white degree paint film is applied to a matte chess card (Fig. 2) with a slot puller provided with a 200-micron aperture (SR EN ISO 6504-3:2007).

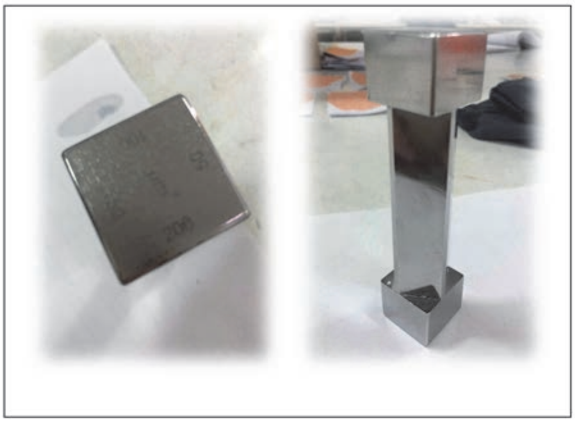


**Fig. 2.** Samples for CR determination

The card shall be kept in an oven thermostatically controlled for 10 minutes at 40°C and the readings shall be made with the Datacolor D110 Spectrophotometer. To determine viscosity was used VK 2000 Viscometer (intern method). The properties of paints obtained were determined and compared with etalon.

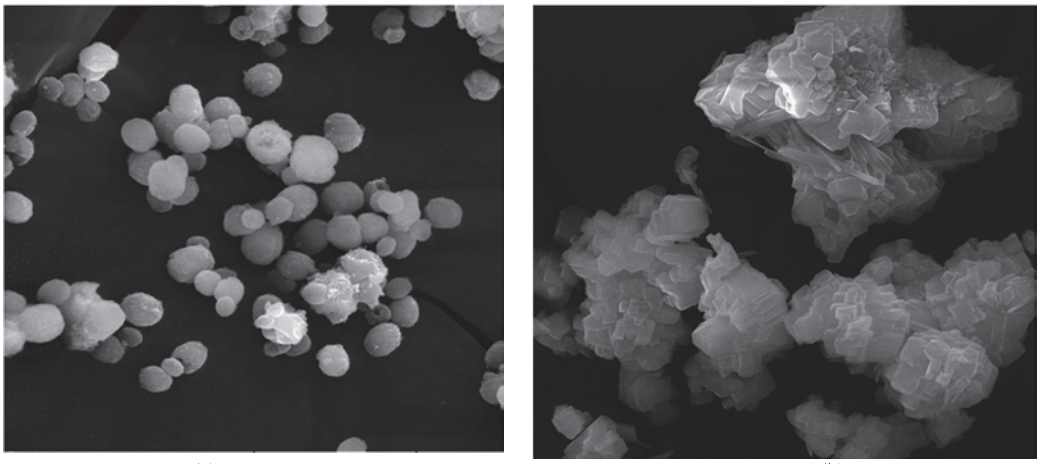
## 3. Results and discussion

### *3.1. Characterization of filler*

The commercial and PCC waste was characterized for morphology. From Fig. 3 it can be observed that the commercial filler contains preponderantly spheroidal particles (it is obtained by milling), therefore waste materials contained rhombohedral particles and a mixture of spheroidal and rhombohedral particles, with irregular and plates form (Fig. 3b). Particle size analysis of the fillers is presented in Fig. 4, where from it can be observed that if the commercial filler is milling at 0.101 μm for 75% of particles, the PCC waste had the particle diameter of 0.475 μm. The relatively large spectrum of particles was obtained for commercial filler, while PCC waste exhibits a more uniform particle, but with a large possibility to agglomeration. The commercial filler was ground at smaller diameters, while PCC waste was used without any processing.

The chemical characterization was carried out by gas-volumetric method (GV), complexometric method (CM), thermogravimetrically (TG) and FTIR spectra. The FTIR spectra of the commercial and waste are represented in Fig. 5. From the analysis of the FTIR spectrum shown in Fig. 5 it is found that the waste is predominantly calcite, as is also presented in the literature (Fortuna et al., 2020; Loghin et al., 2020).

The peaks of 1421.53 cm$^{-1}$, 875.61 cm$^{-1}$ and 711.63 cm$^{-1}$ indicate the presence of the main phase of commercial filler – calcite, while small vaterite phase at 1085 $cm^{-1}$ and 744.52 $cm^{-1}$ appear in PCC waste, together with main phase calcite. XRD, presented in Fig. 6, demonstrated that mineral phases that existent in commercial and PCC waste is calcite and vaterite, in accordance with the literature (Harja et al., 2012; Kontoyannis and Vagenas, 2000). The XRD pattern at Fig. 6 (a) with peaks at 2θ of 28.4°, 35.9°, 39.8°, 45.8° and 56.5°, which represent (112), (104), (110), (202) and (122), indicated that commercial filler is calcite. XRD pattern at Fig. 6(b) indicates mixture of calcite and vaterite.



(a) (b)

**Fig. 3.** SEM micrograph for filler, 20 μm: (a) commercial; (b) PCC waste

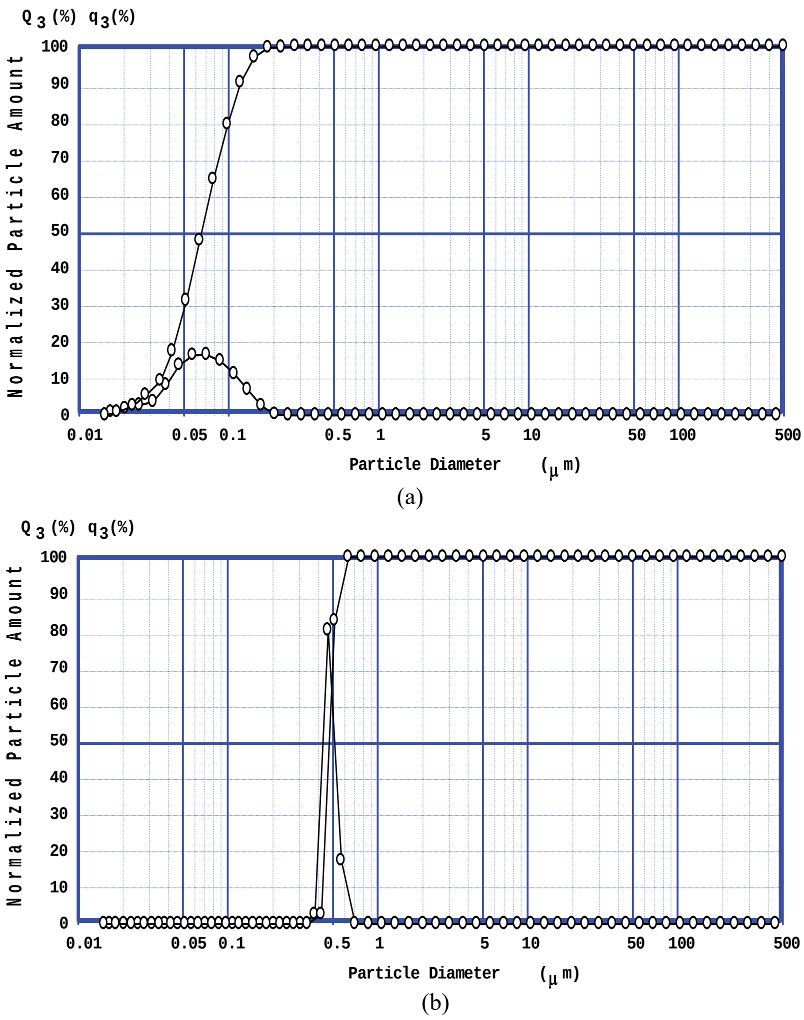
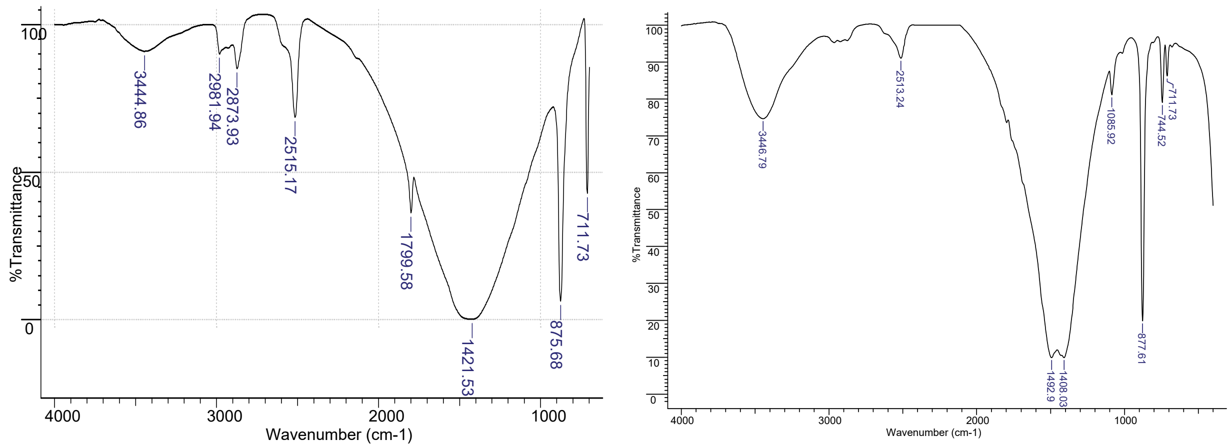



**Fig. 4.** Particles size distribution of filler: (a) commercial; (b) PCC waste




(a) (b)

**Fig. 5.** FTIR spectra for fillers: (a) Commercial; (b) PCC waste

The diffraction peaks located at 2θ of 23.2° (112), 29.5° (104), 35.8° (110) and 45.9° (018) are allocated to calcite crystals; however, the peaks located at 2θ of 25.1° (100), 27.2° (101), 32.7° (114), 39.5° (211), 43.5° (300) and 50.2° (118) are assigned to vaterite crystals (Chong et al., 2014). The calcium carbonate content, determined by gas-volumetric (GV), complexometric (CM) and thermogravimetric (TG) methods, is presented in Table 2.

The samples of PCC waste had closed properties with commercial, that permit capitalisation as filler in waterborne. From the point of view of calcium carbonate content, the experimental determinations, as shown in Table 2, indicate that the PCC waste have calcium carbonate content over commercial filler, does not differ significantly from the natural limestone. The high calcium carbonate content, expressed by the measurement of TG, indicates the presence of other volatile components, this is more obvious in the case of unwashed PCC waste, which can contain ammonium compounds.

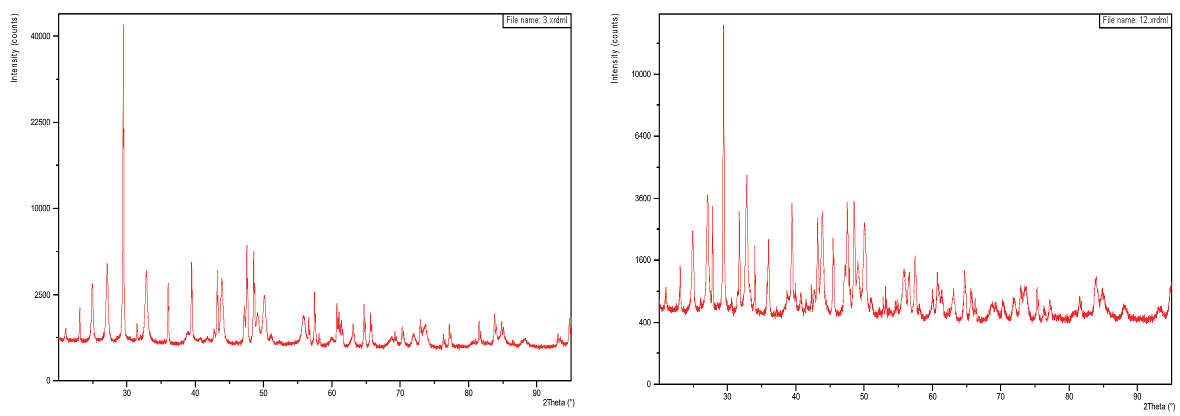
The waste from the manufacture of NPK fertilizers, having diameter particles of 0.5 µm does not allow to obtain relatively stable suspensions, but the crystalline structure, chemical reactivity and high calcite content make it possible to use it to obtain paints, all characterization regarding paint properties is imposed. The humidity of PCC waste is 0.183% and the white degree of 88.8%, compared to commercial calcium carbonate commercial which has a humidity of 0.147% and the white degree of 93.4% (Fig. 7).

### *3.2. Characterization of paint containing commercial calcium carbonate*

The analyzed waterborne paint is a white paint in an acrylico-styrenic aqueous emulsion. Comparison between the properties of the paint with commercial filler and the values imposed by the standards are shown in Table 3. Following the analyses, the paint falls within all the parameters set in the standard.

### *3.3. Characterization of the paint containing calcium carbonate waste*

After characterization of the paint containing commercial calcium carbonate, in this mixture gradually 5, 10, 15, 20, 20 and 30 grams of calcium carbonate residue were introduced in 300 mL resin. At each dose, the characteristics of the paint were determined.



(a) (b)

**Fig. 6.** XRD spectra for fillers: (a) Commercial; (b) PCC waste

**Table 2.** Chemical composition of the investigated carbonates

| *Samples* | *Commercial* | | | *PCC Waste* | | |
|---|---|---|---|---|---|---|
| | *GV* | *CM* | *TG* | *GV* | *CM* | *TG* |
| Sample 1 | 98.01±0.20 | 99.51±0.15 | 98.01±0.02 | 99.01±0.24 | 99.62±0.38 | 99.01±0.12 |
| Sample 2 | 98.24±0.15 | 98.96±0.17 | 98.24±0.12 | 99.24±0.45 | 99.91±0.35 | 99.24±0.22 |
| Sample 3 | 97.31±0.17 | 98.35±0.23 | 97.31±0.15 | 97.52±0.32 | 98.9±0.40 | 99.91±0.08 |
| Sample 4 | 97.27±0.22 | 98.02±0.25 | 97.27±0.06 | 99.27±0.22 | 98.82±0.51 | 99.07±0.13 |
| Sample 5 | 99.85±0.25 | 98.24±0.22 | 99.85±0.01 | 99.85±0.21 | 98.84±0.28 | 99.05±0.082 |
| Sample 6 | 97.25±0.14 | 98.25±0.12 | 97.25±0.24 | 97.25±0.56 | 99.03±0.32 | 98.25±0.11 |

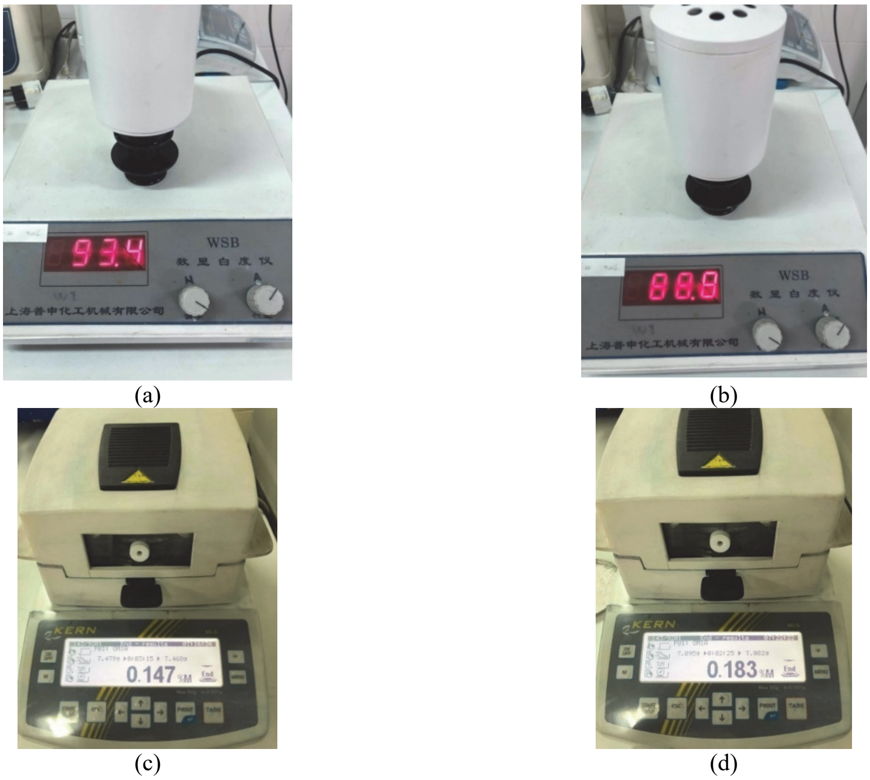



**Fig. 7.** The apparatus for the determination of white degree (a) commercial; (b) PCC waste and humidity; (c) commercial; (d) PCC waste

**Table 3.** The characteristics of a water-based paint

| *Characteristic* | *Unit* | *Standard* | *Real* |
|---|---|---|---|
| Appearance | - | viscous suspension | viscous suspension |
| Product colour | - | White | White |
| Non-volatile content | % | 65-76 | 66.16 |
| Viscosity Stormer (25°C) | Krebs Unit (KU) | 95-110 | 108.9 |
| Density (23°C) | kg/m$^3$ | 1630-1730 | 1683.2 |
| pH | - | 8-8.5 | 8.5 |
| Film appearance | - | Matte film | Matte film |
| White degree | % | 90-100 | 93.29 |
| Contrast ratio | % | 97-100 | 98.00 |

The homogenization was achieved using the paint disperser set to 1200 rpm for 30 minutes for the first 4 samples and 1h in the last test. Fig. 8 shows the variation in the content of the non-volatile substance according to the amount of calcium carbonate added. After the determination of this characteristic, it resulted that the quantity of 30 grams can be used without exceeding the maximum value required in the standard, that of 76 %. Another characteristic was density, its variation being shown in Fig. 9. Also, in this case the specified characteristic does not exceed the required value i.e. 1730 kg/m$^3$. So, in this case it can be used a dosage of 30 grams/300 mL resin. Another specific characteristic, viscosity, is shown in the Fig. 10.

From Fig. 10 it can observe that the viscosity of waterborne paint increases slowly with PCC waste content. When the amount of PCC added is larger, the excess of PCC determines coalescence between $CaCO_3$ particles and consequently increase the viscosity (Zhu et al., 2018). Therefore, the maximum dosage of $CaCO_3$ was established at 10 g/300 mL resin. Over this quantity the higher density of the $CaCO_3$ particles together with the low viscosity led to sedimentation of the $CaCO_3$ particles (Alvarez and Paulis 2017) in the bottom of the film, with obtaining of inappropriate film aspect. White degree and contrast ration of waterborne paint with PCC waste are presented in Table 4. The white degree decreases with the increase of calcium carbonate content, but the obtained value corresponding to requirements (minimum being 90%). CR increases with the increase of the calcium carbonate content; the contrast ratio is classified as standard.

Table 5 shows the properties of the waterborne paints. The results from Table 5 demonstrated that excluding viscosity all properties for obtained paint are in the requirement. For increase PCC waste dosage and respect the standard value it is necessary grinding of PCC waste in order to reduce the particle size, other future researches for establishing grinding parameters will be necessary.

## 4. Conclusions

In this research, the possibility of using precipitated calcium carbonate (PCC) waste to replace commercial fillers in waterborne coatings was investigated. The density, contrast ration, white degree, viscosity, etc., were determined for different PCC waste content.

Precipitated calcium carbonate waste contained main $CaCO_3$ as calcite, particle sizes were even smaller than 1.00 µm, and their shapes exhibited the flake structure, which promotes the formation of coating.

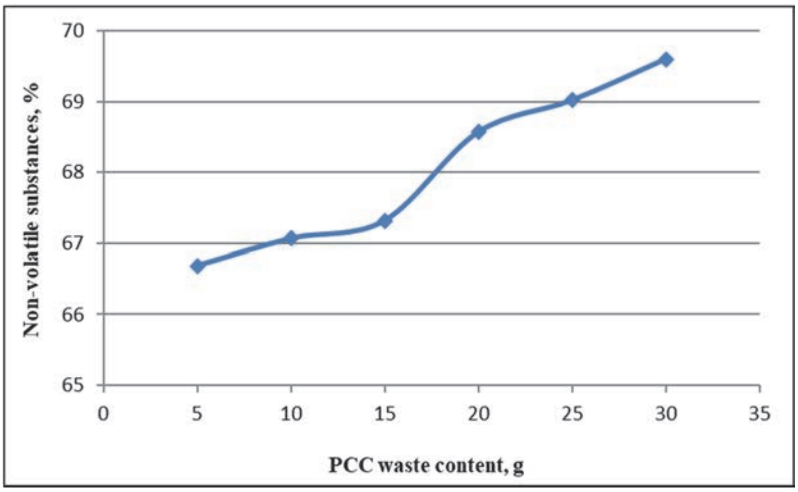



**Fig. 8.** The variation in the content of the non-volatile substance according to the amount of PCC waste added

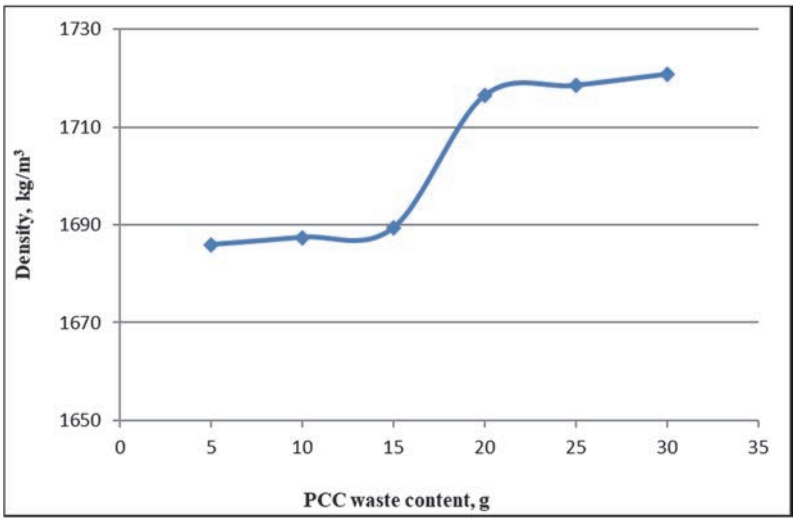



**Fig. 9.** Variation of density function of PCC waste content

**Table 4.** Characteristics of paint containing PCC waste

| *PCC waste content* | *5 g* | *10 g* | *15 g* | *20 g* | *30 g* |
|---|---|---|---|---|---|
| White degree, % | 93.05 | 92.72 | 92.49 | 92.14 | 91.70 |
| Contrast ration (CR) | 97.80 | 98.16 | 98.18 | 98.56 | 98.72 |

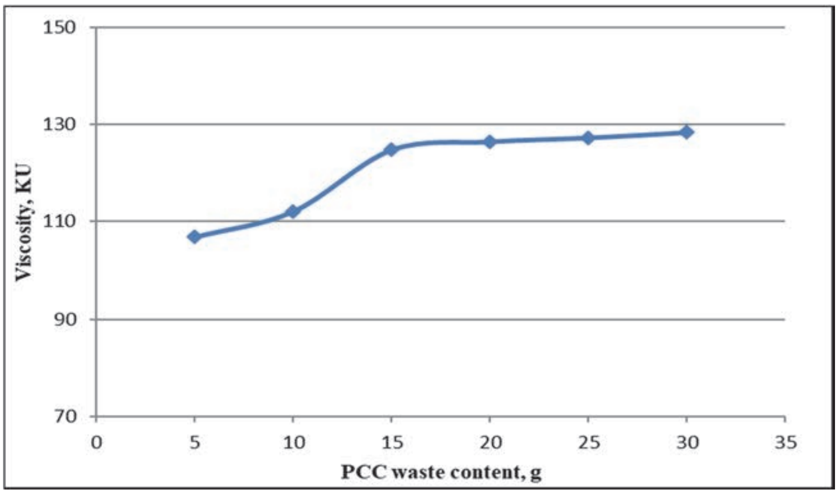



**Fig. 10.** Viscosity changes as a function of the amount of PCC

**Table 5.** Comparison between standard and real values

| *Characteristics* | *Standard value* | *5 g $CaCO_3$/300 mL* | *30 g $CaCO_3$/300 mL* |
|---|---|---|---|
| Appearance | slurry | slurry | slurry |
| Colour | white | white | white |
| Non-volatil content, % | 65–76 | 66.69 | 69.6 |
| Viscosity Stormer, KU | 95 –110 | 106.8 | 128.4 |
| Density, kg/m$^3$ | 1630–1730 | 1686 | 1721 |
| pH | 8–8.5 | 8.5 | 8.5 |
| Film aspect | matte | appropriate | appropriate |
| $W_i$ - White degree, % | 90–100 | 93.05 | 91.70 |
| CR - Contrast ration, % | 97–100 | 97.8 | 98.72 |

After the experimental analyses the following conclusions can be drawn:

– the value of the non-volatile substance content shall not deviate from the value required in the standard;

– the density as in the case above remains within the required values, the maximum variation being 1.7208%;

– the addition of calcium carbonate waste causes an increase of viscosity that deviates from the required values. The maximum quantity of PCC that can be used without viscosity modification is 10 g/300 mL;

– the white degree was negatively influenced, because with the increase in the amounts of PCC decreases the white degree, but its value remains in the imposed interval, close to the minimum value;

– regarding the contrast ratio (CR) it was found that adding the filler increases its coverage power, but not with relevant values (values between 0.5-1 %);

– the paint film isn't very uniform, because it has agglomerations of un-dispersed calcium carbonate, for increase PCC waste content the grinding is recommended.

After the analyses were carried out, precipitated calcium carbonate from the NPK fertilizer industry can be used to prepare water-based paints since the properties are within the values imposed by the standard as well as economically because it can be purchased at the lower price in that way reducing final costs.

These findings indicate that they are potential candidates for replacing traditional fillers in waterborne coatings.

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