Formulations for Gypsum Production

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Dissertação para obtenção do Grau de Mestre em

Engenharia Química

realizado em

Govi Engineered Chemicals

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Resumo

O gesso é um dos mais antigos materiais usados para construção. Sendo um material poroso, absorve, tendencialmente, grandes quantidades de água, quando em contacto com esta. A absorção de água por parte do gesso é prejudicial, uma vez que se traduz numa perda da sua resistência mecânica.

De modo a contrariar este efeito, emulsões contendo cera são, comumente, adicionadas à pasta de gesso, no processo de produção de blocos de gesso, melhorando a sua propriedade de repelência de água. O objectivo inicial deste projecto é a obtenção de dispersões/emulsões que, adicionadas ao gesso, o tornem repelente de água. Ao longo do projecto, foi sendo revelada a importância de diversas variáveis no processo de produção de blocos de gesso. A análise da influência destes parâmetros assumiu, então, uma relevância significativa no presente estudo.

Foram também testados aditivos com a intenção de promover uma melhoria no escoamento da pasta de gesso, propriedade de grande importância que determina a maior ou menor facilidade de manuseamento durante a aplicação.

Sumarizando, neste projecto foram obtidas diversas emulsões dentro da categoria de repelentes de água e, após a análise da influência de diferentes variáveis, o método de produção de blocos de gesso foi melhorado. Como trabalho futuro, sugere-se o uso destas emulsões repelentes de água na optimização deste mesmo método, com vista a reduzir a quantidade de aditivo requerido para a obtenção de resultados exigidos.

Palavras Chave: *gesso, emulsão, absorção de água, escoamento, variáveis do método.*

Abstract

Gypsum is one of the most ancient building materials. Due to its porous surface, when contacting with water, has great water uptake values. The water uptake by gypsum is harmful, since it leads to mechanical properties losses. In order to counteract this effect, wax emulsions are, commonly, added into gypsum slurry, during gypsum blocks manufacture, improving its water repellency feature. The main aim of this project is the achievement of dispersions/emulsions that make gypsum water repellent. During the course of the project, several variables proved to be relevant in the process of gypsum blocks manufacture. Thus, the analysis of these parameters assumed a relevant significance during the course of the current study.

In order to boost the gypsum slurry flow, an important property determining its workability during application, different additives have been tested.

Summing up, several water repellent emulsions were obtained and, after analyzing the influence of each variable, the method of gypsum blocks manufacture was improved. Combination of both, emulsions and method improvement is suggested as future development in order to optimize the process of gypsum blocks manufacture.

Keywords: *gypsum, emulsion, water uptake, flow, method variables*

Index of Tables

Index of Figures

List of Abreviations and Symbols

WU	Water uptake
WU1	Water uptake measured after 1 hour of immersion
WU2	Water uptake measured after 2 hours of immersion
w/w	Water by water ratio
G/W	Gypsum / Water ratio (w/w)
EVA	Ethylene vinyl acetate
VA	Vinyl Acetate
PVA	Polyvinyl alcohol
MEA	Monoethanolamine
KOH	Potassium hydroxide
min	Minutes
s	Seconds
ºC	Celsius degree
cm	Centimeter
g	Grams
cP	Centipoise
σ	Standard deviation

Contents

1 Introduction

Govi (*Gentse Olie en Vet Industrien*) is a family-owned company, incorporated in 1910, that supplies a variety of industries.

Govi produces about 40 thousand ton per year, being specialist in emulsions and colloidal systems. The current business units comprise applications in wood, insulation, printing, dust binding, rope & netting and textiles.

The *Govi Engineered Chemicals* embraces this project with the main objective of obtaining an emulsion for making gypsum blocks water-repellent.

Natural gypsum consists mainly of calcium sulfate dehydrate and it is a common non-metallic mineral that occurs as a deposit of fairly soft and often impure rock [1]. Synthetic gypsum is identical to natural gypsum from a chemical and crystallographic point of view. The main difference between both lies primarily in their physical state, which depends on the origin or manner of their formation.

Over the ages, natural gypsum has been used as blocks for construction purposes, because of its excellent fire resistance, aesthetics and low price. From an environmental point of view, gypsum has a lower emission of carbon dioxide, during his industrial process of production, if compared with Portland cement [1]. More recently, utilizations of uncalcined gypsum have involved application as setting time regulator for Portland cement, as fertilizer and for soil amelioration. However, the most modern application for gypsum is for the manufacture of gypsum board on a large scale. The set of applications of gypsum, and their respective relevance, is illustrated in the picture below.

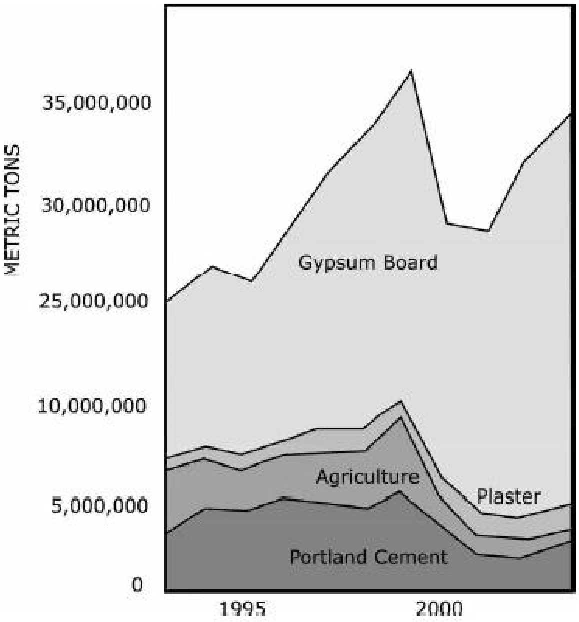

Figure 1 – End use of gypsum [1]

However, the utilization of gypsum has some limitations that affect your application.

When absorbing liquid water, rehydrated gypsum loses strength up to 50%, which is much greater than that of other cementitious materials. This is due to the higher solubility of gypsum in water, reinforced by its higher porosity. It has also been speculated that the loss of hydrogen bonds is the reason for this relatively large loss of strength.

Figure 2 shows the effect of the increase of the water in the compressive strength of the gypsum.

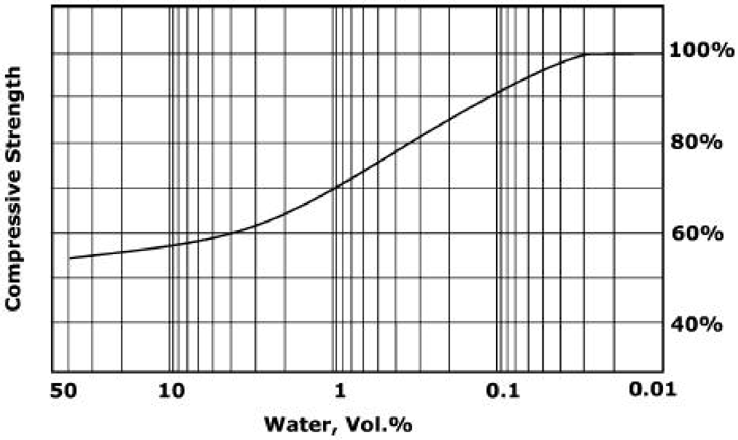

Figure 2 – Compressive strength variation with the water uptake by gypsum. [1]

Actually, the two major commercial methods to make gypsum wallboard water resistant are by incorporating hydrocarbon wax or polymethylhydrogensiloxane (siloxane) into the gypsum slurry, during board/block manufacture.

Currently, wax emulsions and siloxane represent 55% and 45% of the US market, respectively. [2]

An important factor that can change the actual market paradigm in the next years has to do with the Volatile Organic Compound (VOC) emissions. Although blocks made with wax or siloxane generated VOCs during the kiln drying process, the contribution of VOC emissions levels from siloxane blocks were higher by as much as a factor of ten times that of wax-containing blocks. Moreover, siloxane generates one of the more toxic pollutants (HCBD) on the TO-15 list [2].The higher emissions are thought to be due to reactions and subsequent volatilization that occurs as the siloxane raw material is converted to the water resistant block manufacture process. If government emissions permitting and storage/disposal requirements are a concern for a manufacturing plant, wax emulsion use is recommended over siloxanes [2].

On the other hand, it is estimated that wax emulsion is more expensive than siloxane by a factor of 2,5 times more [11].

However, in addition to water repellency, there are other relevant properties that the desired product should confer, such as a good flow and certain hardening/setting time of the gypsum slurry.

Thus, to evaluate the performance of each emulsion in the gypsum slurry application, several tests were made:

- <u>Water uptake test</u>

As mentioned before, the higher the water content, the lower the compressive strength of the gypsum block. This feature is definitely the most important and, such as, greater emphasis was given to this test.

Standard EN520 defines three different water-repellent categories, depending on the two-hour water uptake performance, as shown in the Table 1.

Table 1 – Categories for gypsum plasterboards according to EN520.

Category	***Water Uptake***
H1	≤ 5%
H2	≤ 10%
H3	≤ 25%

- <u>Flow test</u>

The flow property is also an important characteristic of the gypsum. This feature is intended to reflect the workability of the wet plaster and it is perhaps the most important and least understood of all plasters properties. [1]

- <u>Hardening time test</u>

A major hurdle in the use of gypsum plaster, in the building industry, has been the quick setting time. A plaster has to possess sufficient time so that the masons could apply it with ease. However, more rarely and in some applications, it could be desired to shorten the setting time in order to speed up manufacturing processes [5].

The detailed description of the tests mentioned above will be presented in the chapter 3.1.

2 Background

Most applications of gypsum are based on the fact that it can be calcined when subjected to heat treatment at fairly low temperatures. This results in the formation of stucco as the first calcinations stage or insoluble anhydrite as the second calcinations stage.

Frequently, the manufacturing process of gypsum board/block production is based on stucco alone and does not involve insoluble anhydrite.

Under atmospheric conditions, the dehydration of calcium sulfate dehydrate involves exposure to increasing temperatures with corresponding stepwise loss of water. This process is indicated below.

Figure 3 – Calcium Sulfate process steps.

Soluble anhydrite, CaSO4 (sol.), is a special case, but not a separate phase. It may be considered an extension or an anhydrous variation of hemihydrates. Furthermore, soluble anhydrite is unstable and reverts rapidly into hemihydrate when exposed to water vapor or when coming into contact with liquid water.

The rehydration of hemihydrate and of insoluble anhydrite refers to their solution in water and subsequent crystallization.

$$Hemihydrate + water \rightarrow Dihydrate + Heat \quad (rapid\ process)$$

$$Insol.Anhydrite + water \rightarrow Dihydrate + Heat \quad (slow\ process)$$

This process consists of the incorporation of water during crystallization and is featured by a release of heat.

For blocks, gypsum is heated to calcine and remove some of the water of crystallization to generate calcium sulfate hemihydrate ($CaSO_4{*}^{1/2}H_2O$). This stucco is then mixed with other additives and water to give a flowable and pumpable slurry. The stucco then rehydrates to form the starting gypsum dehydrate material. The excess of moisture is finally dried off in an oven. Figure 4 illustrates the industrial gypsum chemistry cycle.

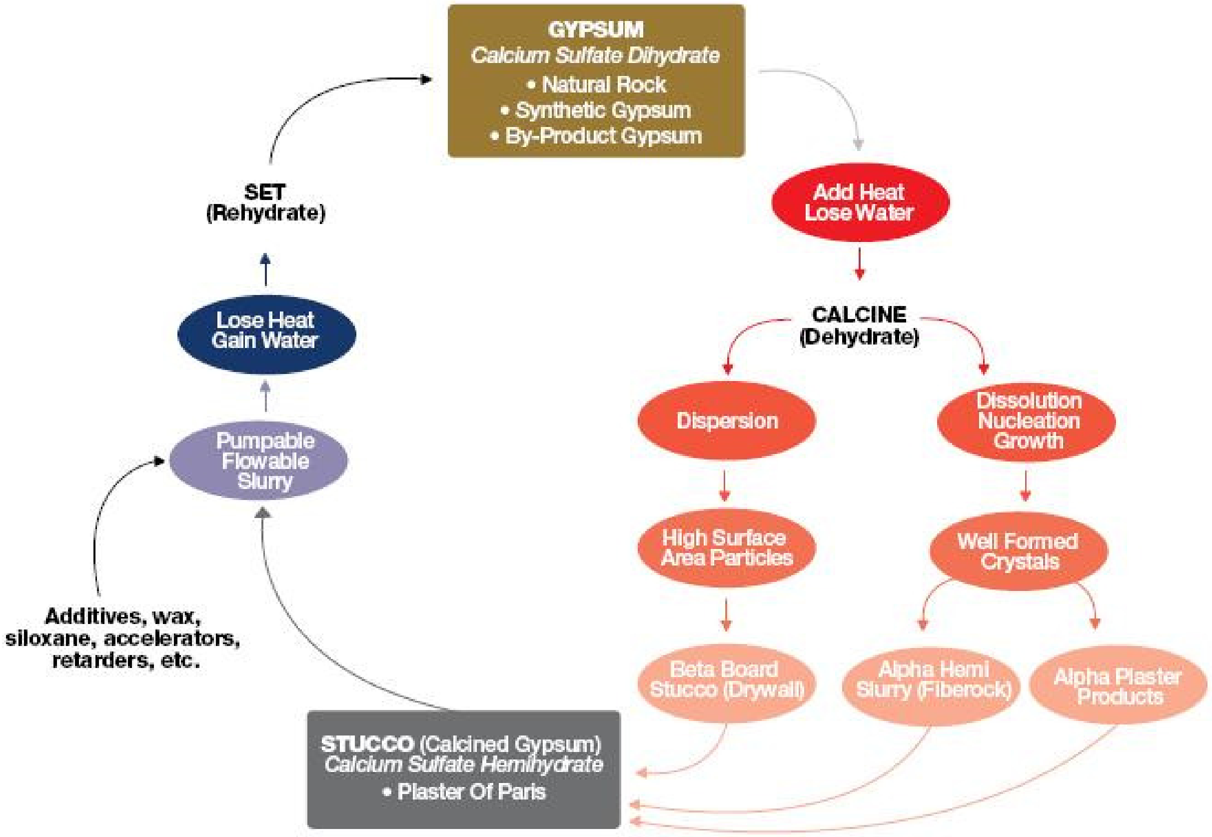

Figure 4 – Industrial gypsum chemistry cycle [2].

To overcome problems of water absorption by the hygroscopic gypsum, which may lead to weakening of the block, hydrophobic components are added into the gypsum slurry, prior to make the blocks. Such hydrophobic components, such waxes, must be provided in the form of an emulsion so as to be miscible in the aqueous gypsum slurry. These emulsions provide the gypsum blocks water repellent characteristics.

Emulsions are part of a more general class of two-phase systems of matter called colloids. Colloid is a mixture in which one substance is dispersed throughout another at the microscopic level. They can be classified according to their particle size, from highest to lowest, and stability, from lowest to highest as follows: dispersion, general suspension, colloidal suspension, lyophobic suspension, lyophilic colloid, emulsion and solution. In this last state, the dispersed phase is totally solvated and the system is considered homogeneous [12].

In the specific case of emulsions, both the continuous and the dispersed phase are liquid. Emulsions are unstable and thus do not form spontaneously. To form an emulsion, energy input through homogenizing, stirring or shaking is needed. Over the time, emulsions tend to revert to the stable state comprising both phases. Thus, a third component, a surfactant, must be present to prevent coalescence of the dispersed phase [15].

A surfactant means a surface active agent. In other words, surfactant is defined by its tendency to adsorb at surfaces and interfaces [14] The driving force for a surfactant to adsorb at an interface is to lower the free energy on that phase boundary. The term interfacial tension is often used instead of interfacial free energy per unit area, which represents the amount of work required to expand the interface. When that boundary is covered by surfactant molecules, the surface tension (or the amount of work required to expand the interface) is reduced. [4]

There are different classes of surfactants. Emulsifiers and dispersing agents (or dispersants), both can be used with the same main function: to increase the stability of an emulsion. Emulsifier is an agent that stabilizes an emulsion by increasing its kinetic stability. However, emulsifiers are not preferred for this kind of emulsions since they can help water penetrating into the pores, due to the reduction of the surface tension.

As mentioned above, hydrocarbon wax emulsions are added into the gypsum slurry during block manufacture in order to improve its water repellency.

Waxes for gypsum board/blocks applications are typically melt blended and then emulsified in water to allow room temperature transport to gypsum board/blocks plants plus increases the compatibility with aqueous gypsum based slurries.

Mixtures of waxes tend to be used to tailor the wax formulation to the target application. One commonly used blending in gypsum blocks/wallboard manufacture is a combination of a paraffin and a montan wax. The molten waxes are mixed with hot water and alkali to saponify the Montan components to form a soap. After higher shear mixing and rapid cooling, the wax droplets solidify and form a finely divided dispersion.

For *waterproofing* of gypsum-based substrates, silanes, siloxanes and siliconates have also been used historically.

For gypsum wallboard slurry, the lower molecular weight silanes tend to be more mobile in the gypsum slurry and during the drying process. This poses retention problems during setting and drying, which means that larger amounts will be required to achieve an acceptable performance. Siliconates tend to be alkaline and alkaline nature tends to retard the setting reactions of stucco hemihydrate calcium sulfate. Siloxanes have more typically been used for gypsum wallboard production.

The siloxane method is more complex than wax emulsions one, with chemical reactions occurring during the wallboard manufacture process.

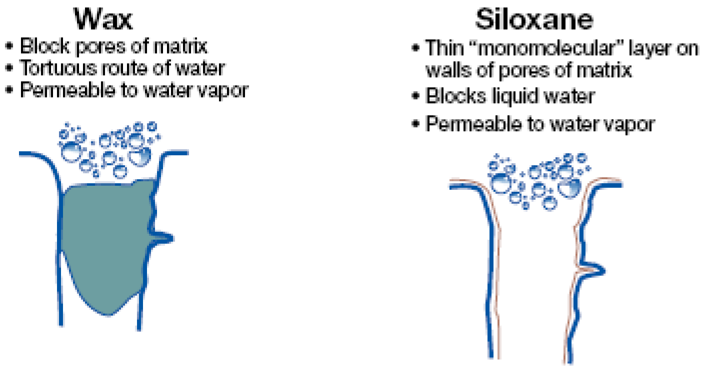

Figure 5 – Longitudinal section of typical gypsum matrix pore having Wax (left) or Siloxane (right) water resistance additive [2].

Although these materials accomplish the same task, their chemistry and water resistant mechanisms are different. Wax is non-reactive and considered to have a bulk, pore blocking effect in the gypsum matrix which controls water mobility. Siloxane is a complex, reactive mechanism thought to create a thin, low surface tension in the matrix to protect the block from moisture.

3 Technical Description and Results Analysis

This chapter consists of two sections. Sub-chapter 3.1 presents the methods/materials that were followed/used in the course of this project. The results and respective discussion is presented in sub-chapter 3.2.

3.1 Materials and Methods

In the following figures, it is illustrated some of the equipments used to prepare and perform the methods described in this chapter.

Figure 6 – High pressure homogenizer.

Figure 7 – Analytical scale (±0.01 g) used to assess boards water uptake by difference to the initial test sample weight.

Figure 8 – Moisture analyzer used to assess solids content in each emulsion.

Figure 9 – Moisture analyzer used to assess solids content in each emulsion.

3.1.1 Preparation of Emulsions

Literature [6] refers aqueous emulsions comprising a paraffinic hydrocarbon, montan wax, polyvinyl alcohol (PVA) and, optionally, additives conventionally employed in emulsions to different purposes, including emulsifiers to assist in formation of the emulsion and stabilizers to assist in stabilization of the emulsion.

The paraffinic wax is indicated as one having a melting point of 40 to 80ºC, since melting points above 80ºC require higher drying temperatures in the manufacture of gypsum wallboard and this results in a poor water resistance in the wallboard.

The current study contemplated a blend of a fully refined paraffin, with a melting point between 68 and 70ºC, and a slack wax with a 50-70ºC melting point range. Slack wax is a semi-refined wax, darker and with a higher oil content, but, on the other hand, cheaper than fully refined paraffin.

The polyvinyl alcohol is typically obtained by hydrolysis of polyvinyl acetate. It is soluble in water in a 65-95ºC temperature range, thus it could be added in the aqueous phase. Polyvinyl alcohol provides adhesive characteristics as well as increased stability in the gypsum slurry, while providing superior water repellency in the final gypsum product. The PVA coats the gypsum crystals/particles such that, during the setting, the coated gypsum particles are prevented from returning to the hemihydrate state from the dihydrate.

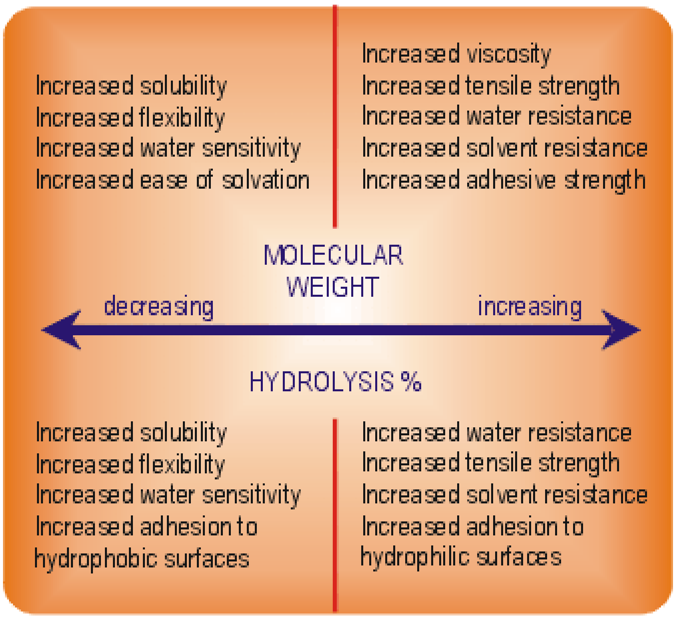

Figure 10 – PVA Hydrolysis and Molecular Weight Effects [9]

Literature [9] refers that higher molecular weight and higher hydrolysis degree lead to increased block resistance, as well as an increased water resistance, respectively. On the contrary, higher molecular means higher viscosity, which may have a negative effect in the flow property of the gypsum slurry, decreasing its workability. The emulsions tested comprised a 98,8% hydrolysis degree and a 31000-50000 average molecular weight range.

Taking into account the Bakor's patent [6], it was formulated alternative emulsions, presented below. In the method of preparation of the aqueous emulsions, the paraffinic hydrocarbon and other waxes are heated to the molten state and then blended together. A hot aqueous solution of the PVA containing the emulsifiers and stabilizers is passed through the homogenizer and the resulting emulsion should be rapidly cooled.

For the development of new emulsions for gypsum blocks production, it was applied an iterative reformulation, based on experimental results.

For intellectual property (IP) matters, the real and trade names of most of the compounds used in the formulations described hereinafter has been replaced by some code and generic names. That should not represent a problem to understand the goals of this project, since what is true for the specific molecules used may also be true for other similar molecules. This also allows this study to cover a broader view on the chemistries that may or may not be interesting to use in the gypsum blocks or panels manufacturing.

The preparation of all emulsions followed the Method 1.

Method 1 – Preparation of emulsions

1. Prepare the organic phase: join every waxes in a vessel and warm up the mixture, while mixing, until all the waxes are totally melted;
2. Prepare the water phase: join every ingredients and mix until the solution is completely homogeneous;
3. Join the water phase to the organic phase in the homogenizer's reactor, stirring the mixture;
4. Heat or cool down the mixture until the desired temperature is reached (10-15 ºC above the highest melting point of the waxes);
5. Pass the mixture through the homogenizer at a pressure of 200 bar, during 4min15s;
6. Use the cooling system integrated in the installation to rapidly cool down the mixture;
7. Collect the emulsion in 1L plastic bottle and keep it in a water bath at room temperature until the emulsion temperature stabilizes.

3.1.1.1 Amount of Dispersant A

Dispersing agents or dispersants are commonly used in the production of suspensions of particulate solids in water. The effect of a dispersing agent is evident in a sharp reduction in the viscosity of a dispersion if the optimum quantity is added. This makes it possible for highly concentrated slurries to be produced which are much easier to handle, because they can be stirred and pumped more easily and with less use of energy.

Other potentialities of these additives are proven: the fact they stabilize dispersions and emulsions (e.g. of polymers, resins and paraffin) against physical and chemical influences that could impair their stability during processing; and the effect that the solid components of the dispersions remain finely dispersed if any flocculation occurs.

The effect of the addition of different amounts of a dispersant in the water uptake of the gypsum blocks and in the flow of the gypsum slurry was studied for two different standard emulsions. Thereunto, as example, Dispersant A, a naphthalene sulfonic acid formaldehyde condensate, was used.

The formulations comprising the influence of the amount of Dispersant A are expressed in Table 2 and Table 3.

Table 2 – Formulations of the emulsions 182, 183 and 184.

	182	***183***	***184***
Water	45,39%	44,94%	44,50%
Fully Refined Paraffin Wax	23,32%	23,09%	22,86%
Slack Wax	10,00%	9,90%	9,80%
Radia 7268 (EGDS)	1,44%	1,43%	1,41%
Dispersant A	**1,00%**	**1,98%**	**2,94%**
PVA: celvol 107 15%	14,23%	14,09%	13,95%
MEA 90%	0,55%	0,54%	0,54%
Acticide LA	0,10%	0,10%	0,10%
Polar Wax A	3,97%	3,93%	3,89%
Solids Content	41,52%	40,82%	41,93%

Table 3 – Formulations of the emulsions 185, 186 and 187.

	185	***186***	***187***
Water	45,11%	44,66%	44,23%
Fully Refined Paraffin Wax	23,17%	22,94%	22,72%
Slack Wax	9,94%	9,84%	9,74%
staybelite E	0,99%	0,98%	0,97%
Dispersant A	**0,99%**	**1,97%**	**2,92%**
PVA: celvol 107 15%	14,14%	14,00%	13,86%
KOH 50%	1,61%	1,60%	1,58%
Acticide LA	0,10%	0,10%	0,10%
Polar Wax A	3,94%	3,91%	3,87%
Solids Content	41,85%	41,09%	42,83%

3.1.1.2 Alternative Polar Waxes

Literature [6] refers aqueous emulsions containing a montan wax as being useful in the manufacture of water resistant gypsum wallboards. Crude montan wax is a hard dark brown extracted from lignite or brown coal capable of being emulsified and saponified, providing plasterboard waterproofing. Notwithstanding, montan wax exhibit some discouraging issues.

Montan wax is known to cause a build-up of dark or black sludge in process tanks used for emulsification. Moreover, many wax emulsions based on montan wax tend to separate during storage, creating inconsistent performance features [7], as well as the variety of components that this wax may contain from one geographic region to another [13].

The current shortage of montan wax it is also a relevant issue, making it worthwhile to find an alternative to these waxes. With this aim, polar waxes were tested as substitutes of this component.

- Polar Wax A is a hydrocarbon polymer, with a 96ºC melting point, that compatibilizes polar and non-polar waxes, resins and additives, due to its polar and non-polar segments.
- Polar Wax B is a polyvinyl ether wax, with a melting point between 47ºC and 51ºC.
- Polar Wax C has random copolymers of ethylene and vinyl acetate. Its melting point is 74ºC.
- Polar Wax D is an ethylene copolymer wax, with high viscosity.
- Polar Wax E is a very viscous polyamide resin, with a softening point of 118ºC.

The same background formulation was used in order to enable the comparison between each polar wax. Nevertheless, there are some differentiating points: emulsions 188, 189 and 190 contain stearic acid, in order to have some extra emulsifying power, and, simultaneously, MEA to neutralize those acid groups; emulsion 183 does not contains stearic acid; emulsion 192 does not contain MEA because there are no acid groups to neutralize.

The formulations of these series of emulsions are presented in the Table 4.

Table 4 – Formulations of the emulsions 183, 188, 189, 190 and 192.

	183	*188*	*189*	*190*	*192*
Water	44,94%	44,79%	44,79%	44,79%	45,19%
Fully Refined Paraffin Wax	23,09%	23,01%	23,01%	23,01%	23,21%
Slack Wax	9,90%	9,87%	9,87%	9,87%	9,95%
Radia 7268 (EGDS)	1,43%	1,42%	1,42%	1,42%	1,43%
Dispersant A	1,98%	1,97%	1,97%	1,97%	1,99%
Stearic Acid		0,59%	0,59%	0,59%	
PVA: celvol 107 15%	14,09%	14,04%	14,04%	14,04%	14,17%
MEA 90%	0,54%	0,29%	0,29%	0,29%	
Acticide LA	0,10%	0,10%	0,10%	0,10%	0,10%
Polar Wax A	**3,93%**				
Polar Wax B		**3,92%**			
Polar Wax C			**3,92%**		
Polar Wax D				**3,92%**	
Polar Wax E					**3,95%**
Solids Content	40,82%	41,14%	41,04%	43,42%	41,30%

3.1.1.3 Half amount of Polyvinyl Alcohol

Polyvinyl alcohol is prepared by the alcoholysis, saponification or hydrolysis of a polyvinyl ester such as polyvinyl acetate, so as to convert at least about 70 percent of the ester groups of the latter to hydroxyl groups. The extent to which such conversion is effected is commonly referred to as the degree of hydrolysis, which is frequently expressed as percent hydrolysis. A polyvinyl alcohol that is 99 to 100 percent hydrolyzed, i.e., 99 to 100 percent of the ester groups are converted to hydroxyl groups, is generally referred to as a fully hydrolyzed polyvinyl alcohol, while one that is hydrolyzed to a lesser extent is referred to as a partially hydrolyzed polyvinyl alcohol. Polyvinyl alcohols of various degrees of hydrolysis are available commercially in high, medium and low viscosity grades. The viscosity of a polyvinyl alcohol depends upon the degree of polymerization of the polyvinyl ester: the higher the degree of polymerization of the parent ester, the higher will be the viscosity of the polyvinyl alcohol. [3]

Polyvinyl alcohol provides adhesive characteristics as well as increased stability in the gypsum slurry, while providing superior water repellency in the final gypsum product. Nevertheless, its molecular weight plays also an important role in terms of the final rheological properties. Being so, it is important to find a good commitment between the water repellency and flow capability features.

This series of tests aims to understand the effect on the water uptake / flow test 1 results by halving the amount of the PVA content. It was considered once again a commercially available polyvinyl alcohol, Celvol 107, having a degree of hydrolysis of 98.0 to 98.8% and a viscosity from 5.5 to 6.6 cP at a 4% (w/w) concentration aqueous solution.

Polyvinyl Alcohol is soluble in water in a 65-95ºC temperature range, so it could be added in the aqueous phase. Thus, it was replaced half of the amount of the PVA by the tantamount of water.

The formulations 195, 196 and 197 correspond to emulsions 183, 188 and 189, respectively, comprising the previously mentioned replacement.

Table 5 – Formulations of the emulsions 195, 196 and 197.

	195	***196***	***197***
Water	51,99%	51,81%	51,81%
Fully Refined Paraffin Wax	23,09%	23,01%	23,01%
Slack Wax	9,90%	9,87%	9,87%
Radia 7268 (EGDS)	1,43%	1,42%	1,42%
Dispersant A	1,98%	1,97%	1,97%
Stearic Acid		0,59%	0,59%
PVA: celvol 107 15%	**7,04%**	**7,02%**	**7,02%**
KOH 50%	0,54%	0,29%	0,29%
Acticide LA	0,10%	0,10%	0,10%
Polar Wax A	3,93%		
Polar Wax B		3,92%	
Polar Wax C			3,92%
Solids Content	39,91%	39,90%	40,79%

3.1.1.4 Ethylene - Vinyl Acetate Copolymers

Ethylene - Vinyl Acetate (EVA) and wax are two components that complement each other in a variety of uses, including hot melt adhesives and curtain coatings for paper. EVA has high cohesive strength and allows the wax to maintain its water barrier properties in folds and creases.

In this experiment were considered EVA copolymers with different properties, namely in terms of VA content and melt index.

Higher Vinyl Acetate content determines increased solubility, improved creased barrier and higher seal strength. Besides, lower content provides improved gloss retention, blocking resistance and paraffin wax compatibility.

According to ASTM D1238, melt index is a measure of the ease the flow of the melt of a thermoplastic polymer. It is defined as the mass, in grams, that flows in through a capillary in 10 minutes. Higher melt index leads to a lower melt viscosity, improved gloss retention and increased solubility, while lower melt index gives improved creased barrier, increased toughness and flexibility and higher seal strength [10].

The emulsions 189 and 202 to 205 aimed to study the performance of different types of EVA, keeping the remaining composition constant.

- Polar Wax C has 18% VA content, a 74ºC melting point, with a melt index of 450-550 g/10min.
- Copolymer A has 18% VA content, a 88ºC melting point, with a melt index of 135-175 g/10min.
- Copolymer B has 28% VA content, a 66ºC melting point, with a melt index of 370-470 g/10min.
- Copolymer C has 18% VA content, a 88ºC melting point, with a melt index of 2,5 g/10min.
- Copolymer D has 28% VA content, a 75ºC melting point, with a melt index of 6.0 g/10min.

The formulations of the emulsions tested are presented in the Table 6. Note that it was also tested a new formulation containing the previous mentioned Polar Wax C (also an EVA copolymer).

Table 6 – Formulations of the emulsions including different types of EVA.

	189	***202***	***203***	***204***	***205***
Water	45,39%	45,39%	45,39%	45,39%	45,39%
Fully Refined Paraffin Wax	23,32%	23,32%	23,32%	23,32%	23,32%
Slack Wax	10,00%	10,00%	10,00%	10,00%	10,00%
Polar Wax C	**3,97%**				
Copolymer A		**3,97%**			
Copolymer B			**3,97%**		
Copolymer C				**3,97%**	
Copolymer D					**3,97%**
Radia 7268 (EGDS)	1,44%	1,44%	1,44%	1,44%	1,44%
Dispersant A	2,00%	2,00%	2,00%	2,00%	2,00%
stearinezuur	0,60%	0,60%	0,60%	0,60%	0,60%
PVA : celvol 107 15%	14,23%	14,23%	14,23%	14,23%	14,23%
MEA 90%	0,29%	0,29%	0,29%	0,29%	0,29%
Acticide LA	0,10%	0,10%	0,10%	0,10%	0,10%
Solids Content	41,04%	39,33%	39,48%	39,32%	39,47%

3.1.1.5 Costumer Drying Conditions: 70ºC during 36 hours

With a potential costumer rising up, some of the previously manufactured emulsions were sent for client tests. The studies were conducted at costumer's usual conditions, which require 70ºC during the 36 hours drying step.

In order to maintain a parallel with the client evaluation, drying conditions were defined as the same.

This series of tests includes the emulsions 195, 196, 197 and 203, sent to the customer, and a new formulation, emulsion 209.

Emulsion 209 comprises the use of a different water soluble polymer, instead of the PVA. Water Soluble Polymer A contains silanol groups in its molecular structure and has a viscosity of 20 to 30cP.

At the same time, it was introduced a 3,76% (w/w) of a montan wax to the detriment of a polar wax in the composition of the referred emulsion.

Emulsion 209 formulation is described in Table 7.

Table 7 – Formulation of the emulsion 209.

	209
Water	54,24%
Fully Refined Paraffin Wax	22,12%
Slack Wax	9,48%
Montan Wax	**3,76%**
Dispersant A	1,90%
Radia 7268 (EGDS)	1,37%
Water Soluble Polymer A	**6,76%**
MEA 90%	0,28%
Acticide LA	0,09%
Solids Content	38,52%

3.1.2 Test Methods

Method 2 – Water uptake test

In order to obtain the water repellency performance of each emulsion, it was followed the Method 2. This method consists in adding the previously prepared emulsion to the gypsum. The gypsum slurry is then disposed into the block mold, being the blocks dried in the oven. Four gypsum blocks are manufactured per each series. Finally, the water repellency is tested for each block, after being submersed in water during 1 and 2 hours.

The procedure for the water uptake test is the following:

1. Weigh 683,10 g of water and 63,80 g of emulsion and mix them until an homogenous phase is formed;
2. Weigh 1036,20 g of gypsum;
3. Lubricate the metal plates with lubricant oil.
4. Assemble the mold with the metal plates.
5. Join the gypsum into the water and emulsion and stir violently the mixture during 1 min.
6. Dispose the gypsum slurry in the mold, prepared for 4 blocks.
7. After the setting of the gypsum slurry, remove the metal plates;
8. Dry the blocks in the oven at 80ºC;
9. 2h later, change the temperature of the oven to 40ºC;
10. 5 days later, remove the blocks from the oven and let them stay at room temperature during 30 min;
11. Weigh each block and write down the value (m_{dry});
12. Submerge the blocks in water;
13. Weigh each block and write down the value after 1h (m_{1h}) and 2h (m_{2h}).
14. Calculate the water uptake after 2h (and analogously for 1h) through the equation 1:

$$WU_{2h} = \frac{(m_{2h} - m_{dry})}{m_{dry}} \qquad \text{(Equation 1)}$$

Method 3 – Flow Test A

This tests aims to give a measure of the flow capability that each emulsion gives to gypsum slurry. This is also an important property during the manufacturing of gypsum panels or blocks, since it determines the greater or lesser difficulty in molding the gypsum slurry during the application.

Test A consists in dispose the gypsum slurry on a slide and measure the distance achieved before setting.

The procedure is described below:

1. Weigh 207,24 g of gypsum and put it on a 500 mL plastic bottle;
2. Weigh 136,62 g of water and 12,70 g of emulsion and mix them until an homogenous phase is formed;
3. Add the set water-emulsion into the gypsum, close the bottle and shake very well during 1 min;
4. Place the bottle on a metal plate, inclined with an angle of 7,3º and lift the bottle.
5. The liquid flows down the plate. Measure and write down the length reached by the gypsum slurry.

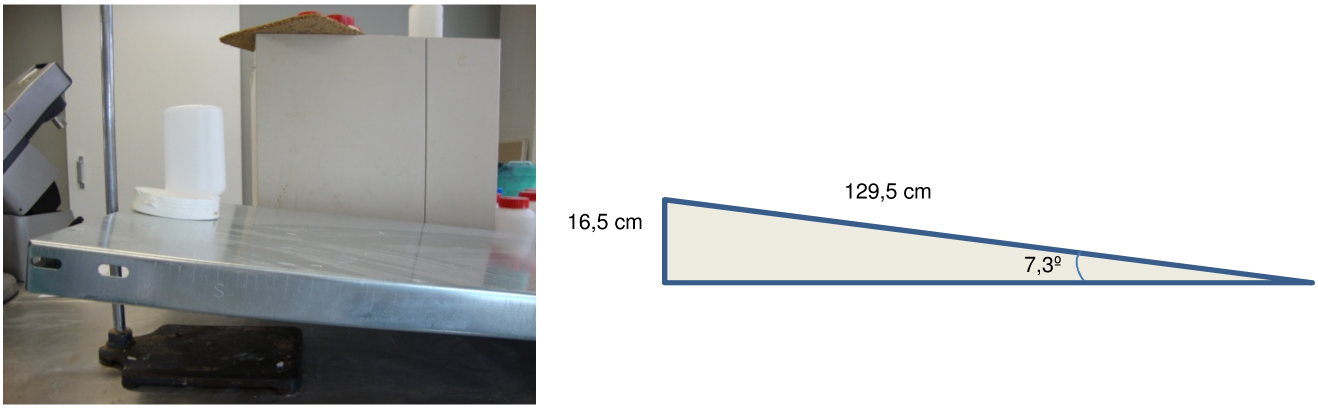

Figure 11 – Slide used during the Flow Test A.

Method 4 – Flow Test B (Hardening Test)

Such as the Test A, this test aims to give a measure of how each emulsion affects the workability of the gypsum slurry during its application.

Test B consists in making cuts, with a knife, in a gypsum layer until the cut does not close upon itself. The greater the time between the disposal of the gypsum slurry and the last cut, the greater the workability of the gypsum.

Test B procedure is the following:

1. Weigh 138,16 g of gypsum and put in on a 500 mL plastic bottle;
2. Weigh 91,08 g of water and 8,51 g of emulsion and mix them until an homogeneous phase is formed;
3. Add the set water-emulsion into the gypsum, close the bottle and shake very well during 1 min;
4. Cast the gypsum in between the metal plates in order to get a layer of nearly 5 mm;
5. Cut the gypsum layer at regular times with a knife;
6. When the cut does not close upon itself, write down the time.

3.2 Results Analysis

This section starts to present the results obtained for the different series of blocks made, comprising different emulsions. A tentative of improvement in terms of gypsum slurry rheological properties, by adding a superplasticizer, is described analyzed here.

After that, the results and respective analysis for the study of the influence of several operative variables in the method of gypsum blocks manufacturing is displayed.

Finally, it is presented a comparative analysis between wax emulsions and siloxanes.

3.2.1 Formulation of Emulsions

This chapter comprises the water uptake and flow results of the formulation of emulsions presented in chapter 3.1. As mentioned in the Method 2, the mold used allowed the manufacture of 4 gypsum blocks per each series. Thus, the average water uptake and the standard deviation, σ, are calculated taking into account the 4 results obtained for the 4 blocks.

Together with the emulsions formulated, a commercial product was also tested every day, working as a reference. This allows to measure the performance of the formulated emulsions versus the commercial ones, but also the comparison between the emulsions made in different days, i.e. presumably in different conditions. Two different commercial products were defined as reference:

- **Reference 1**, a Romonta product which consists on a montan wax dispersion with an interesting water repellency performance.
- **Reference 2**, or Coreshield® from Walker Industries, combines moisture resistance with a great flow property.

Both were applied as references due to the short availability of each one in the laboratory. The deviation evidences the difference, in terms of water uptake after 2 hours (WU2h), between the emulsion and the reference, according to the equation 2.

$$Deviation(\%) = \frac{WU2h - Reference}{Reference} \times 100 \qquad \text{(Equation 2)}$$

3.2.1.1 Amount of Dispersant A

This study was made in two different days: one comprised the inclusion of the emulsions 182 and 184 and the other when was included emulsion 183. Both were accompanied by the Reference 1.

The results are shown in the Table 8 and Figure 12.

Table 8 – Water Uptake results for the emulsions 182, 183 and 184.

Emulsion	***WU2h***	***σ Emulsion***	***Reference 1***	***σ Reference 1***	***Deviation***
182	1,50%	0,13%	1,81%	0,40%	-17,13%
183	2,34%	0,51%	2,52%	0,35%	-7,14%
184	2,02%	0,22%	1,81%	0,40%	11,60%

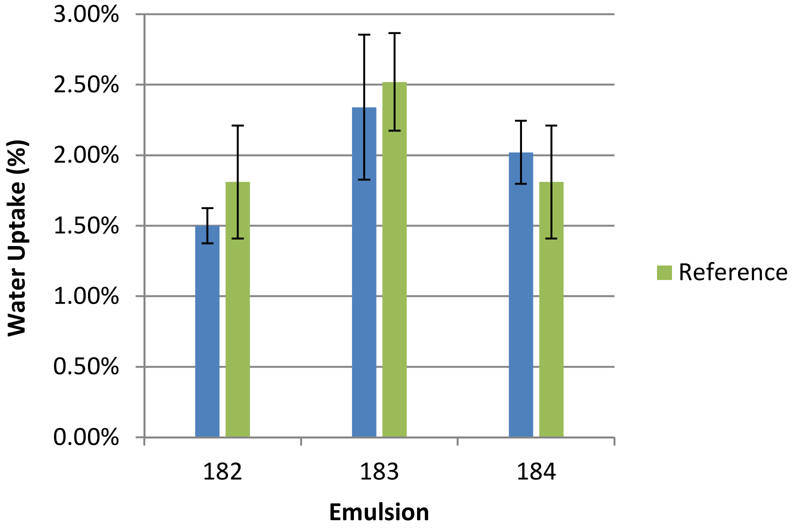

Figure 12 – Water uptake results for emulsions 182, 183 and 184.

Through Figure 12, all the emulsions present a H1 category water uptake result, according to EN520.

Relatively to the reference, it is noticeable the fact that increasing the amount of Dispersant A has a negative effect, increasing the water uptake. Despite this component has an excellent dispersing action, it is not surface-active, therefore it has a bad performance in terms of water repellency. It is also noteworthy the fact that the reference 1 assumed some discrepancy from the one day to the other.

In parallel, it was made the study of the amount of Dispersant A on the flow properties of the gypsum slurry. It was made both flow tests, FT1 and FT2, described in the chapter 3.2. The results are presented in Table 9, Figure 13 and Figure 14.

Table 9 – Flow Test 1 and Flow Test 2 results for emulsions 182, 183 and 184.

Emulsion	***FT1(cm)***	***Reference 2(cm)***	***FT1 Deviation***	***FT2 (s)***	***Reference 1(s)***	***FT2 Deviation***
182	21,1	26,7	-21,0%	188	195	-3,7%
183	24,6		-7,9%	N/A	N/A	N/A
184	33,0		23,6%	223	195	12,6%

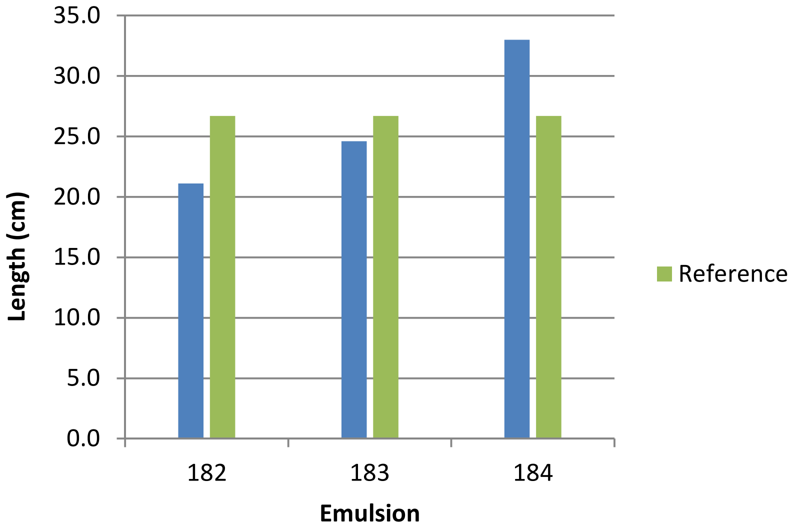

Figure 13 – Flow Test 1 results for emulsions 182, 183 and 184.

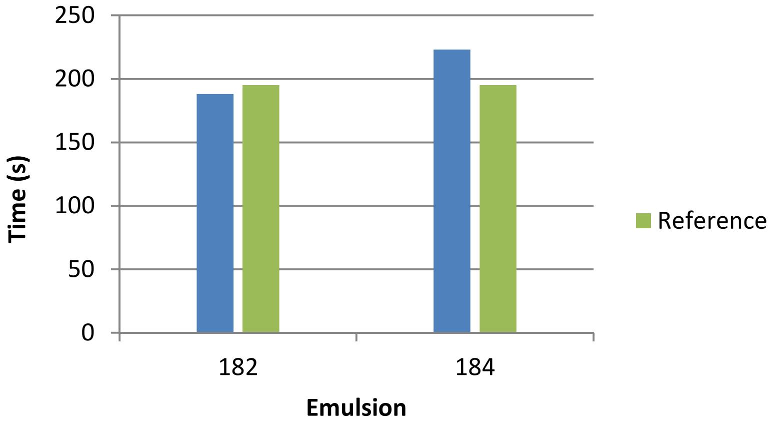

Figure 14 – Flow Test 2 results for emulsions 182 and 184.

Through the analysis of the results it is clear that flow test 1 and flow test 2 are congruent: increasing the amount of Dispersant A the flow also increases. Indeed, this result was already expected, due to the dispersing potential of this additive, by reducing the viscosity of the gypsum slurry. The flow test 2 was not made for the emulsion 182, due to the unavailability of this emulsion that time.

The same experiment was also carried out using a different background formulation. The results corresponding to Table 3 formulations are evidenced in the Table 10 and Figure 15.

Table 10 – Water Uptake results for the emulsions 185, 186 and 187.

Emulsion	WU2h	σ Emulsion	Reference 1	σ Reference 1	Deviation
185	2,35%	0,31%	2,79%	0,19%	-15,77%
186	2,09%	0,33%			-25,09%
187	2,12%	0,17%			-24,01%

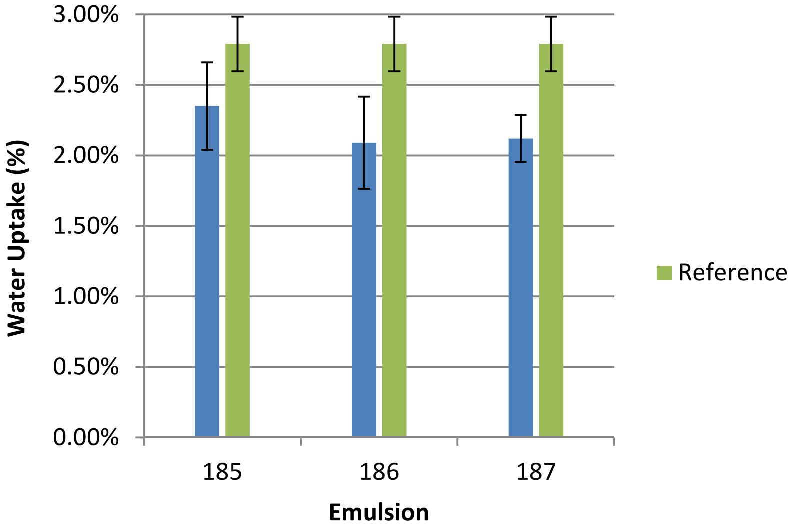

Figure 15 – Water uptake results for emulsions 185, 186 and 187.

Through the analysis of Figure 15, it is not possible to conclude about the effect of Dispersant A in the water uptake for this kind of emulsions. There is a relatively small difference between the water uptake values for each amount of Dispersant A and there is no visible trend. On the other hand, we can see that the three emulsions have a better and promising water uptake result, if compared to the value presented by the reference.

Additionally, it was studied the influence of the increase of Dispersant in flow features. Table 11, Figure 16 and Figure 17 express these results.

Table 11 – Flow Test 1 and Flow Test 2 results for the emulsions 185, 186 and 187.

Emulsion	FT1(cm)	Reference 2 (cm)	FT1 Deviation	FT2 (s)	Reference 1(s)	FT2 Deviation
185	19,6	26,7	-36,2%	178	195	-9,6%
186	19,0		-40,5%	188		-3,7%
187	17,3		-54,3%	164		-18,9%

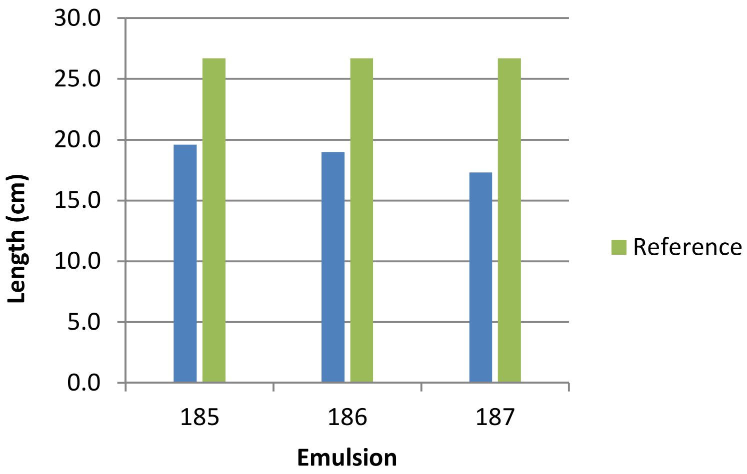

Figure 16 – Flow Test 1 results for emulsions 185, 186 and 187.

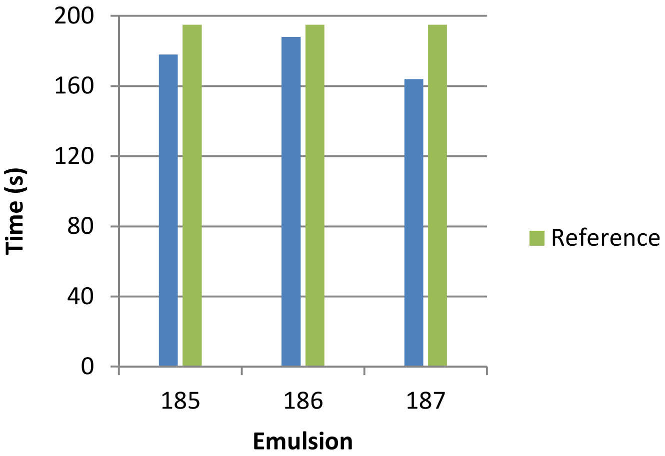

Figure 17 – Flow Test 2 results for emulsions 185, 186 and 187.

The results shown in Table 11 do not reveal a clear trend in the flow property by increasing the amount of Dispersant A in this type of emulsion, like has occurred in the water uptake test, within the range of this product amount. Taking into consideration the information displayed in the technical data sheet of this product, it suggests that the effect of the dispersant, improving the flow feature, is just evident if the optimum quantity is added. Thus, in order to have a more consistent trend and more effective conclusions, the experiment should be made within other amount of Dispersant A range.

3.2.1.2 Alternative Polar Waxes

The results of the comparison between the formulations listed in Table 4 are revealed in Table 12 and Figure 18.

Table 12 – Water Uptake results for the emulsions 183, 188, 189, 190 and 192.

Emulsion	***WU2h***	***σ Emulsion***	***Reference 1***	***σ Reference 1***	***Deviation***
183	2,34%	0,51%	2,52%	0,35%	-7,14%
188	1,42%	0,32%	2,79%	0,19%	-49,10%
189	1,39%	0,24%	2,79%	0,19%	-50,18%
190	2,60%	0,27%	2,79%	0,19%	-6,81%
192	2,75%	0,23%	2,52%	0,35%	9,13%

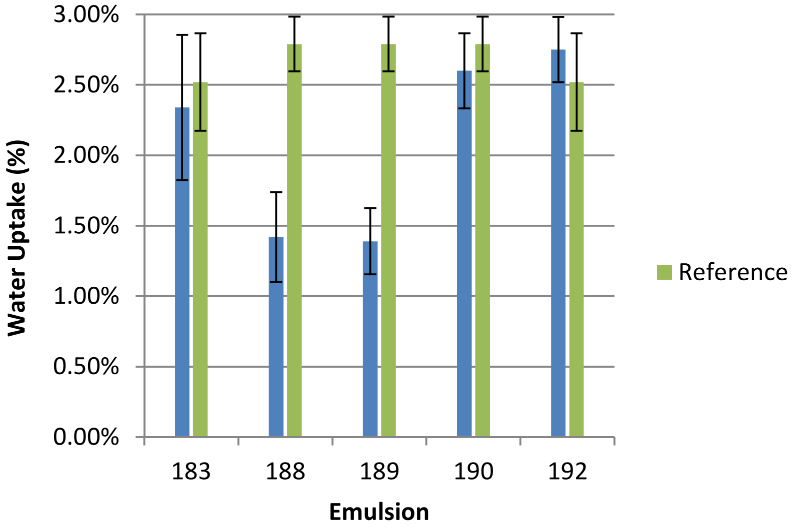

Figure 18 – Water uptake results for emulsions 183, 188, 189, 190 and 192.

As first analysis it is interesting to observe that all the emulsions are located below 5%, which is an important remark for water absorption values.

Even so, the results above highlight the emulsions 188 and 189 by having a very prominent performance in terms of water uptake. The water uptake value obtained for both emulsions is about half the value that Reference 1 achieved, which means that Polar Wax B and Polar Wax C are presented as good components for those water repellent wax emulsions, constituting an effective potential substitute for montan wax.

Emulsion 183 and 190, comprising Polar Wax A and Polar Wax D, obtained a slightly lower value than reference as well and, being so, these components should not be discarded.

The flow properties of those emulsions, when applied to the gypsum slurry, represent also a relevant parameter. In order to understand their behavior in this field, it was made the Flow Test 1.

Table 13 – Flow Test 1 results for the emulsions 183, 188, 189, 190 and 192.

Emulsion	***FT1 (cm)***	***Reference 2 (cm)***	***FT1 Deviation***
183	24,6	26,7	-7,9%
188	16,5		-38,2%
189	9,5		-64,4%
190	8,1		-69,7%
192	7,9		-70,4%

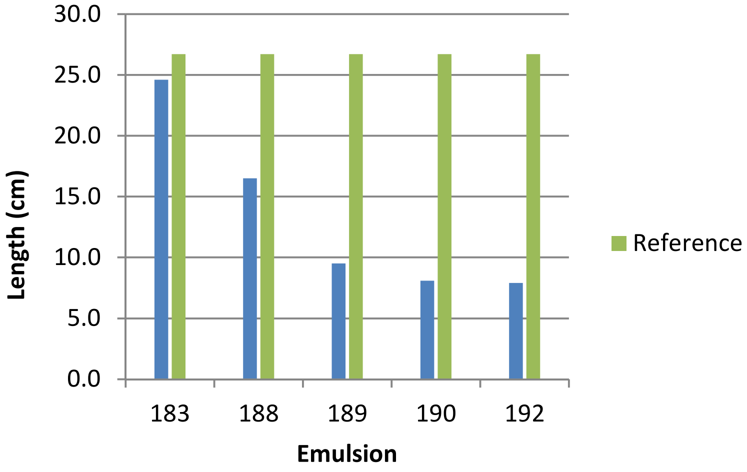

Figure 19 – Flow Test 1 results for emulsions 183, 188, 189, 190 and 192.

Table 13 and Figure 19 illustrate that all the emulsions tested have a poorer performance than the reference. However, since the reference is taken as an emulsion with a great flow capability, the result presented by the emulsion 183 could be considered interesting. The emulsions 188 and 189, which had a good performance as water repellent agents, had a weaker behavior in terms of flow, creating some critical handling problems during the manufacture.

Emulsions 190 and 192 combine their higher water uptake result with their incapability of generating a good flow to the gypsum slurry.

3.2.1.3 Half amount of Polyvinyl Alcohol

In this experiment, it have been taken the emulsions that had obtained better results earlier and it has been reduced the amount of PVA by half in the water phase. That way, emulsion 195, 196 and 197 were created.

The water uptake results for the emulsions 195 to 197 are displayed in the Table 14 and Figure 20, as well as the Reference 1 used during the tests.

Table 14 – Water Uptake results for the emulsions 195, 196 and 197.

Emulsion	**WU2h**	**σ Emulsion**	**Reference 1**	**σ Reference 1**	**Deviation**
195	1,23%	0,27%	1,53%	0,58%	-19,61%
196	1,74%	0,47%			13,73%
197	3,31%	0,67%			116,34%

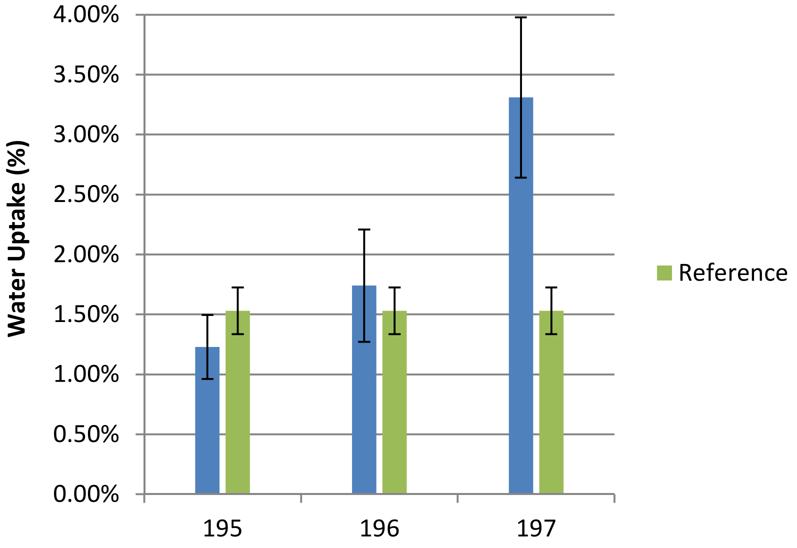

Figure 20 – Water uptake results for emulsions 195, 196 and 197.

The results illustrated in Figure 20 demonstrated a very interesting performance by emulsion 195, achieving better results than the Reference 1. This result shows that the reduction of PVA amount did not affect negatively this emulsion in terms of water uptake, maintaining the upper performance verified for the equivalent emulsion 183 (with the double PVA amount), when compared with the Reference 1.

On the opposite side, halving the amount of PVA reflected in higher water uptake values for emulsion 196 and, particularly for emulsion 197.

It is also interesting to note that the Reference 1 considerably improved the water repellency during this series of blocks, if compared with the previous trials. This occurrence attests the importance of including a commercial product as reference. As a well proven product, this reference could help finding some incongruities due to variables not taken into account.

3.2.1.4 Ethylene – Vinyl Acetate Copolymers

This study comprised the emulsions 202 to 205, whose formulations were described in Table 6, and were performed together with the previous tested emulsion 189 and with the Reference 1. This test aimed to compare the performance of ethylene – vinyl acetate with different characteristics and to try to reduce the amount of emulsion used in the gypsum slurry preparation (Method 2) to 80% of the original amount, taking into reference the emulsion 189, which has already demonstrated a good performance.

The results are shown in the Table 15 and Figure 21.

Table 15 – Water Uptake results for the emulsions 189, 202, 203, 204 and 205.

Emulsion	***WU2h***	***σ Emulsion***	***Reference 1***	***σ Reference 1***	***Deviation***
189	6,01%	1,29%	3,97%	0,61%	51,39%
202	6,43%	0,59%			61,96%
203	3,56%	0,81%			-10,33%
204	N/A	N/A			N/A
205	N/A	N/A			N/A

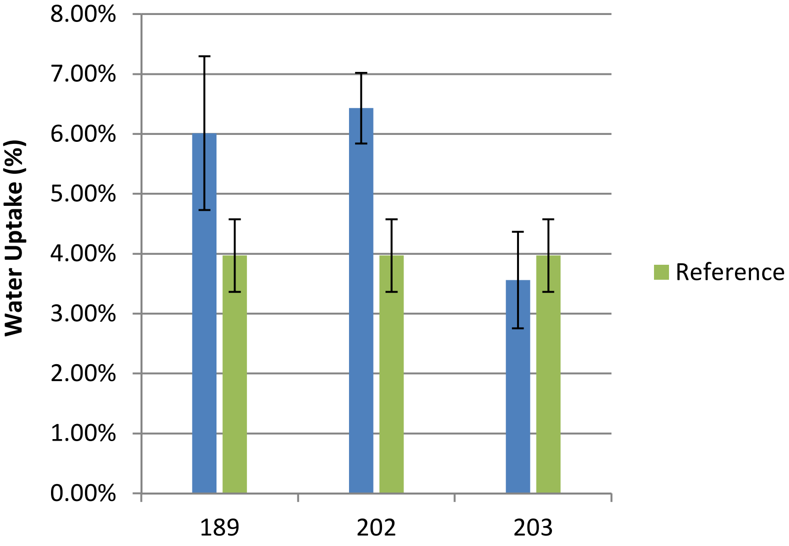

Figure 21 – Water uptake results for emulsions 189, 202 and 203.

It was not possible to conclude about emulsions 204 and 205, since, during its formulation, they have solidified through the homogenizer cooling system. This can be explained by the fact that both EVA used have a low melt index. Lower melt index leads to lower solubility and higher melt viscosity, being so, it is inadvisable the use of EVA with lower melt index.

Regarding the remaining ones, it is noticeable that the emulsion 189 had a poorer performance when compared with the reference. Those results are inconsistent, since this emulsion have demonstrated a better performance than the Reference 1 before. Besides that, Figure 21 shows that the emulsion 203 performed better than the others, which may lead us to believe that higher VA content results in a positive impact in the water uptake value.

Furthermore, it is clear that the water uptake was affected by the reduction of the emulsion added to the gypsum slurry, since emulsion 189 and the Reference 1 increased significantly the water absorption.

3.2.1.5 Costumer Drying Conditions

The studies were conducted at costumer's conditions, which require 70ºC during the 36 hours drying step, instead of the previously drying conditions used (2 hours at 80ºC plus 5 days at 40ºC).

This series of tests includes the emulsions 195, 196, 197 and 203, previously tested as described in Method 1, and a new formulation, emulsion 209.

It was also tested the Reference 1, as mean of comparison. The water uptake results may be found in Table 16 and Figure 22.

Table 16 – Water Uptake results for the emulsions 195, 196, 197, 203 and 209.

Emulsion	***WU2h***	***σ Emulsion***	***Reference 1***	***σ Reference 1***	***Deviation***
195	5,23%	9,40%	0,52%	0,06%	905,77%
196	1,84%	1,69%			253,85%
197	0,80%	0,35%			53,85%
203	2,61%	3,38%			401,92%
209	3,67%	4,56%			605,77%

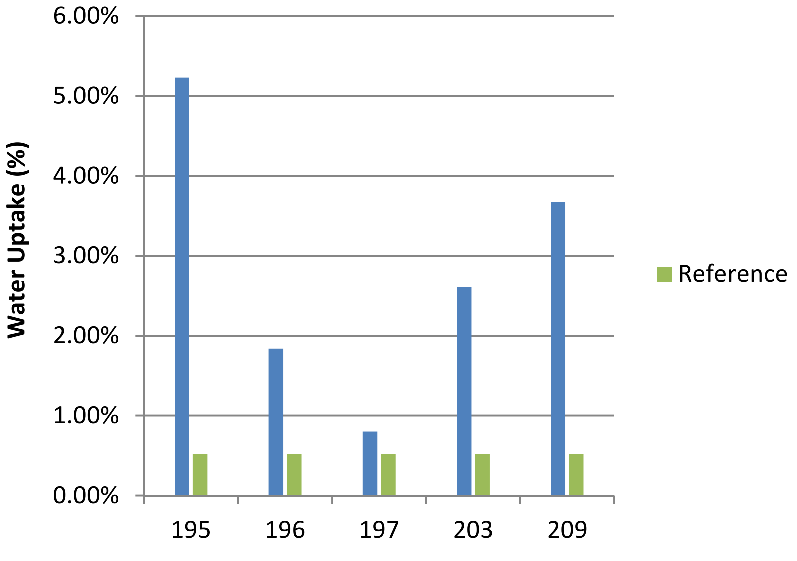

Figure 22 – Water uptake results for emulsions 195, 196, 197, 203 and 209 dried at 70ºC during 36h.

All the emulsions tested presented very poor results, when compared with the Reference 1, which contradicts some of the previous results obtained, where emulsions 195 and 203 performed better than this same reference. Furthermore, Reference 1 presented a great performance, obtaining 0,52% water uptake.

These results indicate that these drying conditions were previously optimized for montan wax based emulsions.

Comparing these results with the results obtained for emulsions 195, 196 and 197 in section 3.2.1.3, where it was studied the impact of halving the amount of PVA, it is discernible significant differences. Emulsion 195, comprising Polar Wax A, worsened from 1,23% to 5,23%; emulsion 196, containing Polar Wax B, presented approximately the same result (1,74% to 1,84%); the emulsion 197, including Polar Wax C, improved from 3,31% to 0,80% in terms of water uptake. Polar Wax A is a hydrocarbon polymer, with a 96ºC melting point, so the lower temperature and less time of drying may have not favored a polymer with this characteristic.

Moreover, it is noticeable that standard deviation was unduly, exceeding inclusive the absolute average value of water uptake. This inconsistence between blocks from the same series of 4, suggests that other variables, beyond the drying conditions, may have affected this experiment.

3.2.1.6 Superplasticizer addition

As previously mentioned, the gypsum slurry flow is a very relevant feature during the gypsum blocks production. This characteristic reflects the workability of the wet plaster. In order to obtain free-flow slurries that spread evenly during the application, dispersing agents are added to the gypsum slurry, which may lead to a decrease in the water demand. Consequently, the both density and strength move toward higher values.

In the current investigation, it was tested the influence of the addition of different amounts of a superplasticizer, Melment®, to the gypsum slurry in its flow property. Melment® is a sulphonated polycondensation product based on melamine, manufactured by BASF. In liquid form typically is used for water reduction and cost optimization in gypsum panel production and to improve flow characteristics in concrete applications. [8]

Melment® avoids particle aggregation in the slurry, making sure that the particles move independent of each other and, therefore, the viscosity keeps being low for longer times.

It was also made the comparison between the performance, in terms of flow, of the gypsum slurries comprising the dispersant (emulsion 188) and the reference Coreshield®.

The current study was made through the Flow Test 1, being the Melment® added expressed by the equation 3.

$$Melment\ added\ (\%) = \frac{Melment\ (g)}{Melment\ (g) + Emulsion\ (g)} \times 100 \qquad \text{(Equation 3)}$$

As starting point, no Melment® was added; after that, different portions were mixed with the emulsion 188.

The results are shown in the Table 17.

Table 17 – Flow Test 1 results for different amounts of Melment® added to emulsion 188.

Melment® added	***FT1 (cm)***	***Deviation vs Reference 2***
0,0%	17,3	-19%
0,5%	18,0	-15%
1,0%	22,2	4%
1,5%	25,7	21%
2,5%	29,1	37%

Figure 24 and Figure 23 show the influence of the addition of Melment® in the gypsum slurry rheological properties.

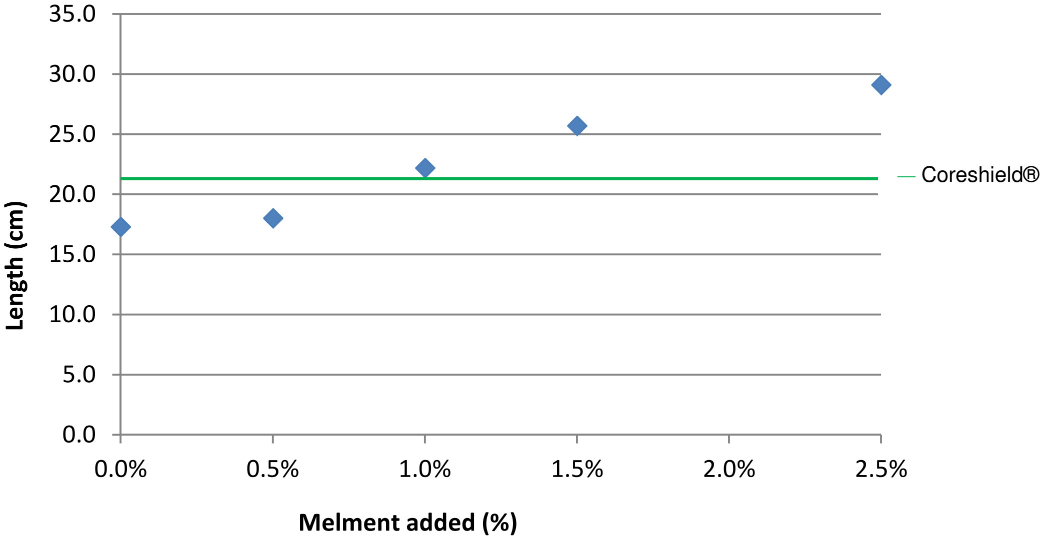

Figure 23 – Flow Test 1 results for different amounts of Melment® added to emulsion 188.

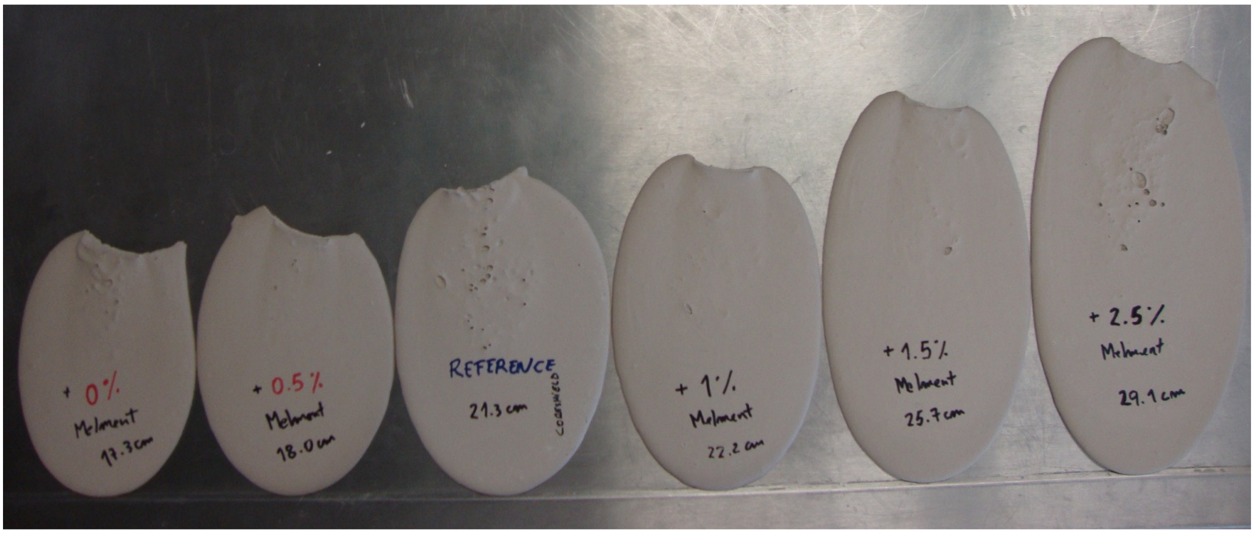

Figure 24 – Flow Test 1 results for different amounts of Melment® added.

Through the analysis of the Figure 23, it is possible to conclude that the addition of Melment® promotes a clear improvement in the gypsum slurry flow.

The length achieved increased 28% by adding just 1% of Melment® and, if we add 2,5% of this superplasticizer, we can improve about 68% the flow capability of the gypsum slurry.

The superplasticizer avoids particle aggregation and improves the wetting of inorganic particles in aqueous medium, reducing the water/gypsum ratio.

As mentioned before, superplasticizers are widely used in concrete applications to improve it rheology. The results show that the use of superplasticizers should be also considered for gypsum blocks production.

3.2.2 Study of Operative Variables

Analyzing the results presented in the chapter 3.2.1, we can find some inconsistencies over the different trials. The water uptake values for the reference do not remain nearly constant, showing variations of over 50%. The increasing in the amount of Dispersant A, keeping the remainder composition, led to an increasing of water uptake for the emulsions 182 to 184, but has a different behavior and consequence in terms of water uptake for the emulsions 185 to 187. Moreover, blocks from the same series (which means blocks made simultaneously, containing the same emulsion) obtained water uptake values discrepant.

At this point, these inconsistencies have to be justified and, subsequently, avoided, in order to preserve the scientific rigor and to better understand the variables that play an important role in the gypsum blocks production and how they influence the water uptake of those blocks.

Being so, this chapter focus the analysis of different variables, which have been identified as may have influence along the gypsum blocks manufacturing.

This study included four different parameters: two of them were variable during previous trials, and, as such, may have affected the performance and the results analysis; and the other two did not affect the previous results, since they were kept constant for all the series, for all the blocks.

The time since the beginning of mixing until the beginning of drying (time between mixing and drying) and the time since the end of the drying until the beginning of the submersion of the blocks in water for the evaluation (time between drying and evaluation) were not the same for the different series. Even for blocks from the same series, the time between drying and evaluation was not constant, which can explain the disparities in blocks from the same series. The drying time and the gypsum/water ratio used in the gypsum slurry making were also subject of study, although they have not been variable in the previous trials.

Obviously, during the study of each variable, the parameters that were not being tested remained unchanged for the different series of blocks. The temperature selected for the blocks drying process was 70ºC. This choice is intimately related with the fact that the company's customer uses this drying temperature in its process. Indeed, as explained above, the wax present in the blocks should be melted during the drying process. All the emulsions tested had a paraffin wax with a 68-70ºC melting point range, which means that the drying temperature must be at least 70ºC. On the other hand, it is also known that prolonged exposure to high temperatures leads to strength losses and must be avoided because gypsum converts into hemihydrate and soluble anhydrite. It is often believed that staying below 100ºC is a safe procedure.[1]

3.2.2.1 Time between mixing and drying

In this experiment, the blocks remained at room temperature and atmospheric conditions between mixing and drying process, during different periods of time. Other conditions were the same for each series of blocks, presented in Table 18.

Table 18 – Conditions used for the time between mixing and drying variable study.

Drying Time	46h
Drying Temperature	70ºC
Time between drying and evaluation	1h
Gypsum/Water ratio	1,2
Additive	Emulsion 196
Amount added (g)	41,47

Table 19 and Figure 25 present the results obtained applying the conditions referred in Table 18.

Table 19 - Water uptake results for different times between mixing and drying.

Mixing-Drying	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
2h	28,78%	8,74%	30,73%	7,77%
3h	25,51%	7,90%	28,61%	8,12%
4h	21,32%	10,20%	23,64%	9,86%

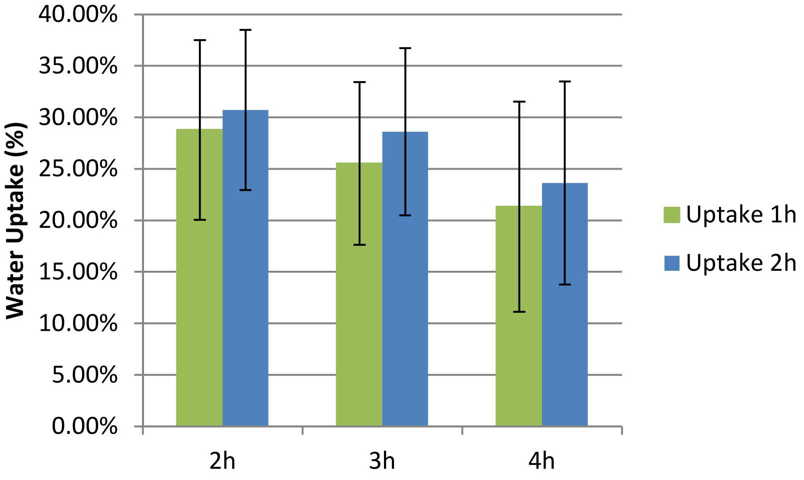

Figure 25 – Water uptake results for different times between mixing and drying.

In order to confirm the previous results and extend the range in test, another experiment was carried out using the conditions listed in Table 20.

Table 20 - Conditions used for the time between mixing and drying variable study.

Drying Time	18h
Drying Temperature	70ºC
Time between drying and evaluation	4h
Gypsum/Water ratio	1,2
Additive	Emulsion 209
Amount added (g)	41,47

The results found using the conditions described in Table 20 are shown in Table 21 and Figure 26.

Table 21 - Water uptake results for different times between mixing and drying.

Mixing-Drying	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
1h	43,01%	2,56%	45,40%	1,82%
4h	8,40%	0,60%	11,91%	0,78%
24h	1,33%	0,22%	1,36%	0,22%
47h	1,33%	0,12%	1,65%	0,19%

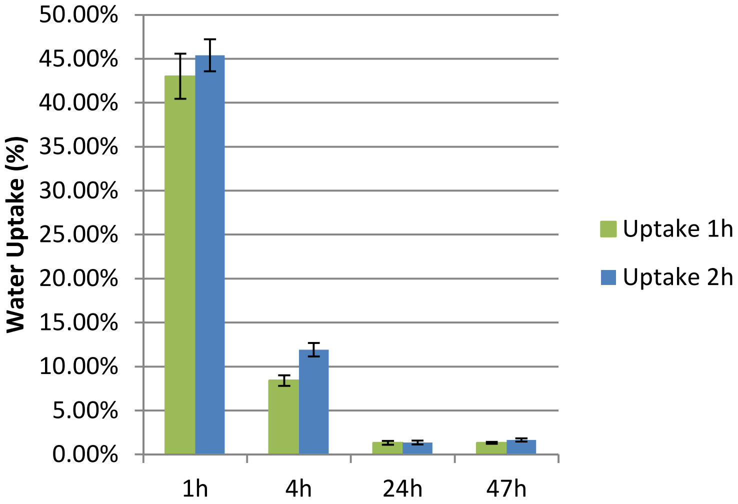

Figure 26 - Water uptake results for different times between mixing and drying.

From the analysis of the Figure 25 and the Figure 26 it is possible to conclude that the time since the mixing of the components to form the gypsum slurry until the beginning of the blocks' drying plays an important role in the water uptake final result. The less time we wait until start drying, the lower the water repellency of the gypsum block. This is verified by two different wax emulsions and it becomes critical if the time between mixing and drying is lower than 4h. After 24h, there is no advantage in waiting longer times before drying. It would be interesting to verify the behavior in the range of 4 to 24 hours of time between mixing and drying. Notwithstanding, it was not possible to make tests in that range, due to incompatibility with the work schedule.

3.2.2.2 Time between drying and evaluation

The analysis of this variable, using a wax emulsion, was made under the conditions expressed in the Table 22. During the time between drying and evaluation, blocks have cooled down at room temperature and atmospheric conditions.

Table 22 - Conditions used for the time between drying and evaluation variable study.

Drying Time	44h
Drying Temperature	70ºC
Time between mixing and drying	4h
Gypsum/Water ratio	1,2
Additive	Emulsion 196
Amount added (g)	41,47

The water uptake results for each time between drying and evaluation are shown below in the Table 23 and in the Figure 27.

Table 23 - Water uptake results for different times between drying and evaluation (Wax emulsion).

Drying-Evaluation	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
1h00	15,06%	8,57%	18,28%	8,47%
1h45	13,34%	9,35%	16,32%	9,84%
2h30	10,41%	3,51%	13,89%	3,97%
3h15	9,40%	6,51%	12,21%	6,96%

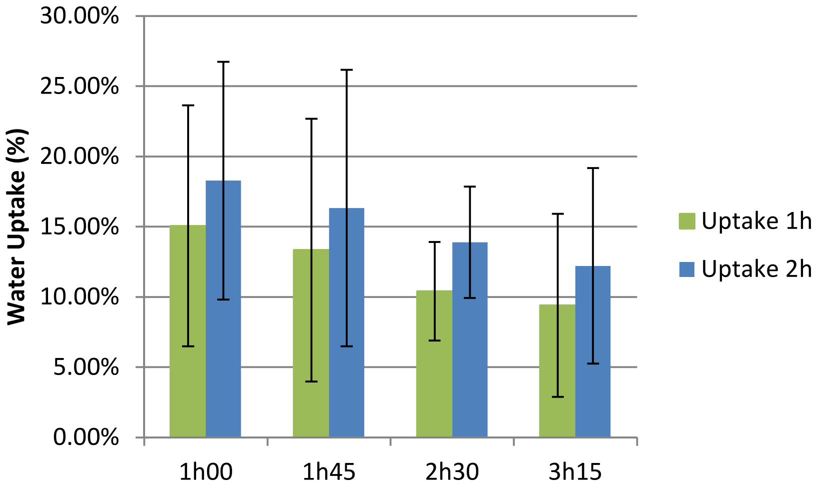

Figure 27 - Water uptake results for different times between drying and evaluation (Wax emulsion).

The analysis of this variable, using a siloxane, was made under the conditions expressed in the Table 24.

Table 24 - Conditions used for the time between drying and evaluation variable study.

Drying Time	19h
Drying Temperature	70ºC
Time between mixing and drying	4h
Gypsum/Water ratio	1,2
Additive	Wacker Silres BS 94
Amount added (g)	6,50

The results are presented in the Table 25 and Figure 28.

Table 25 - Water uptake results for different times between drying and evaluation (Siloxane).

Drying-Evaluation	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
30 min	3,36%	0,74%	4,56%	0,93%
1h15	2,22%	0,22%	3,12%	0,28%
2h	2,31%	0,48%	3,32%	0,76%
3h30	1,56%	0,14%	2,17%	0,18%

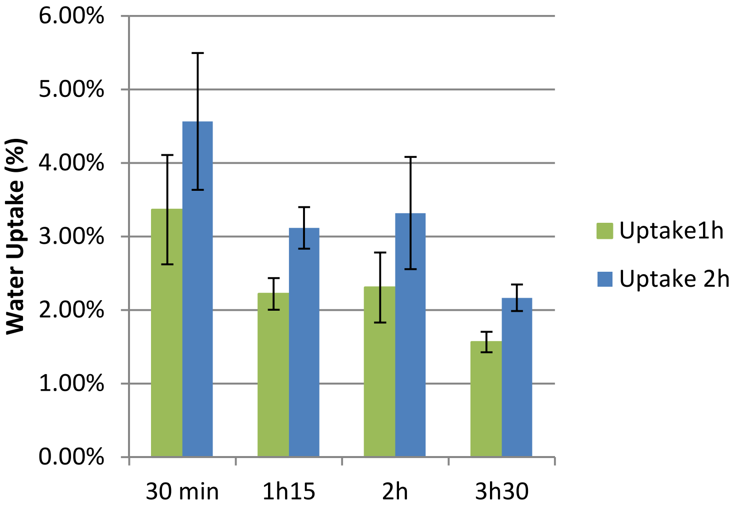

Figure 28 - Water uptake results for different times between drying and evaluation (Siloxane).

Figure 27 and Figure 28 show that the time since the blocks end drying until the beginning of the evaluation is, also, a relevant parameter with direct influence in the water uptake result. Those tests were made with two different types of additives: wax emulsions and siloxanes. The results show that the variable studied has the same effect for both types of additives: the lower the time we let the blocks out of the oven until the beginning of the evaluation, the lower the ability of the gypsum block to repel water.

3.2.2.3 Drying Time

The evaluation of the influence of the drying time in the water uptake by the gypsum blocks was made, firstly, using the conditions referred in the Table 26.

Table 26 - Conditions used for the drying time variable study.

Drying Temperature	70ºC
Time between drying and evaluation	4h
Time between mixing and drying	4h
Gypsum/Water ratio	1,2
Additive	Emulsion 196
Amount added (g)	41,47

Table 27 and Figure 29 display the results obtained by employing the conditions described in Table 26.

Table 27 - Water uptake results for different drying times.

Drying Time	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
16h	3,14%	0,16%	5,28%	0,24%
21h	6,06%	1,37%	9,12%	2,00%
42h	13,25%	0,68%	18,84%	0,56%
68h	34,74%	3,53%	36,56%	4,14%

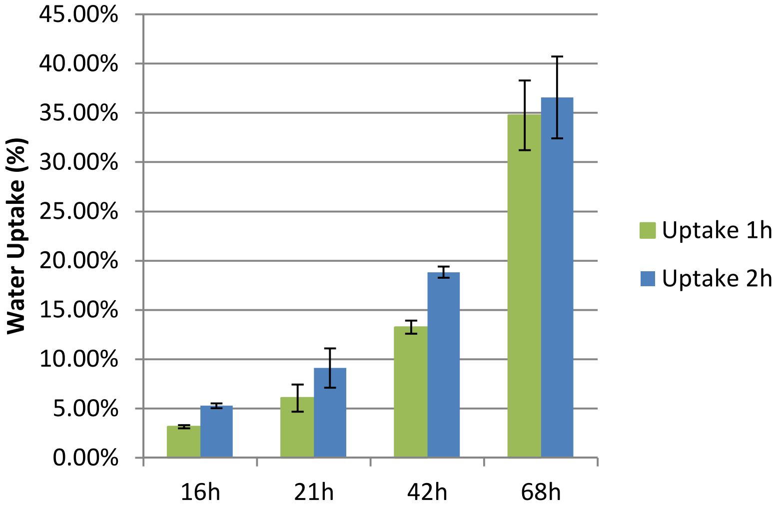

Figure 29 – Water uptake results for different drying times.

Other trial was carried out using conditions shown in Table 28.

Table 28 - Conditions used for the drying time variable study.

Drying Temperature	70ºC
Time between drying and evaluation	4h
Time between mixing and drying	4h
Gypsum/Water ratio	1,2
Additive	Emulsion 209
Amount added (g)	41,47

Table 29 and Figure 30 exhibit the results obtained using the conditions displayed in Table 28.

Table 29 - Water uptake results for different drying times.

Drying Time	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
16h	6,63%	0,74%	10,86%	0,97%
21h	9,21%	2,46%	13,15%	2,95%
42h	33,82%	5,23%	39,60%	4,16%
68h	48,30%	1,73%	50,77%	1,46%

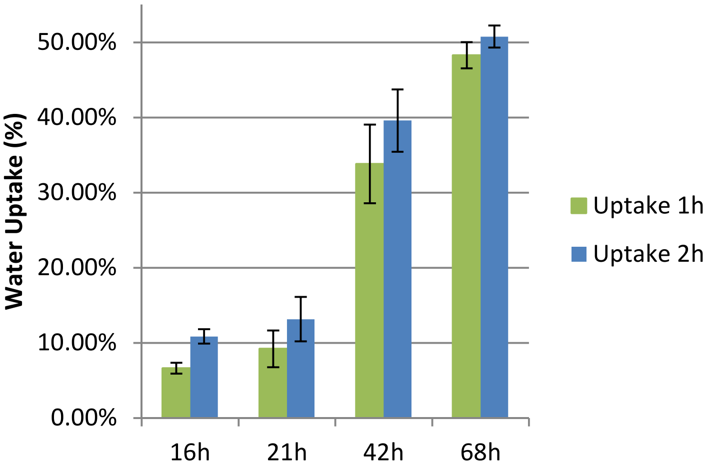

Figure 30 - Water uptake results for different drying times.

The results illustrated in the Figure 29 and in the Figure 30 show that, from 16 hours, the longer the drying process, the greater the water uptake. Indeed, in the drying process it is required the removal of the excess water, remaining in the block just the stoichiometric amount to form the dihydrate (two molecules of water per molecule of calcium sulfate). If the drying process is prolonged, part of the water required to form the dihydrate starts being removed. This may be avoided since longer drying time hinder the formation of the stronger calcium sulfate dihydrate. A quicker drying time enables the formation of this stronger compound and, therefore, leads to a stronger gypsum product.

Furthermore, the drying time should be enough to remove the free water contained in the block.

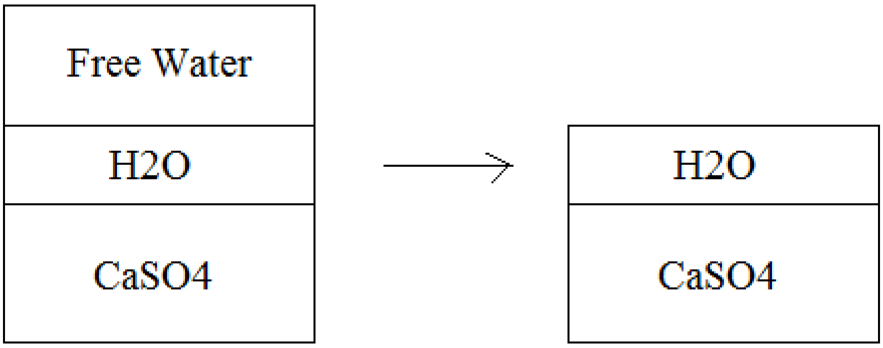

Figure 31 – Water removal required from the gypsum block.

In order to estimate the amount of water removed during the drying process, it was weighed the blocks after setting and after being taken out of the oven. Thus, it was possible to estimate the calcium sulfate/water ratio (g/g) for each block. Two molecules of water per molecule of sulfate calcium, required to form the dehydrate, means around 3,8 grams of calcium sulfate per gram of water. This procedure was followed for the second experiment. The results are shown in the Table 30.

Table 30 – Calcium Sulfate/Water ratio (g/g), after drying, for different drying times.

Drying Time	***m ($CaSO_4$)/m (H_20) (g/g)***
16 hours	4,02
21 hours	4,10
42 hours	4,20
68 hours	5,43

Table 30 shows that all the free water has been evaporated during the drying process. However, those results indicate that part of the stoichiometrically required water has also been removed. This effect has been truly drastic just after 68 hours of drying.

3.2.2.4 Gypsum/Water (G/W) Ratio

The Gypsum/Water (G/W) ratio was also subject of study. This parameter has only to do with proportion between the gypsum powder and water added (with the emulsion) when making the gypsum slurry, as shown in the equation 4.

$$G/W\ ratio = \frac{mass_{Gypsum}}{mass_{Water}} \qquad \text{(Equation 4)}$$

The first experiment comprising the analysis of the influence of the G/W ratio in the water uptake was done under the conditions expressed in the Table 31.

Table 31 - Conditions used for the G/W Ratio variable study.

Drying Temperature	70ºC
Time between drying and evaluation	4h
Time between mixing and drying	4h
Drying Time	19h
Additive	Emulsion 196
Amount added (g)	41,47

The results of the first experiment, in terms of water uptake, for each G/W ratio, are illustrated in Table 32 and Figure 32.

Table 32 - Water uptake results for different G/W Ratios (Wax Emulsion).

G/W Ratio	*WU 1 (%)*	*σ*	*WU 2 (%)*	*σ*
1	4,03%	0,14%	6,35%	0,28%
1,1	3,91%	0,30%	6,25%	0,36%
1,2	3,59%	0,13%	5,50%	0,17%
1,5	3,22%	0,53%	4,52%	0,60%

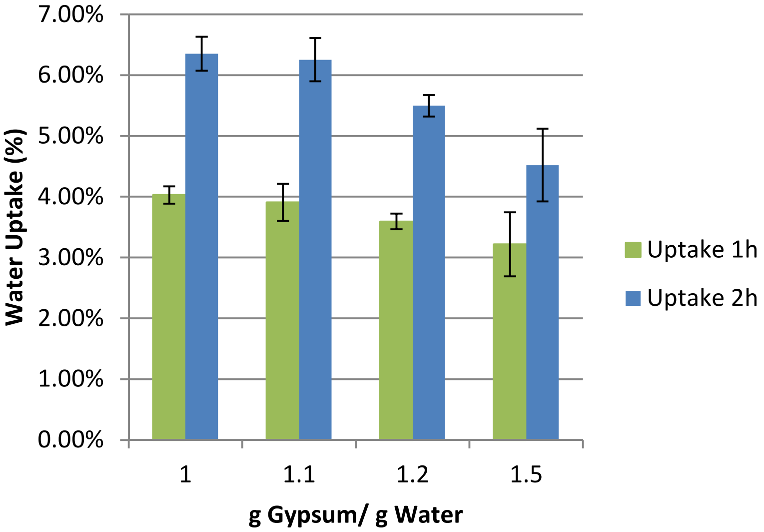

Figure 32 - Water uptake results for different G/W Ratios (Wax Emulsion).

The second experiment comprising the study of this variable was done under the conditions presented in the Table 33.

Table 33 - Conditions used for the G/W Ratio variable study.

Drying Temperature	70ºC
Time between drying and evaluation	4h
Time between mixing and drying	4h
Drying Time	19h
Additive	Wacker Silres BS 94
Amount added (g)	6,50

The results of the second experiment, in terms of water uptake, are represented in Table 34 and Figure 33.

Table 34 - Water uptake results for different G/W Ratios (Siloxane).

G/W Ratio	***WU 1 (%)***	***σ***	***WU 2 (%)***	***σ***
1	2,90%	0,97%	4,52%	1,59%
1,1	2,03%	0,20%	3,13%	0,35%
1,2	1,94%	0,25%	2,89%	0,43%
1,5	1,38%	0,15%	1,92%	0,21%

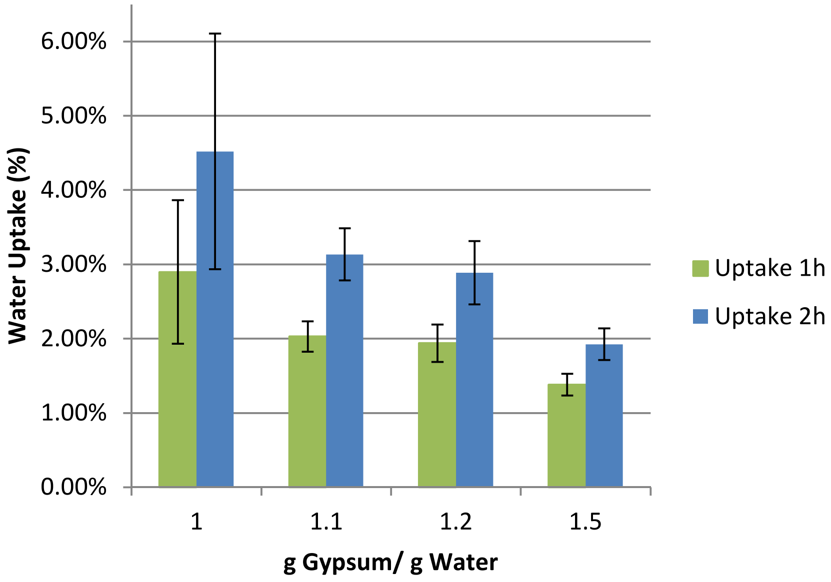

Figure 33 - Water uptake results for different G/W Ratios (Siloxane).

Through the analysis of the Figure 32 and the Figure 33, it is evident that, increasing the G/W ratio, decreases the water uptake of the gypsum blocks, for both types of additive. Increasing the G/W ratio more nuclei of crystallization of dihydrate per unit volume are created, which leads to a more resistant plaster, since there are fewer spaces available for the water between the crystals of dihydrate. So, increasing the G/W ratio will result in a lower porosity of the block, after the drying process and, consequently, in a lower water uptake. However, it is also worth noting that extremely high G/W ratios will conduct to poor workability conditions, due to setting time shortening. Thus, it is a compromise between the amount of water required to have workable slurry and the amount of nuclei of crystallization of dihydrate per unit volume.

3.2.2.5 Oven Positioning

The positioning of the blocks in the oven was also a parameter and a variable, since the temperature inside the oven, during the drying process, could have differences from the wall to the center of the oven. It was made a series of blocks, all comprising the same emulsion, keeping the variables pointed out in the chapter 3.2.2 constant. The conditions are described in the Table 35.

Table 35 – Conditions used for oven positioning variable study.

Time between mixing and drying	24h
Drying Temperature	70ºC
Drying Time	24h
Time between drying and evaluation	24h
Gypsum/Water ratio	1,2
Additive	Emulsion 209

The blocks were distributed in the oven into four layers, A to D, as illustrated in Figure 34. The top layer is identified as *A* and the bottom layer marked as *D*. Also, *L* refers to the left side of the oven, while *R* refers to its right side.

The position of the ventilation area, situated in the back wall of the oven, is also schematized in the following cross section.

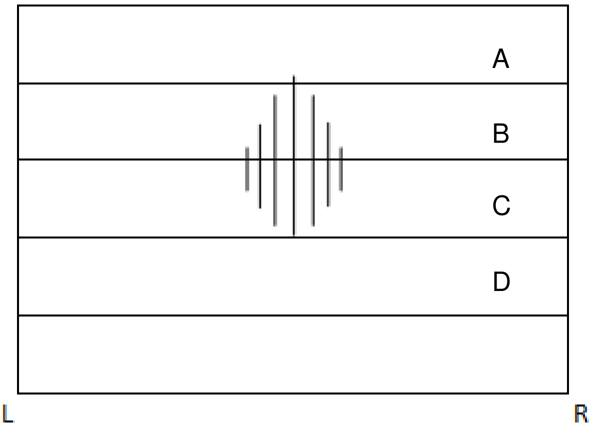

Figure 34 – Cross-section schematizing the distribution of the layers in the ventilated oven.

The disposal of each block in the different layers is demonstrated through horizontal planes.

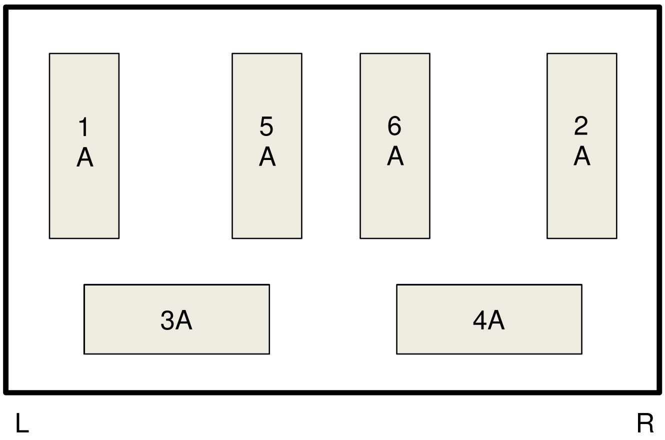

Figure 35 – Disposal of the blocks in the layer A.

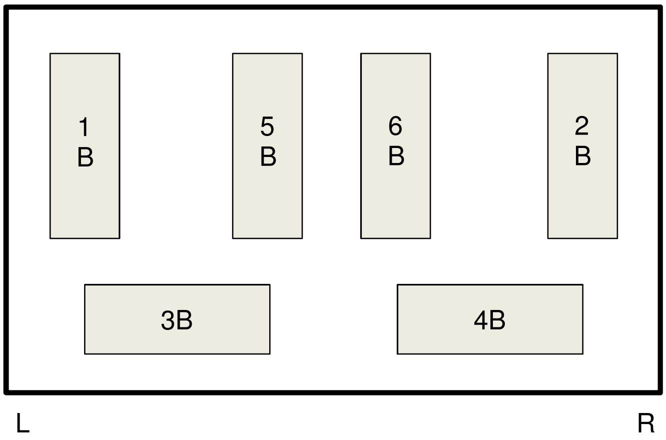

Figure 36 - Disposal of the blocks in the layer B.

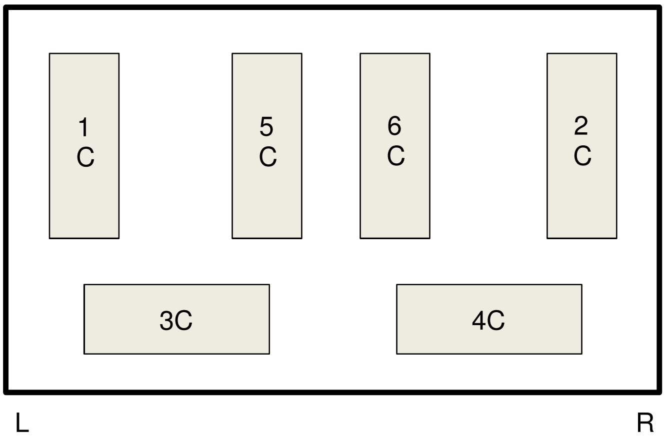

Figure 37 - Disposal of the blocks in the layer C.

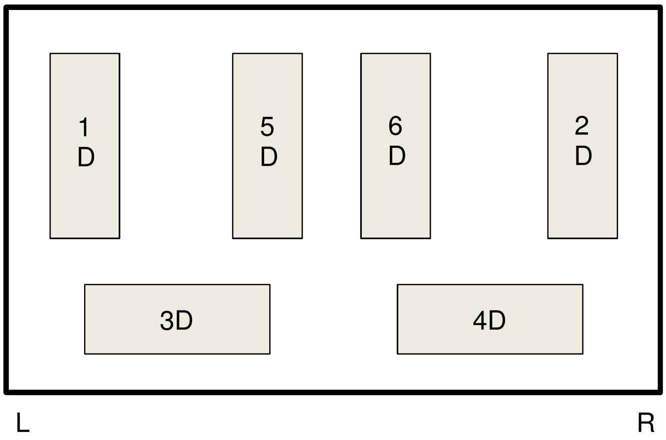

Figure 38 - Disposal of the blocks in the layer D.

The water uptake results for each block are described in Table 36.

Table 36 – Water uptake results for each block.

	Water Uptake after 2 hours			
	A	B	C	D
1	1,64%	1,52%	1,47%	1,35%
2	1,28%	0,89%	0,90%	0,80%
3	0,87%	0,86%	0,68%	0,63%
4	0,66%	0,83%	0,67%	0,67%
5	0,77%	0,71%	0,85%	0,79%
6	0,73%	0,66%	0,69%	0,63%

The results presented above are not conclusive regarding the layer height. Also, there are no significant differences between the water uptake values obtained for the blocks placed on the left side of the oven, if compared with the blocks disposed on the right side. These evidences could be explained by the fact the ventilation is located in the center of the oven.

However, it is possible to identify a trend regarding the position, since positions 1 and 2 present higher water uptake values. Locations 1 and 2 correspond to the nearest from the oven wall. In these positions it is likely that the temperature is higher than in the center of the oven. Being so, the drying process could be accelerated and generate an equivalent effect to the one obtained for a larger drying time. If the drying process is prolonged, part of the water required to form the dihydrate starts being removed.

3.2.3 Wax Emulsion vs Siloxane

As mentioned above, the two major commercial methods to make gypsum water resistant are by incorporating wax emulsions or siloxanes into the gypsum slurry, during block manufacture. However, as explained in chapter 2, they have different ways to accomplish this task. Consequently, the amount required to achieve the category H1 Table 1 is also a relevant issue.

This experiment aimed to study the amount required for each one to achieve the higher category for water repellent gypsum products and was made under the conditions listed in the Table 37.

Table 37 – Conditions used in Wax Emulsion/Siloxane amount required to achieve H1 study.

Drying Temperature	70ºC
Time between drying and evaluation	4h
Time between mixing and drying	1h
Drying Time	19h
G/W ratio	1,2
Wax Emulsion	PD-352-209
Siloxane	Wacker Silres BS 94

The results obtained for each amount of additive added is shown in Table 38 and Figure 39.

Table 38 – Water Uptake results for each amount of Wax Emulsion/Siloxane added.

Wax Emulsion added (g)	***WU2h***	***Siloxane added(g)***	***WU2h***
41,59	19,58%	2,87	11,85%
45,04	7,08%	3,88	8,71%
50,03	2,40%	5,00	6,64%
55,01	1,36%	6,97	4,59%
60,01	0,85%		
63,85	0,95%		

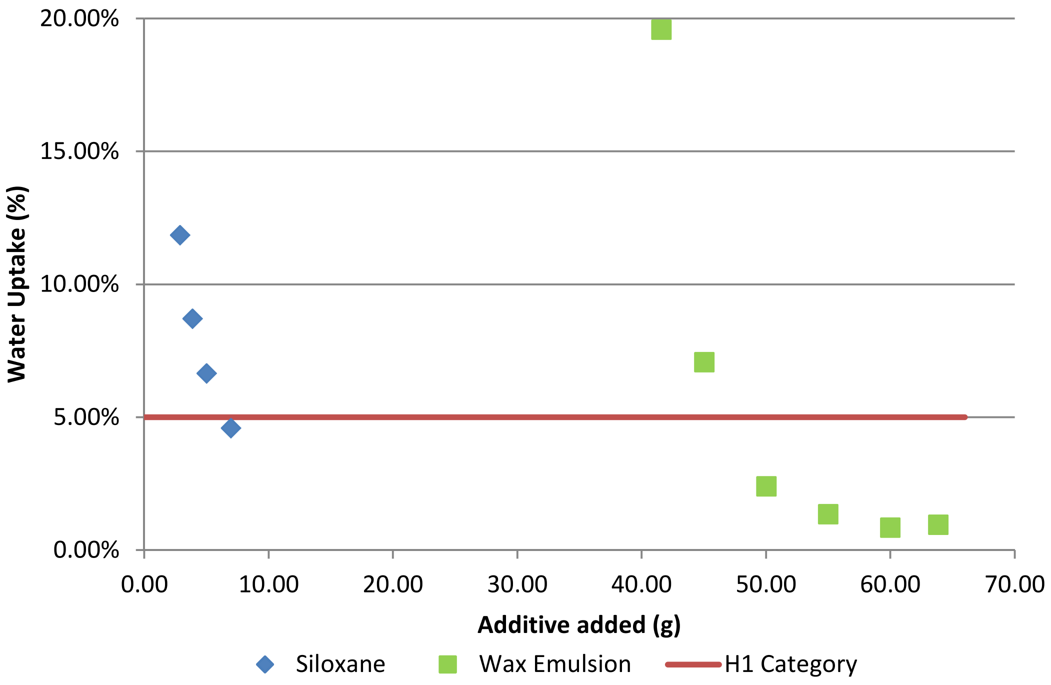

Figure 39 - Water Uptake results for each amount of Wax Emulsion/Siloxane added.

Adjusting a trend line, it was estimated the minimum amount required to reach the H1 for each additive. In both cases, the best adjustment was a potential regression. The equations obtained through the Microsoft Excel® tool are shown below.

$$WU2h(\%) = 0{,}369\ siloxane\ added(g)^{-1{,}07}; R^2 = 0{,}9995 \qquad \text{(Equation 5)}$$

$$WU2h(\%) = 6{,}491 \times 10^{10}\ wax\ emulsion\ added(g)^{-7{,}22}; R^2 = 0{,}9247 \qquad \text{(Equation 6)}$$

Replacing the water uptake after 2 hours by 5%, in each equation, it is possible to obtain the minimum quantity of siloxane/wax emulsion required to reach the H1 category.

For siloxane we need about 6,5 g to meet the target, while for wax emulsion we need 47,7g.

Taking into account that silicon oil price it is estimated to cost 2.5 times more than paraffin [11], wax emulsion cost as additive for gypsum blocks would be higher than siloxane cost.

4 Conclusions

The *Govi Engineered Chemicals* embraced this project with the main objective of formulating emulsions for making gypsum blocks water-repellent, through the study of the effect of different stabilizing additives. Thereunto, laboratory production of gypsum probes for comparative prediction of the performance were made, following an iterative reformulation system, based on experimental results.

Briefly, the gypsum blocks manufacture consists in mixing the calcium sulfate with water amongst the emulsion, spread the mixture in the mold, unmold after setting and dry the block in the oven. Afterward, the water uptake performance is evaluated by submerging the blocks into a water bath during two hours (by weight difference to the initial sample mass). According to EN520, it is considered 5% as a good performance in terms of water uptake.

In parallel, flow properties were tested as well, by measuring the length achieved by the gypsum slurry when disposed on a slide or through the measurement of the time required by the gypsum slurry to close upon itself after being made a cut with a knife.

In a general manner, wax emulsions provide a greater water repellency to gypsum blocks, since the EN520 H1 category was achieved for several formulations.

The first experiment comprised the study of the influence of the amount of a naphthalene sulfonic acid formaldehyde condensate (named Dispersant A) in the gypsum properties.

The first series indicate that the increasing of the dispersant amount had a negative effect in the water uptake, since this is not a surface-active agent. Although, the dispersing potential of this additive revealed a trend to improve the flow characteristics of the gypsum slurry, by reducing its viscosity.

Nevertheless, the second series were not conclusive, which may indicate that this is a sensitive variable and an optimum quantity should be added in order to achieve a commitment between water repellency capability and a good performance in terms of flow ability.

The next experiment aimed to find alternatives to montan wax. The results were very promising for polyvinyl ether wax and for copolymers of ethylene and vinyl acetate, from the water uptake point of view, performing considerably better than the montan wax dispersion commercial product used as reference. Nevertheless, flow tests indicate that for both, polyvinyl ether wax and copolymers of ethylene and vinyl acetate, flow properties should be improved in order to promote a better workability of the gypsum slurry. Adding this characteristic, both demonstrated that can constitute an effective potential substitute for montan wax.

Hydrocarbon polymer combined a reasonable water uptake result with a good performance during the flow tests and should also be considered as a viable alternative.

On the contrary, ethylene copolymer wax and polyamide resin were discarded, due to their poorer performance from the water repellency and flow properties point of view.

Reducing 50% the amount of PVA in three emulsions, differing only in one type of polar wax, brought antagonistic effects: emulsion containing hydrocarbon polymer obtained better results if compared with original one, emulsion including a polyvinyl ether wax slightly increased the water absorption, while emulsion comprising random copolymers of ethylene and vinyl acetate worsened it performance.

Relevant remarks were achieved when different EVA copolymers were tested. EVA copolymers with low melt index were not practicable and emulsion containing EVA copolymer with higher VA content, 28%, performed better than the remaining two, with 18% VA content.

When subjected to costumer drying conditions of 36 hours at 70ºC, gypsum blocks containing wax emulsions previously tested were negatively affected. On the opposite, Reference 1, based on montan wax, reacted considerably better.

Furthermore, great deviations in blocks from the same series of 4 suggested that other variables, beyond the drying conditions, may have affected this experiment.

Beyond the water repellency of gypsum blocks/boards, gypsum slurry flow capability is another relevant parameter, since it determines the easiness in its employment. Adding superplasticizers to the water repellent wax emulsions resulted in an impressive improvement in gypsum slurry flowability and, thus, demonstrated superplasticizers as a component to take into account for the emulsions that confer more viscous properties.

Probably the major conclusion that was possible to extract all over the different series of trials until this point, was the fact that many variables could affect the gypsum blocks water repellency. This finding changed the focus of the project for the study of the influence of some variables pointed out regarding water uptake performance.

The time between mixing and drying, time between drying and evaluation, drying time, gypsum/water ratio and the position of the blocks in the oven during drying were identified as possibly being affecting the water uptake of the gypsum blocks.

After analyzing the influence of each variable it was possible to conclude that: 1) the higher the time between mixing and drying, the lower the water uptake; 2) higher drying time reflects in poorer performance in terms of water uptake; 3) the higher the ratio gypsum/water present in the mixture the lower the water uptake; 4) when evaluating the performance, higher times between drying and evaluation lead to better results in terms of water uptake; 5) the position in the oven did not reveal significant differences in the water uptake, however, the blocks located near the oven wall have presented results slightly worse.

Moreover, for the *G/W ratio* and *time between drying and evaluation* experiments, comprising wax emulsions and a commercial siloxane, was found a similar trend using either a wax emulsion either a siloxane.

Finally, in order to potentiate an economic evaluation, as a starting point, further tests were made comparing one of the wax emulsions that have performed better and a commercial siloxane. The tests were conducted under the same conditions (taking into consideration the variables mentioned above). The results obtained allow to conclude that it is necessary to add about 7 times more wax emulsion than siloxane to achieve the 5% water uptake (EN520 H1 category).

In the end of the developed work, to understand at the molecular level the consequent phenomena of adding the compounds here described to the wax emulsions, and their influence on the output obtained at a macroscopic level, it was probably the major shortcoming of this project. Indeed, such study was not presented, since it was comprised within the proposed goals. The major purpose was the achievement of water repellent emulsions for gypsum blocks and, from that point of view, very satisfactory results were obtained.

For future development, it is suggested to include the study of other molecules and products that may improve the water repellency on gypsum blocks or boards, taking into account the results here obtained as a starting point for research. In the case of setting the drying temperature at 70ºC, as it is widely common, it is suggested to study paraffin waxes with a melting point lower than 68ºC – 70ºC.

It would be also interesting to expand the study of different operative variables, such as drying temperature, and their influence on the water uptake performance.

Another relevant issue, regards an evaluation of the costs vs benefits resulting from the different wax emulsions here formulated, the economic analysis between wax emulsions and siloxanes, taking into consideration the amounts required for each additive and the influence of each operative variable here identified on the operational costs of a company.

Last, but also very interesting, would be the challenge of scaling up the formulation of oil in water dispersions for gypsum board/blocks production, from a laboratorial to an industrial manufacturing area, in order to try to replicate the results obtained during the laboratory experiments.

5 Other Studies Conducted

Obtaining water-repellency for Perlite

Perlite is an amorphous volcanic glass that expands and becomes porous when heated. This expansion is due to the water molecules trapped in the rock that turn into vapor, which causes the expansion of the rock. This increase of volume leads to a very low density of expanded perlite.

Perlite has been used in several different situations. The majority of perlite is applied in ceiling tiles and roof insulation products, but also as piping insulator and filling in masonry block construction. It can work as sound insulator as well and, since it is non-combustible, it also improves the fire resistance of different construction component in buildings.

However, expanded perlite absorbs moisture rapidly and is readily dispersible in an aqueous medium. These features strongly restrict the commercial applications of expanded perlite.

The main goal of this project is to render hydrophobic the expanded perlite, as well as to reduce its solubility in aqueous media, through the inclusion of an additive comprising an aqueous siloxane emulsion.

The aqueous siloxane emulsion typically contains silicone oil (or a mixture of different silicone oils), an emulsifier, water and a biocide.

The method followed is described below:

1. Put 100 g of perlite in an empty 5 L can;
2. Make a dilution of the emulsion to be tested in a beaker of 1 L: 200 g of soft water and 0,40 g of emulsion. Turn the beaker manually until the emulsion is homogeneously diluted;
3. Add all of the diluted emulsion into the perlite in the 5 L can;
4. Close the can and shake until all water (and emulsion) is taken by the perlite;
5. Put the perlite in a bowl;
6. Put the bowl in the oven at 80ºC for 24h;
7. Weigh an empty 1 L bottle (m_b);
8. Take 35 g of the dried perlite (m_{dp}) and put it in the 1 L bottle;
9. Fill the bottle with tap water until completely full;
10. Empty the bottle after 1h over a filter of 400 microns;
11. Weigh the bottle + wet perlite and write down the value (m_{b+wp}). The water taken up by the perlite (m_{wtu}) is given by:

$$m_{wtu} = m_{b+wp} - m_b - m_{dp} \qquad \text{(Equation 7)}$$

12. Fill again the bottle with water and repeat after 2h, 4h, 6h and 24h;

The result can be expressed as % of water taken up versus 35g of perlite.

$$Water\ Uptake\ (\%) = \frac{m_{wtu}}{35g\ of\ \ perlite} \times 100 \qquad \text{(Equation 8)}$$

The results obtained are displayed in the Figure 40.

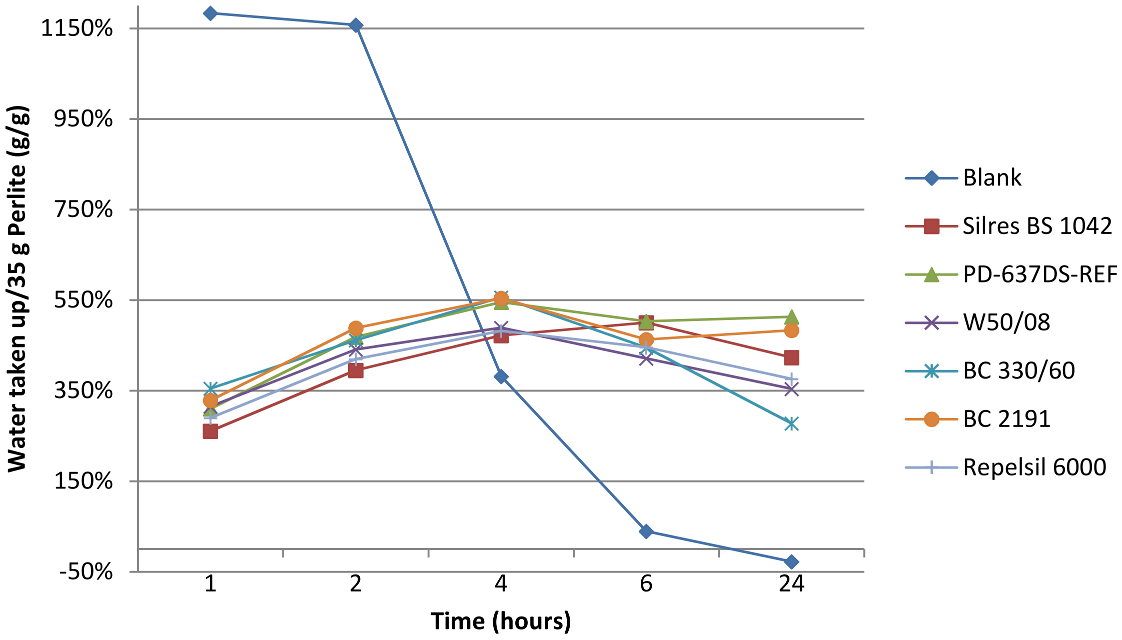

Figure 40 - Water taken up / 35 grams of perlite.

As expectable, the blank does not assume the same behavior as the emulsions, having a decrease of the amount of water per initial amount of perlite over the time. Initially, the decrease is not so pronounced due to the fact that the absorption of water by the perlite partially compensates the dissolution occurred.

The results show that the emulsions tested behave in a typical way. Primarily, the amount of water in perlite starts increasing, due to absorption of water by the perlite, but after some hours the curve assumes an inverse slope because the amount of perlite is no more the initial one, since it starts dissolving in water.

Through the evolution illustrated in the previous figure, it is possible to verify that, while the absorption phenomenon prevails against dissolution phenomenon, the reference Silres BS 1042 is the one with a lower water amount per initial weight of perlite ratio. It means that Silres BS 1042 is the emulsion that provides the lower water uptake. Through the analysis of the same graph, it is also possible to find that the emulsion whose time of effectiveness is higher is the reference Silres BS 1042.

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