Integrated Master in Chemical Engineering

Formulation of an Antifoam Agent for the Paper Making Process

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Resumo [Abstract in Portuguese]

O principal objectivo deste projecto é elaborar um anti-espumante para aplicar na indústria do papel reciclado.

No processo do papel reciclado existe uma etapa chamada flotação onde a tinta é removida a partir dos resíduos de papel. Antes desta etapa, a tinta é primeiramente separada das fibras através do processo de produção da polpa. Em seguida, a flotação toma lugar, com o intuito de remover a tinta separada da suspensão de fibras injectando bolhas de ar, assumindo que as partículas hidrofóbicas de tinta se irão fixar às bolhas de ar durante a colisão. A tinta é depois removida quando a espuma de bolhas com tinta flutua no topo da célula de flotação e finalmente é rejeitada.

Durante o processo da referida etapa grandes quantidades de espuma são produzidas, que precisam de ser removidas do processo. Assim, a separação da espuma é feita e um agente anti-espumante é usado para reduzir o volume deste resíduo. O mesmo anti-espumante é adicionado à fracção de polpa sem tinta para evitar a presença de ar no papel final, o que pode causar buracos no produto final e assim levar a uma qualidade de papel inaceitável.

No decorrer do projecto, várias emulsões foram realizadas recorrendo a matérias-primas tais como óleos, ácidos gordos, ceras, entre outros. Equipamentos tais como o homogenizador, banho de ultra-som e o Ultra-Turrax® foram usados para preparar as referidas formulações. De modo a avaliar a eficiência destas emulsões, três tipos de testes foram realizados: um teste de destruição de espuma (*defoaming*) para determinar o quão rápido um anti-espumante consegue destruir a espuma existente; um teste de remoção de ar (*deaeration*) para avaliar a capacidade das bolhas de ar coalescerem de modo a formarem espuma mais rápido à superfície; e um teste anti-espuma (*antifoaming*) para verificar a capacidade do anti-espumante em prevenir a formação de espuma espontaneamente ou após agitação.

A emulsão PD-985-142, composta por *Solvent*, *Fatty Ester 2*, *Oleic Acid* e *PVA 4*, é a melhor em termos gerais. Conduziu aos melhores resultados no teste anti-espuma, tendo-se revelado tão eficiente como o produto de referência. A mesma emulsão teve também um dos melhores desempenhos no que diz respeito ao teste de remoção de ar. Um estudo sobre o desempenho da remoção de ar do produto de referência mostrou uma percentagem de ar óptima após 5 minutos seguido de um suave e assimptótico aumento durante 60 minutos. Nenhuma das emulsões consideradas no mesmo estudo mostrou um comportamento semelhante.

Palavras-chave: Papel, Flotação, Espuma, Anti-espumante, Remoção de Ar

Abstract

The main objective of this project is to elaborate an antifoam to apply in the recycled paper industry.

In the recycled paper process there is a stage called Flotation deinking where ink is removed from wastepaper. Before this stage the ink is firstly detached from fibers through the pulping process. Then, the flotation process takes place, aiming to remove the detached ink from the fiber suspension by injecting air bubbles, with the assumption that the hydrophobic ink particles will stick to air bubbles on collision. Ink is then removed when the ink-attached bubble froth floats to the top of a flotation cell and is finally rejected.

In the course of the mentioned stage large amounts of foam are produced, which needs to be removed from the process. As a result, separation of the foam is accomplished and an antifoam agent is used to reduce the volume of this waste material. The same antifoam product is also added to the deinked pulp fraction to avoid the presence of air in the finished paper product, which can lead to holes in the final product and thus an unacceptable paper quality.

In the course of the project, several emulsions were made using raw materials such as oils, fatty acids, waxes, among others. Equipment such as a homogenizer, a sonicator and an Ultra-Turrax® were used to prepare the aforementioned formulations. To evaluate the efficiency of these emulsions, three kinds of tests were carried out: a defoaming test to determine how fast a defoamer can destroy existing foam; a deaeration test to evaluate the air bubbles capacity to coalescence so that they can cream faster to the surface; and the antifoaming test to verify the ability to prevent the natural or upon agitation foam formation.

The emulsion PD-985-142, composed of *Solvent*, *Fatty Ester 2*, *Oleic Acid* and *PVA 4*, is the best tested emulsion in general terms. It led to the best results in the antifoam test, in which it was as good as the reference. The same emulsion had also one of the best performances regarding the deaeration test.

An accomplished study of deaeration performance in time of the reference product, showed an optimum percentage of air after 5 min and then a soft and asymptotic increase during 60 minutes. None of the emulsions considered in the same study had a similar behavior.

Keywords: Paper, Flotation, Foam, Antifoam, Deaerator

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1 Introduction

1.1 Project Context and Presentation

Foams appear as an integral part of various technological applications, such as ore and mineral flotation, tertiary oil recovery, production of porous insulating materials, fire fighting and many others. Foams are also encountered in certain types of consumer products, e.g. the mousses and ice-creams as food products and shaving and styling foams in cosmetics. It has been known for many years that the presence of oil droplets and/or hydrophobic solid particles in the aqueous foaming solutions can strongly reduce the foaminess and foam stability, which might be a problem in various applications. For example, the fat particles in food products and the droplets of silicone oil used in personal care products (such as shampoos and hair/skin conditioners) have a strong antifoam effect, which should be suppressed to achieve an acceptable product quality from a consumer viewpoint (Binks & Horozov, 2006).

On the other hand, excessive foaming might create serious problems in many industrial processes. Typical examples are during fermentation in drug and food manufacturing, the processing of drug emulsions and suspensions, pulp and paper production, industrial water purification, beverage production and packaging, textile dyeing, oil rectification and many others. That is why special additives called “antifoams” or “defoamers” are widely used in these and other industrial applications to suppress foam formation or to destroy already formed foam. The antifoams are also indispensable components of several everyday commercial products, such as washing machine detergents and paints, among others (Binks & Horozov, 2006).

Foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase. Foam bubbles usually have diameters greater than 10 µm and may be larger than 1000 µm.

A two-dimensional slice of a general foam system is depicted in Figure 1. The general foam structure is contained by the bulk liquid on the bottom and on the upper side by a second bulk phase, in this case gas. The gas phase is separated from the thin liquid film, by a two-dimensional interface (Schramm, 2005).

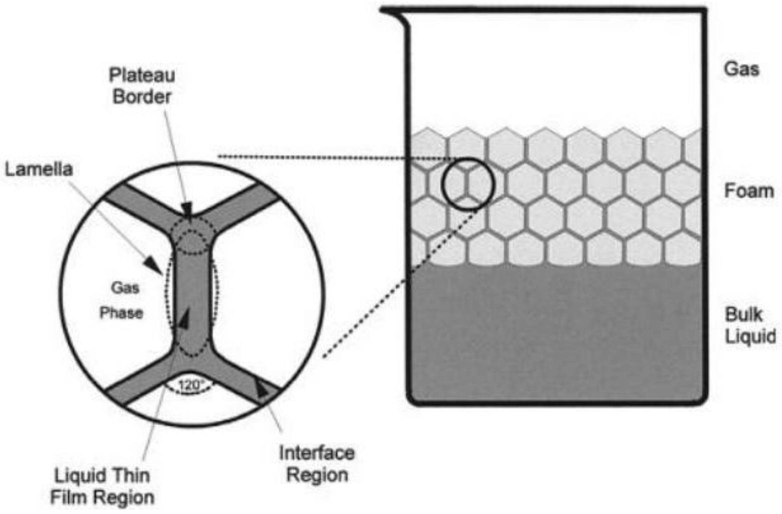

Figure 1 – Illustration of a generalized foam system showing aspects of a foam lamella (Schramm, 2005)

The process for reusing waste paper to make new paper involves a flotation step to remove foreign substances like ink from the paper pulp. Usually soap is used to stabilize the air bubbles that adsorb at their interfaces hydrophobic substances like inks. Due to their low density, the air bubbles rise with the ink to the top where they can be separated. Large amounts of foam are produced in this step. Immediately after the separation of the foam, an antifoam agent is used here to reduce the volume of this waste material. The same antifoam product will also be added in the deinked pulp fraction to avoid the inclusion of air in the finished paper product, causing holes in the final product and thus an unacceptable paper quality. In this respect, the main objective of this project is to create an efficient antifoam for the recycled paper industry.

A typical antifoam or defoamer consists of oil, hydrophobic solid particles, or a mixture of both. Antifoams are substances which are predispersed in the foaming solution as solid particles, oil drops, or mixed oil-solid globules. Therefore, the main role of the antifoam is to prevent formation of excessive foam (Denkov, 2004).

The oil should be surface active and exhibit the property of spreading fast at the air-liquid interface, whereas the hydrophobic particles should bridge opposite liquid-air interfaces. A scheme of the antifoam action is presented in Figure 2.

The project comprises a study of the different variables affecting the production of antifoam, namely the type of oil, the type of solid particles, the particle sizes, the particle shapes and the emulsifier system.

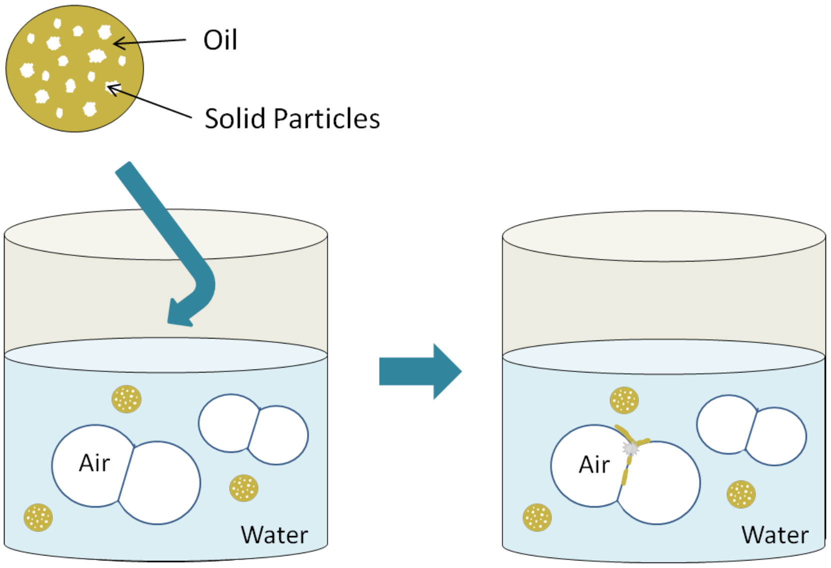

Figure 2 - Scheme of the antifoam action

The first step of the lab experiments is to create a dispersion of solid particles in oil. Then, the mixture is dispersed in water, creating emulsions.

All the emulsions made in this project are oil-in-water (o/w) emulsions.

After that, some tests have to be accomplished in order to check if the antifoams formulations succeeded in terms of the three main objectives for antifoam, which are: defoaming, antifoaming and deaeration (TOUCH CHEM).

- Defoaming performance of a defoamer is determined from how fast a defoamer can destroy existing foam;
- Deaeration is the process of air bubbles coalescence so their size increases and they cream faster;
- Antifoaming is the ability to prevent the natural or upon agitation foam formation.

The antifoaming tests require pulp and foam to be performed. I visited a company, which produces newspaper and magazines paper from recycled paper, and some samples of foam, micro-, pre- and postflotation foam, were collected as well as a sample of pulp.

GOVI (Gentse Olie en Vet Industrien) is a family-owned company incorporated in 1910, currently with 36 employees. Moreover it is an international manufacturing company, supported by R&D and customer oriented creation of added value, which is also present in Russia, Serbia, Budapest and Italy.

GOVI manufactures and commercializes different chemical products, being specialist in emulsions and colloidal systems. The production capacity is about 40 000 ton per year and has a turnover of 25 M€. It is noteworthy that 85 % of the company's production is exported. In Figure 3 the current business units of the company are presented.

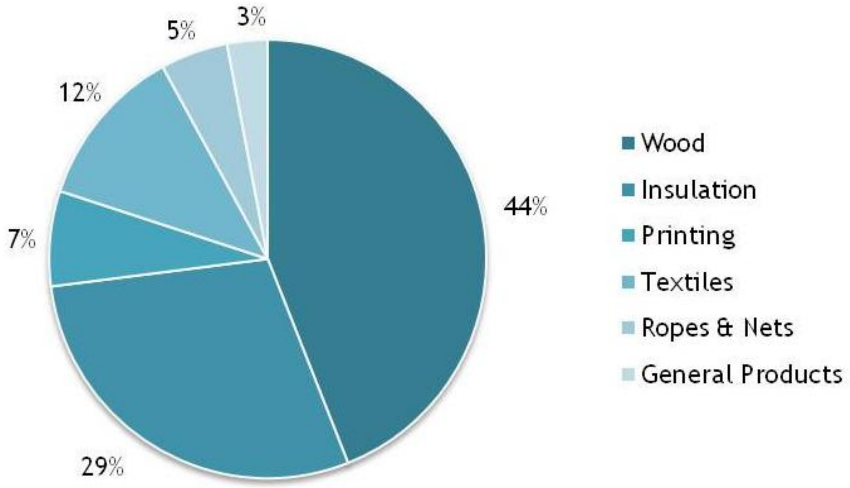

Figure 3 - Current business units of GOVI

1.2 Contributes of the Work

Before starting this project, the R&D team of the company worked on the subject for over a year, with partial success, as only the defoaming property, desired for any antifoam, was achieved.

The most relevant innovation accomplished in this project is the exploration of different types of raw materials to use in the formulations as well as the use of different emulsifying equipments and techniques, namely the sonicator and the Ultra-Turrax®, apart from the homogenizer which was the typical equipment used in the lab.

Therefore the scope of the project is broader than before as not only the testing of the different formulations will be studied but also the different working conditions at which emulsions can be made and the consequences of these working conditions to the final properties and features of the emulsions.

This work also will take into account the variable time for the efficiency of the emulsions and not only the instantaneous activity of the antifoam product.

1.3 Thesis Organization

Apart from this chapter, the document is divided in four additional chapters.

In this respect, the second chapter is the Background, where the state of art is presented regarding literature sources as well as existing knowledge in the company.

Moreover, the third chapter is divided in two sub-chapters: in the first one the raw materials and methods used for the experiments are presented and in the second sub-chapter the obtained results of the experiments are presented and discussed.

The fourth chapter exhibits the main conclusions of the project.

Finally, the fifth chapter contains the evaluation of the accomplished work where achievements, possible future work and the final considerations are expressed and identified.

2 Background

Various nonpolar oils (mineral oils, silicone oils) and polar oils (fatty alcohols, acids and esters, alkylamines and alkylamides, tributylphosphates, thioethers and many others) are used as antifoam components. In cosmetic, personal care and some pharmaceutical products, the silicone oil polydimethylsiloxane (PDMS) has found wide application under the commercial name “dimethicone”. The solid particles are usually hydrophobized inorganic oxides (silica, Al_2O_3, TiO_2) or wax particles (e.g., Mg stearate) (Binks & Horozov, 2006).
It was found empirically that mixtures of oil and hydrophobic solid particles (typically, 2-6 wt % of particles dispersed in the oil phase) often have much higher antifoam efficiency, in comparison with each of the individual components. Such antifoam compounds, if properly formulated, could prevent foam formation or destroy entirely the foam for seconds, at concentrations as low as 0.01 to 0.1 wt % (Binks & Horozov, 2006).

Those antifoams also contain dispersants, emulsifiers, and other key components that modify the surface activity of either the products or the process liquors in which they may function (Thorn & Au, 2009).

Many commercial antifoam compounds are sold in the form of oil-in-water emulsions, because the latter are more convenient for dosing during application (Denkov, 2004).

An emulsion may be defined as a heterogeneous system consisting of two immiscible liquid phases in which one is intimately distributed in the other as minute droplets whose diameters exceed 0.1 micrometer. In most cases one of the liquids is water. A third component, known as a surfactant (emulsifying agent or stabilizer), must be present in adequate amounts to prevent coalescence of the dispersed phase.
When oil is dispersed as extremely fine droplets in a continuous phase of water, the emulsion would be oil-in-water (O/W). Emulsions of this type are water-dilutable. When the oil is the continuous phase with the water distributed in the oil as small droplets, the emulsion is water-in-oil (W/O). This type of emulsion is not dilutable with water but will dilute with oil.
The type of emulsion formed is greatly dependent upon the nature of the surfactant used in the formulation. The two main functions of the surfactant are (1) reducing the interfacial tension of the oil and water phases, and (2) preventing agglomeration, coalescence and breaking of the dispersed droplets after they are formed (APV).

Many factors that destabilize foams are known to destabilize emulsions as well. That is why only a few emulsifiers (such as PVA, and some nonsoluble surfactants which make a shield of solid particles on the surface of the compound globules) have been found to stabilize efficiently the antifoam emulsions (Denkov, 2004).

There are some performance concepts about antifoaming products that might be useful to understand, namely:

- *Antifoam activity* characterizes the antifoam generation (during agitation) and/or the antifoam ability to destroy rapidly foam that is already generated (i.e., after stopping the agitation).
- *Antifoam exhaustion* is a process in which the antifoam loses its activity in the course of foam destruction.
- The term *antifoam durability* characterizes the antifoam ability to destroy a certain total amount of foam, before the antifoam ability is lost.

The term *antifoam efficiency* is used to characterize the antifoam in a qualitative sense with respect to both antifoam activity and durability (Denkov, 2004).

It was shown experimentally and theoretically that hydrophobic particles can rupture the foam films by the so-called “bridging-dewetting mechanism. This mechanism implies that, first, the solid particles comes in contact with the two opposite surfaces of the foam film, forming a “solid bridge” between them as it is exemplified in Figure 4 (Denkov, 2004).

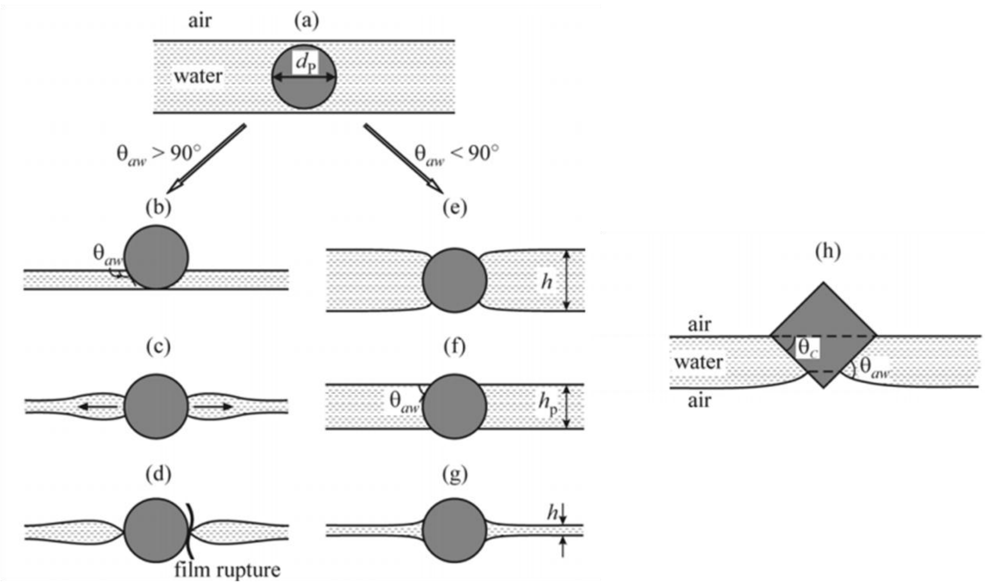

Figure 4 - Scheme of the bridging of foam film surfaces by a solid particle. (a)-(d) When the spherical particle has contact angle θ_{aw} > 90°, it is dewetted by the liquid perforating the foam film at the particle surface.(e)-(g) If θ_{aw} < 90°, the particle is not dewetted and the foam film remains stable. (h) Cone-shaped particle with slope angle θ_C can be dewetted if $\theta_{aw} > \theta_C$. (Denkov, 2004)

If the particle is sufficiently hydrophobic ($\theta_{aw} > 90°$), it is dewetted by the liquid and the three-phase contact lines eventually come in direct contact with each other – the foam film gets perforated at the particle surface. Some experiments showed that foam film rupture can be induced by less hydrophobic particles ($\theta_{aw} < 90°$) if the latter have sharp edges and are properly oriented in the foam film (Denkov, 2004).

There are some important factors, such as the size of antifoam globules, oil spreading, kinetics of surfactant adsorption, hydrophobicity of solid particles in mixed oil-solid antifoams, and the presence of amphiphilic additives (foam boosters) that affects the efficiency of the antifoam (Denkov, 2004).

For instance, part of the role of the particles is to penetrate any electrical double layer between oil droplets and air bubbles, then clearly the particle size should be at least of the same order as the double layer thickness, i.e., > 0,1 mm. If the particle size is appreciably smaller than this, then the oil droplet will in effect be smooth so that the presence of particles will be irrelevant (Garrett, 1993).

Paper Industry: Formation of foam

Increased pulp mill chemical carry-over and the use of recycled fiber as well as high yield pulps elevate the levels of detrimental substances in the papermaking system. These detrimental substances are a source of surface active products that directly contribute to problems caused by air in the system, resulting in the creation of foam. The surfactant concentrates at the boundary of the water and air, resulting in a stabilizing effect. These surface active substances (surfactants) consist of two distinct components: a hydrophobic component and a hydrophilic component. The hydrophobic (water repelling) component generally is a hydrocarbon chain while the hydrophilic (water loving) component is an ionized group or a water-soluble polar moiety. As the concentration of these substances increases, there is a reduction in the surface tension of the pulp suspension resulting in high foaming capacity.

This orientation of the surfactant molecules around the air bubble creates a very thin film around the air bubble that can be strong enough to preserve the bubble. In the pulp and papermaking process, these types of bubbles can either appear in the water phase as entrained air or on the surface as foam (Thorn & Au, 2009).

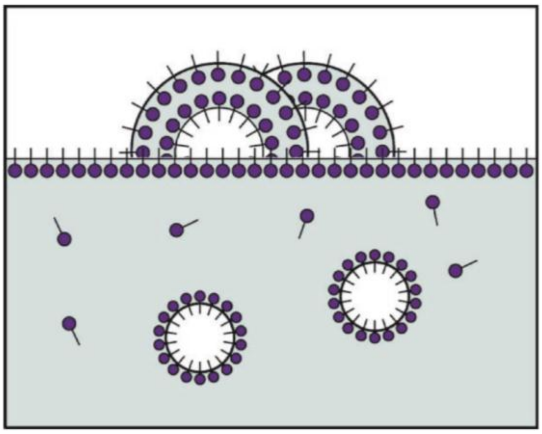

Figure 5 – Surfactant stabilized entrained air and surface foam (Thorn & Au, 2009)

Apart from paper, air, water and detrimental substances or surfactants that stabilize foam and entrained air are present in the papermaking process. A fourth component that further enhances foam stabilization is the presence of fines in the white-water system and papermaking process. Fines are finely divided particles that are often the result of the pulping or papermaking process, or they may be filler or pigment particles added to provide key paper properties. These particles tend to insert themselves between bubbles to interrupt the processes of foam or bubble destruction (Thorn & Au, 2009).

Paper Industry: Main stages

Paper recycling is becoming active part of the paper industry because of growing environmental concerns and economic reasons. The paper recycling process is a way to wash, remove, and bleach unwanted particles from collected printed paper so that it can be sold as an alternative to virgin paper. In modern paper recycling plants, the process of removing unwanted particles from the pulp can take as much as three times the amount of steps that it does in the mineral processing industry due to the fact that a higher quality product is needed to compete with the virgin paper (Drelich et al., 2001).

To stay on the cutting edge of technology, testing is always being done to try to improve the paper recycling technology at different stages of screening, washing, bleaching, and flotation operations (Drelich et al., 2001).

The main stages of a typical recycled paper factory are illustrated in Figure 6.

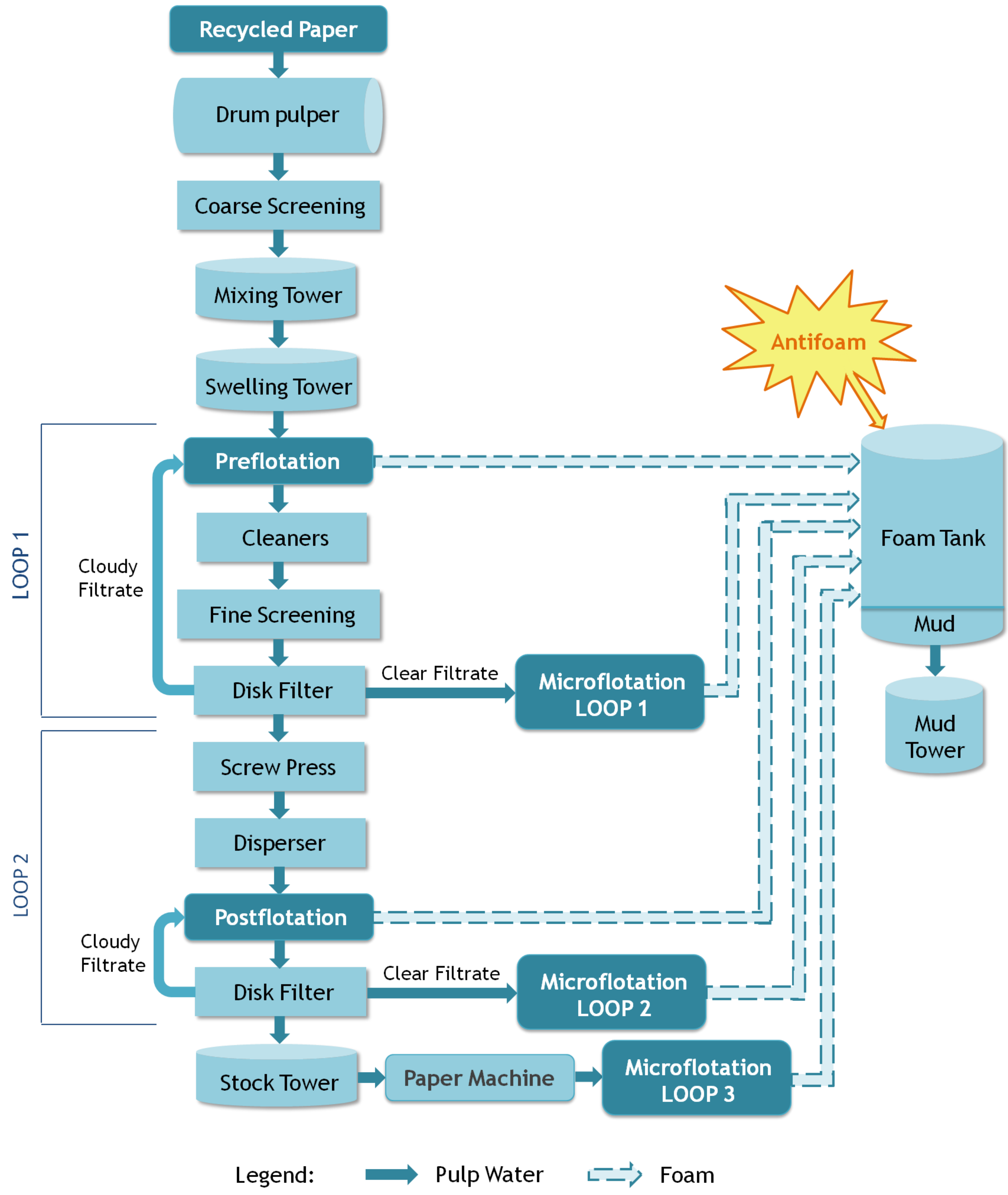

Figure 6 - Scheme of the recycled paper process

Paper Industry: Flotation

First the recovered paper is pulped followed by various processes that have the objective to remove various types of contaminants as ink, plastic materials (stickies), metal objects and other types of garbage. Two methods for separating the ink from the paper fibers are used: washing and flotation (Ek et al., 2009).

A sequence of these two processes is also possible. Nevertheless, since its introduction in the 1980s, flotation is the most common method used.

In both processes the first step is to detach the ink from the fibres using chemical and mechanical processing. In the washing process the difference in size between the dispersed ink and the fibres is used. The small ink particles are separated from the fibre suspension by the use of wires or screens. The flotation process uses surface chemical differences between ink and fibre (Ek et al., 2009).

The objective of the flotation process is to remove the detached inks from the fiber suspension by injecting air bubbles, with the assumption that the hydrophobic ink particles will stick to air bubbles on collision. Ink is removed when the ink-attached bubble froth floats to the top of a flotation cell and is removed (Zhu et al., 2004).

Subsequently, the froth is cleaned in a secondary stage to recover good fiber.

Foam Destruction

Garrett (1993) contends that the oil in oil-based defoamers is present at the water-air interface causing bubble coalescence. He also states that the hydrophobic particles used in defoamers are lodged in the oil-water interface.

To act as an effective defoamer or deaerator, the surface tension of the product has to be lower than that of the foaming liquid. The product must disperse uniformly and quickly and not be soluble into the water phase. The defoamer also must interact with the foam and air bubbles, then destabilize the foam (immediate effect of foam knockdown and reduction in entrained air levels), and it should additionally maintain effectiveness for some time.

Other factors that contribute to a product's efficacy are:

- Particle or droplet size
- Concentration of emulsifiers in the formulation
- Formulation components, such as surfactant used
- Degree of hydrophobicity
- For defoamers containing particles (silicone, EBS wax, Fatty alcohol wax, silica):
    - Size, surface area, and shape of the particle
    - Molecular weight and molecular weight distribution
- Process conditions such as pH, temperature, and conductivity (Thorn & Au, 2009)

Of the large number of defoamer or antifoam products available, most will perform according to one of the following principles:

- **Reduction of surface unity**: All defoamers could be said to operate by disrupting the surface layer. Some defoamer chemistries are made of particles that migrate to the bubble surface and disrupt the regular packing of molecules at the water/air interface. Some particles may absorb surfactant molecules onto their surface. This reduces the surface cohesion. Examples are hydrophobic silica particles, EBS particles, or silicone particles.
- **Spreading**: The defoaming agents, because of their lower solubility, enter the foam lamella by spreading over the bubble surface. Foam-stabilizing surfactants are influenced by the defoamer, which causes them to move towards a position in which surface tension is higher and where air bubble stabilization is affected. The result is a weak area on the lamella and bubble ruptures (Thorn & Au, 2009).

3 Technical Description and Discussion of Results

This chapter is divided in two sections. In section 3.1 the materials and methods that were used and followed in the course of the project are described. In section 3.2 the main results and the respective discussion are presented.

3.1 Materials and Methods

To start, the next tables are presented the code names for the components that were used in the project as well as the general chemical description.

Table 1 – Code names and principal properties of the used Polymers, Biocide and the Inorganic Solid

Group	Code	Chemical description	Degree of hydrolysis
Biocide	Biocide	Biocide	–
Polymers	PVA 1	Polyvinylic Alcohol	98.0 - 98.8
	PVA 2	Polyvinylic Alcohol	–
	PVA 3	Polyvinylic Alcohol	88.0 ± 1.0
	PVA 4	Polyvinylic Alcohol	88.0 ± 1.0
	PVA 5	Polyvinylic Alcohol	98.5 ± 0.5
	PVA 6	Polyvinylic Alcohol	98.25 ± 0.75
	PVA 7	Polyvinylic Alcohol	99.20 ± 0.20
	HEC	Hydroxyethylcellulose	–
	Xanthan	Xanthan Gum	–
Inorganic Solid	Inorg Solid	–	–

Table 2 - Code names and principal properties of the Surfactants used in the project

Group	Code	Chemical description	Acid Value mg KOH/g	Iodine Value g I_2/100 g	Melting Point (°C)	Viscosity (mPa.s)	HLB
Surfactants	FA 1	Branched Ethoxylated Fatty Alcohol	–	–	–	50	8
	FA 2	Branched Ethoxylated Fatty Alcohol	–	–	–	150	13
	FA 3	Branched Ethoxylated Fatty Alcohol	–	–	–	40	8
	EO-PO	EO-PO Block Copolymer	–	–	50	5000	–
	FA 4	Branched Ethoxylated Fatty Alcohol	–	–	–	–	–
	Fatty Ester 1	Fatty Ester 1	2.40	0.85	61.4	–	–

Table 3 - Code names and principal properties of the Fatty Acids used in the project

Group	Code	Chemical description	Acid Value mg KOH/g	Iodine Value g I_2/100 g	Saponification Value mg KOH/g
Fatty Acid	Oleic Acid	Oleic Acid	–	–	–
	Isost Acid 1	Isostearic Acid	183.0	3.97	193.9
	Isost Acid 2	Isostearic Acid	182.3	2.85	194.8
	Isost Acid 3	Isostearic Acid	197	0.67	–
	Isost Acid 4	Isostearic Acid	192-202	≤ 5	193-205

Table 4 - Code names and principal properties of the Waxes used in the project

Group	Code	Chemical description	Acid Value mg KOH/g	Iodine Value g I_2/100 g	Melting Point (°C)
Waxy Solid	Fatty Alcohol	Long Chain Fatty Alcohol	0.02	0.17	52-72
	Micro Paraffin 1	Microcrystalline Paraffin	–	–	62 - 66
	Macro Paraffin	Macrocrystalline Paraffin	–	–	–
	FT paraffin	Fisher-Tropsch Paraffin	–	–	54
	Fatty Ester 2	Fatty Ester 2	–	–	55
	Ester C	Cetylpalmitate	0.3	0.75	52.8
	Micro Paraffin 2	Microcrystalline Paraffin	–	–	81.0
	Micro Paraffin 3	Microcrystalline Paraffin	–	–	82.9
	Hydrogenated Fat	Triglyceride	–	–	–
	Fat	Triglyceride	–	–	–
	Fatty Ester 3	Fatty Ester 3	3	3	–

Table 5 - Code names and principal properties of the Oils and the Solvent used in the project

Group	Code	Chemical description	Acid Value mg KOH/g	Iodine Value g I_2/100 g	Viscosity (cSt)
Oil	White Oil	Paraffinic/Naphtenic Oil	–	–	–
	Sil Oil 350	Polydimethylsiloxane	–	–	350
	Sil Oil 10000	Polydimethylsiloxane	–	–	10 000
	Naftenic Oil	Naftenic Oil	0.03	–	40
	Sunflower Oil	Triglyceride	0.08	128.69	–
	Linseed Oil	Triglyceride	–	–	–
Solvent	Solvent	–	–	–	–

As it was said before, it was found empirically that mixtures of oil and hydrophobic solid particles (typically, 2-6 wt % of particles dispersed in the oil phase) often have higher antifoam efficiency.

According to this information, the project started with the preparation of antifoams composed by different oils and solid particles such as paraffin, animal fat and fatty alcohols.

The first method that was used to prepare the antifoams is explained below and the antifoams were prepared using two equipments, namely a mixer and a sonicator. The solutions were prepared in a 250 mL graduated glass with 6.5 cm of diameter. The stirrer has 4 blades that were turned up and 5 cm of diameter.

Method 1

1. Prepare 150 mL of a solution composed of:
    - 10 % of solid particles (weigh 15 g)
    - 90 % of oil (add oil until 150 g)
    - 1 % of stabilizer – optional (weigh 1 g)
2. Warm the solution in the hotplate or in the hot water bath until the particles are completely melted;
3. Write down the temperature when the solid starts melting and when it is completely melted;
4. Let the solution cool while mixing at 300 rpm until at least 20 °C below the melting point of the solid particles;
5. Register the temperature at which the solution starts getting turbid or small particles starts to appear;
6. Heat the solidified solution in the hotplate or in a hot water bath until it is liquid again;
7. Split the solution in two parts: one part will cool while being mixed at 1100 rpm and the other part will cool down in the sonicator.

Following Method 1, ten solutions were prepared. The composition and the melting points are presented in Table 6.

Table 6 – Composition and measured melting points of the samples 1 to 10

Sample	Oil (90%)	Solid Particles (10%)	Stabilizer (1%)	Melting Point (°C)
PD-985-1	White Oil	Micro Paraffin 1	Fatty Ester 3	60 / 72
PD-985-2	White Oil	Fatty Alcohol	Fatty Ester 3	50 / 65
PD-985-3	White Oil	Hydrogenated Fat	Fatty Ester 3	54 / 90
PD-985-4	White Oil	Micro Paraffin 1	-	28 / 69
PD-985-5	Sunflower Oil	Micro Paraffin 1	Fatty Ester 3	31 / 80
PD-985-6	Sunflower Oil	Fatty Alcohol	Fatty Ester 3	28 / 72
PD-985-7	Sunflower Oil	Micro Paraffin 1	-	29 / 78
PD-985-8	Sil oil 350	Micro Paraffin 1	-	37 / 84
PD-985-9	Sil oil 350	Fatty Alcohol	-	58 / 80
PD-985-10	Sil oil 350	Micro Paraffin 1	Fatty Ester 3	34 / 82

Initially the mixtures were heated to melt the particles and after that, the mixtures were clear and homogeneous.

The observations and main notes of the aforementioned lab experiments are presented in *Table 19* in section 3.2.

Subsequently, the best formulations tested by Method 1 (PD-985-1, PD-985-2, PD-985-3, as it is explained in section 3.2) were repeated. They were prepared following the same procedure for making the previous solutions but with less time for cooling so they would not get solid.

From these solutions three samples of each one were taken to be homogenized (H) using an *APV 1000* Homogenizer (see Annex 2) at different pressures: H_1, H_4, H_7 – 200 bar, H_2, H_5, H_8 – 400 bar, H_3, H_6, H_9 – 600 bar. The aim of homogenizing is to obtain even smaller particles in the solution.

After homogenizing at different pressures (H_i), some emulsions (E_i) were made at 60, 100 and 200 bar of each formulation. The emulsions comprise 70% of water phase (water + emulsifier) and 30% of an oil phase (H_i). The phases were mixed and circulated through the homogenizer. The surfactant used for the emulsions was *PVA 1* 15% in water. The composition of the emulsions was 60% of water, 10% of PVA and 30% of the homogenized solutions (H_i).

Figure 7 exemplifies the followed procedure to make the samples from emulsion PD-985-1. The same procedure applies for emulsions PD-985-2 and PD-985-3.

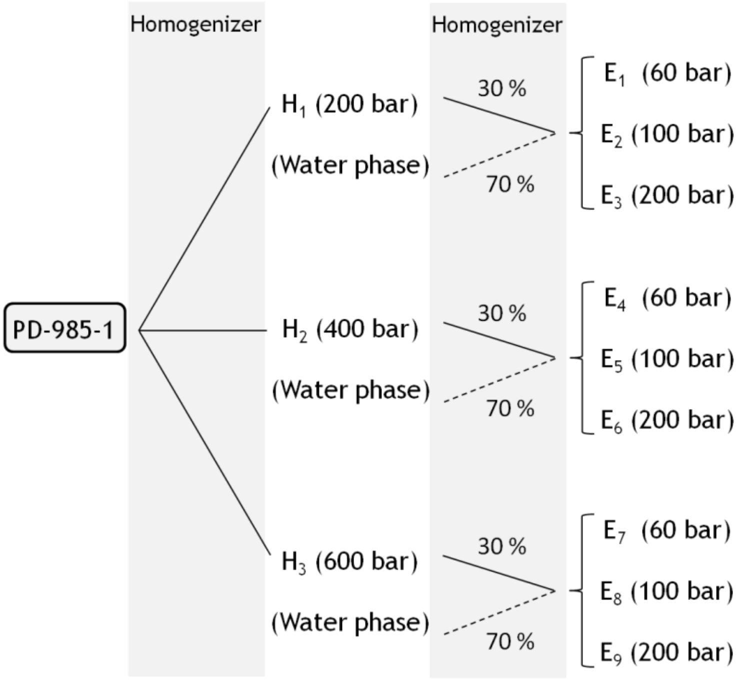

Figure 7 – Scheme of the samples made from emulsion PD-985-1

There are three types of tests that have to be done to analyze the antifoam to check its activity and efficiency and they are explained below. In Table 20 and Table 21 in section 3.2 the results of the mentioned tests are presented.

Antifoam Tests Method for Paper Industry

1st: Deaeration

The diluted pulp that is needed for this test should be around 1.1% of dry mater

The added antifoam should be diluted 100 times (1/100)

1. Warm up a bit more than 1000 mL of diluted pulp in the microwave for ±4 min (temperature should be around 55-57 °C);
2. Weigh 1000 g in a 5 L vessel and shake violently up and down for 25 times;
3. Add 2g of 100 times diluted product;
4. Move the solution 10 times up and down without shaking;
5. Measure the temperature;
6. Put the pulp in the EGT (see Annex 1);
7. Measure the amount of air;

8. Measure the temperature once again;

The percentage of air is calculated by the following equation:

$$\% \text{ air} = (\text{number of turns} - 0.75) * 0.617$$

To the best of the paper company knowledge if the percentage of air is higher than 0.5, undesired holes will be present in the paper. For this reason, the goal is to reach a percentage of air below 0.5.

2nd: Defoaming

The antifoam added should be diluted 100 times (1/100)

1. Prepare a mixture of water from micro-, pre- and postflotation samples (40%, 40%, 20% respectively);
2. Warm up ± 60 mL of the mixture and heat it in the microwave for ±23 s (temperature should be around 52-55 °C);
3. Put 50 mL of the mixture in a 100 mL graduated cylinder with 2.5 cm of diameter;
4. Shake violently for 30 s and let it rest for another 30 s
5. Write down the foam height;
6. Add one droplet of antifoam and turn up and down 3 times. After every turn, let it rest for 30 s and write down the foam height;
7. Add droplets of antifoam until the foam disappears from the surface or the surface is visible.

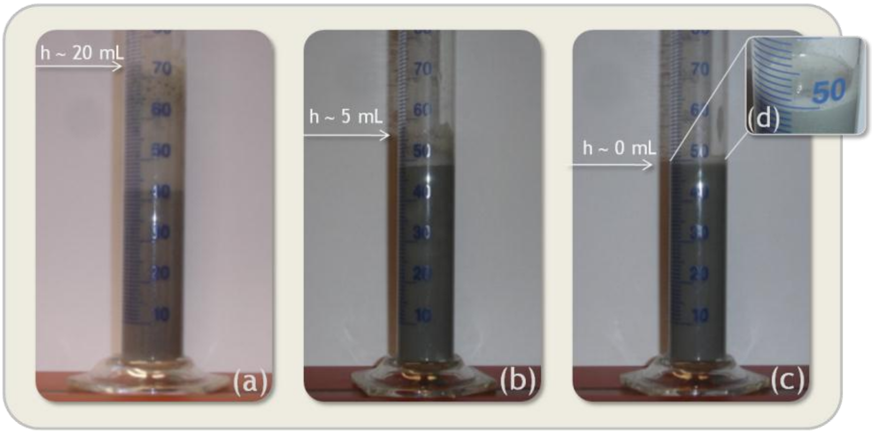

Figure 8 - Defoaming test for the reference. (a) – Without any droplet; (b) – After 1 droplet, 3 turns; (c) - After 2 droplets, 3 turns; (d) – Detail for the surface of (c), the foam is almost completely gone

3rd: Antifoaming

The antifoam added is diluted 1000 times (1/1000)

1. Prepare a mixture of water from micro-, pre- and postflotation samples (40%, 40%, 20% respectively);
2. Warm up ± 60 mL of the mixture and heat in the microwave for ± 23 s (temperature should be around 52-55 °C);
3. Put 50 mL of the mixture in a 100 mL graduated cylinder with 2.5 cm of diameter;
4. Add 1 g of the 1/1000 solution of antifoam;
5. Shake 30 s, let it rest for 30 s and write down the foam height.

Inorganic solid particles were also tried since they could lead to good results according to literature, especially if combined with silicone oil.

Table 7 - Composition of the samples

Sample	Oil (95%)	Solid Particles (5%)	Stabilizer (1%)	Mass (g)
PD -985-11	White Oil	Inorg Solid	-	300
PD – 985-12	Sil Oil 350	Inorg Solid	-	300

To prepare the formulations above only mixing was needed. Thereafter the emulsions were made similarly to the previous ones, but only for two pressures (200 and 300 bar) since the sample was smaller.

The three antifoams tests were made and the results are presented in Table 22 in section 3.2.

Those formulations were not being successful, so it was decided to test a formulation which the company had tested before and that had acceptable results in the antifoaming tests.

The used quantities were the same as in past studies but the emulsions were subjected to three different equipments (sonicator, Ultra-Turrax® and homogenizer) instead of just the homogenizer. The composition is presented in Table 8 and the emulsions were prepared according to Method 2.

The antifoaming tests were made and the results are shown in section 3.2.

Table 8 – Composition of the sample PD-985-13

	Ingredients	wt (%)
Oil phase	White Oil	13.5
	Solvent	13.5
	Fatty Esther 1	2.7
Water phase	PVA 1 15%	10.0
	FA 2 85%	0.3
	Dehardened water	60.0

Method 2

1. Prepare the oil phase: join every ingredients in a vessel and heat it in a heating plate while mixing, until the solid particles are completely melted;
2. Prepare the water phase: join every ingredients and mix until the solution is homogeneous;
3. Join both phases;
4. Stir the mixture with the mixer;
5. Heat or cool down until the desired temperature (10 °C above the melting point of the solids particles);
6. Use the different equipments: sonicator, Ultra-Turrax® and homogenizer at different temperatures, namely 30 °C, 40 °C, 50 °C, 60 °C and 70 °C.

The Ultra-Turrax® (see specifications in Annex 2) is a high-speed dispersing and emulsifying unit capable of handling free flowing and liquid media in batches.

The previous formulation (PD–985-13) failed to work, so that new formulations had to be considered.

It is a fact that the emulsions that were tried before were not very stable, this could be the reason of their failure. For this reason, the new formulations (30% oil phase and 70% water phase) were similar to the previous ones but with more stabilizers in the composition.

They were made in the homogenizer at 70 ºC and at different pressures, namely 50, 100 and 150 bar.

The oil phase was composed by 45.5% of *White Oil*, 45.5% of *Solvent* and 9% of *Fatty Esther 1*. The composition of the water phase is indicated in the Table 9 and in Table 10.

Table 9 – Composition of the emulsions PD-985-101 to PD-985-108

	Samples / Ingredients	101	102	103	104	105	106	107	108
Water Phase	**PVA 1 15%**	10.0	-	5.0	5.0	-	5.0	5.0	5.0
	HEC 1%	-	0.2	-	-	0.2	-	-	-
	FA 2 85%	0.3	0.3	0.3	0.5	-	-	-	-
	FA 1	-	-	-	-	-	0.3	-	-
	FA 3	-	-	-	-	-	-	0.3	-
	EO-PO	-	-	-	-	-	-	-	0.3
	FA 4	-	-	-	-	0.003	-	-	-
	Dehardened water	59.7	69.5	64.7	64.5	69.8	64.7	64.7	64.7

Table 10 – Composition of emulsions PD-985-109 to PD-985-116

	Samples / Ingredients	109	110	111	112	113	114	115	116
Water Phase	**Xanthan 1%**	-	-	-	20.0	20.0	20.0	20.0	20.0
	HEC 1%	20.0	20.0	20.0	-	-	-	-	-
	FA 2 85%	-	-	-	-	-	-	-	0.3
	FA 1	0.3	-	-	-	-	-	0.3	-
	FA 3	-	0.3	-	-	-	0.3	-	-
	EO-PO	-	-	0.3	-	0.3	-	-	-
	FA 4	-	-	-	0.3	-	-	-	-
	Dehardened water	49.7	49.7	49.7	49.7	49.7	49.7	49.7	49.7

The main results obtained for those formulations are related in section 3.2.

In literature (Hamers & Lorenz, 2009) there are studies where is mentioned that paraffin combined with a fatty alcohol can have an antifoaming effect. According to that information, emulsions combining *FT paraffin* and *Fatty Alcohol* in different percentages (50–50%, 20-80% and 80-20%, respectively) were accomplished.

The composition of the emulsions was identical to PD-985-103. In fact, the only difference was the substitution of *Fatty Esther 1* by the combinations aforementioned.

Table 11 – Composition of the emulsions PD-985-117 to PD-985-119

	Ingredients \ Samples	**117**	**118**	**119**
Oil Phase	**White Oil**	13.6	13.6	13.6
	Solvent	13.6	13.6	13.6
	FT paraffin	1.4	0.5	2.2
	Fatty Alcohol	1.4	2.2	0.5
Water Phase	**PVA 1 15%**	5.0	5.0	5.0
	FA 2 85%	0.3	0.3	0.3
	Dehardened water	64.7	64.8	64.8

New formulations with compositions similar to emulsions already tested with some success by the company were prepared. They are listed in Table 12, *Table 13* and in *Table 14*.

Table 12 - Composition of the emulsions PD-985-120 to PD-985-126

	Samples / Ingredients	120	121	122	123	124	125	126
Oil Phase	**White Oil**	27.3	13.6	13.6	13.6	13.6	-	-
	Sunflower Oil	-	-	-	-	-	13.6	-
	Linseed Oil	-	-	-	-	-	-	13.6
	Solvent	-	13.6	13.6	13.6	13.6	13.6	13.6
	Hydrogenated Fat	2.7	2.7	-	-	-	2.7	2.7
	Ester C	-	-	2.7	-	-	-	-
	Fatty Ester 2	-	-	-	2.7	-	-	-
	Fatty Alcohol	-	-	-	-	2.7	-	-
	FA 2 85%	-	-	-	-	-	1.0	1.0
Water Phase	**PVA 1 15 %**	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	Dehardened water	60.0	60.1	60.1	60.1	60.1	59.1	59.1

Table 13 - Composition of the emulsions PD-985-127 to PD-985-132

	Samples / Ingredients	127	128	129	130	131	132
Oil Phase	**White Oil**	27.3	13.6	13.6	13.6	13.6	13.6
	Solvent	-	13.6	13.6	13.6	13.6	13.6
	Isost Acid 3	2.7	2.7	-	-	-	-
	Hydrogenated Fat	-	-	2.7	-	-	2.7
	Micro Paraffin 2	-	-	-	2.7	-	-
	Micro Paraffin 3	-	-	-	-	2.7	-
Water Phase	**PVA 2**	1.5	1.5	1.5	-	-	-
	PVA 1 15 %	-	-	-	5.0	5.0	5.0
	FA 2 85%	-	-	-	0.3	0.3	0.3
	Dehardened water	68.5	68.6	68.6	64.8	64.8	64.8

Table 14 - Composition of the emulsions PD-985-133 to PD-985-136

Ingredients \ Samples		133	134	135	136
Oil Phase	White Oil	12.3	13.0	12.3	13.0
	Solvent	12.3	13.0	12.3	13.0
	Hydrogenated Fat	-	-	2.7	2.7
	Fatty Ester 2	2.7	2.7	2.7	2.7
	Fatty Alcohol	2.7	2.7	-	-
Water Phase	PVA 1 15 %	10.0	-	10.0	-
	Dehardened water	60.0	68.6	60.0	68.6

Table 15 and Table 16 present the compositions of emulsions PD-985-137 to PD-985-148 made with resort to the homogenizer at different pressures.

Moreover, the compositions of emulsions PD-985-149 to PD-985-160 made with resort to the Ultra-Turrax® at 5000 rpm are presented in Table 17 and Table 18.

Table 15 - Composition of the emulsions PD-985-137 to PD-985-143

Ingredients \ Samples		137	138	139	140	141	142	143
Oil Phase	White Oil	13.6	13.6	13.6	13.6	13.6	-	-
	Solvent	13.6	13.6	13.6	13.6	13.6	13.6	-
	Fatty Ester 2	2.8	2.8	2.8	2.8	2.8	2.8	2.7
	Oleic Acid	-	-	-	-	-	13.6	27.3
Water Phase	PVA 4 15 %	10.0	-	-	-	-	10.0	10.0
	PVA 3 15 %	-	10.0	-	-	-	-	-
	PVA 7 15 %	-	-	10.0	-	-	-	-
	PVA 6 15 %	-	-	-	10.0	-	-	-
	PVA 5 13 %	-	-	-	-	10.0	-	-
	Dehardened water	60.0	60.0	60.0	60.0	60.0	60.0	60.0

Table 16 - Composition of the emulsions PD-985-144 to PD-985-148

	Samples / Ingredients	144	145	146	147	148
Oil Phase	**Solvent**	13.6	-	13.6	13.6	-
	Fat	13.6	27.3	-	-	-
	Isost Acid 2	-	-	13.6	-	-
	Naftenic Oil	-	-	-	13.6	27.3
	Fatty Ester 2	2.8	2.7	2.8	2.8	2.7
Water Phase	**PVA 4 15 %**	10.0	10.0	10.0	10.0	10.0
	Dehardened water	60.0	60.0	60.0	60.0	60.0

Table 17 - Composition of the emulsions PD-985-149 to PD-985-155

	Samples / Ingredients	149	150	151	152	153	154	155
Oil Phase	**Solvent**	13.6	13.6	-	-	13.6	13.6	13.6
	Oleic Acid	-	-	-	-	13.6	13.6	13.6
	Isost Acid 4	-	13.6	27.3	27.3	-	-	-
	Fatty Ester 2	2.8	2.8	2.7	-	2.8	2.8	-
	Hydrogenated Fat	-	-	-	2.7	-	-	2.8
	Isost Acid 1	13.6	-	-	-	-	-	-
Water Phase	**PVA 1 15 %**	10.0	10.0	10.0	10.0	10.0	-	10.0
	PVA 4 15 %	-	-	-	-	-	10.0	-
	Dehardened water	60.0	60.0	60.0	60.0	60.0	60.0	60.0

Emulsions PD-985-156 to PD-985-160 only differ from PD-985-149 the polymer that was used.

Table 18 – Polymer used in emulsions PD-985-156 to PD-985-160

Emulsion	**156**	**157**	**158**	**159**	**160**
Polymer	PVA 4 15 %	PVA 3 15 %	PVA 5 15 %	PVA 6 15 %	PVA 7 15 %

3.2 Results and Discussion

The temperature presented in *Table 19* is the measured temperature at which the samples made by Method 1 started getting turbid or small particles started to appear.

Table 19 – Melting point, temperature and viscosity results for the Method 1 experiments

		Mixer at 300 rpm		**Mixer at 1100 rpm**		**Sonicator**	
Sample	**Melting Point (°C)**	**Temp. (°C)**	**Visc. (cP)**	**Temp (°C)**	**Visc. (cP)**	**Cooling Velocity °C/min**	**Visc. (cP)**
PD 985-1	60 / 72	T = 45°C	1520	T = 40°C	3520	_	4640
PD 985-2	50 / 65	T = 60°C (t = 5’)	3520	_	9000	5.2	9200
PD 985-3	54 / 90	T = 43°C (t = 24’)	7720	T = 40°C	13840	3.0	11880
PD 985-4	28 / 69	T = 47°C (t = 14’)	3000	T = 35°C (t = 14’)	4080	3.5	4280
PD 985-5	31 / 80	T = 53°C (t = 8’)	2360	T = 38°C (t = 8’)	3160	0.75	2720
PD 985-6	28 / 72	T = 49°C (t = 14’)	3520	T = 42°C (t = 8’)	9960	4.0	7520
PD 985-7	29 / 78	T = 45°C (t=5’)	3320	T = 49°C	3120	4.0	3960
PD 985-8	37 / 84	T = 62°C (t = 5’)	1240	T = 46°C (t = 11’)	920	6.7	1200
PD 985-9	58 / 80	T = 52°C (t = 13’)	3720	T = 53°C (t = 6’)	3640	5.0	5000
PD 985-10	34 / 82	T = 62°C (t = 8’)	2400	T = 52°C (t = 6’)	2040	7.5	2280

The process of making paper takes place at around 50 °C and the particles should be solid at that temperature. According to this, the formulation should be compatible with this requirement, which implies a melting point of the solid particles above 50 °C. As it is expressed in Table 19, formulations PD-985-1, PD-985-2, PD-985-3 and PD-985-9 are the only samples respecting that requirement.

In the meantime it was known that the silicone oil option, PD-985-9, was an undesired formulation for the costumer of GOVI that is interested in the project. This is due to a stage in the costumer's process regarding water purification, where the final sludge is burned and if it contains silicone oil it will lead to silica deposits which are not desirable.

As a result the three first formulations will be tested as antifoaming agents.

In Table 20 and Table 21 are the values of the antifoam tests for the samples with formulations PD-985-1 and PD-985-2, which were homogenized at different pressures.

By the time it was emulsified, emulsion PD-983-3 was not stable. This could be seen by the presence of agglomerated particles in the solution. As a result, it was not tested. The initial homogenized solutions (H_1-H_3 and H_7-H_9) were not tested because they were solid at room temperature, which implies that they could not be analyzed.

Table 20 – Antifoaming tests results for PD-985-1

Sample	Defoaming	Antifoaming	Deaeration
Blank		hi = 15 mL	% air = 1.48
Reference	2 droplets	h = 9 mL	% air = 0.56
E_1, 60 bar	2 droplets	h = 15 mL	% air = 0.69
E_1, 100 bar	2 droplets	h = 15 mL	% air = 0.66
E_1, 200 bar	2 droplets	h = 14 mL	% air = 0.76
E_2, 60 bar	2 droplets	h = 14 mL	% air = 0.83
E_2, 100 bar	2 droplets	h = 12 mL	% air = 0.86
E_2, 200 bar	2 droplets	h = 13 mL	% air = 0.80
E_3, 60 bar	2 droplets	h = 12 mL	% air = 0.86
E_3, 100 bar	2 droplets	h = 13 mL	% air = 0.85
E_3, 200 bar	2 droplets	h = 13 mL	% air = 0.71

The defoaming test for the emulsions made from PD-985-1 worked as well as the reference. However the deaeration test did not lead to good enough results and the antifoaming test did not have satisfactory results as well.

Table 21 - Antifoaming tests results for PD-985-2

Sample	Defoaming	Antifoaming	Deaeration
Blank		hi = 15 mL	% air = 1.42
Reference	3 droplets	h = 7 mL	% air = 0.31
H_4	3 droplets	h = 14 mL	% air = 0.71
H_5	3 droplets	h = 14 mL	% air = 0.96
H_6	3 droplets	h = 14 mL	% air = 0.80
E_4, 60 bar	4 droplets	h = 15 mL	% air = 0.71
E_4, 100 bar	4 droplets	h = 14 mL	% air = 0.80
E_4, 200 bar	3 droplets	h = 14 mL	% air = 0.93
E_5, 60 bar	5 droplets	h = 14 mL	% air = 0.74

As shown in Table 21, the emulsions E_4-E_6 were not successful. As a result, some emulsions from the series were not tested.

The antifoaming tests results for the samples composed by the Inorganic Solid are shown in Table 22.

Table 22 - Antifoaming tests results

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 1.42
Reference	2 droplets	h = 6 mL	% air = 0.35
Si_1, 200 bar	2 droplets	h = 12 mL	% air = 0.69
Si_1, 300 bar	2 droplets	h = 11 mL	% air = 0.74
Si_2, 200 bar	2 droplets	h = 11 mL	% air = 0.82
Si_2, 300 bar	2 droplets	h = 10 mL	% air = 0.80

Apparently, the defoaming test was better for the samples composed by the Inorganic Solid particles, but the antifoaming and the deaeration were still failing.

Table 23 – Antifoming tests results for sample PD-985-13 with the sonicator

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 1.34
Reference	1 droplet	h = 3 mL	% air = 0.48
30°C	2 droplets	h = 9 mL	% air = 0.43
40°C	2 droplets	h = 10 mL	% air = 0.54
50°C	2 droplets	h = 9 mL	% air = 0.43
60°C	2 droplets	h = 10 mL	% air = 0.35
70°C	1 droplet	h = 8 mL	% air = 0.54

Using the sonicator for the sample preparation, the defoaming and the deaeration tests were acceptable, but the antifoaming test was not successful.

Table 24 – Antifoaming tests results for sample PD-985-13 with the Ultra-Turrax at 70°C

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 1.34
Reference	1 droplet	h = 3 mL	% air = 0.48
1 000 rpm	1 droplet	h = 5 mL	% air = 0.46
4 000 rpm	2 droplets	h = 6 mL	% air = 0.37
6 000 rpm	2 droplets	h = 4 mL	% air = 0.39
8 000 rpm	2 droplets	h = 3 mL	% air = 0.54
10 000 rpm	1 droplet	h = 6 mL	% air = 0.42

Analyzing Table 24 it is clear that all tests seems to have worked, particularly samples of 1000 rpm and 10 000 rpm for the defoaming, sample of 8000 rpm for the antifoaming and sample of 4000 rpm for the deaeration.

Table 25 - Antifoaming tests results for sample PD-985-13 with the Ultra-Turrax at 60°C

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 1.54
Reference	2 droplets	h = 5 mL	% air = 0.54
1 000 rpm	2 droplets	h = 14 mL	% air = 0.80
4 000 rpm	2 droplets	h = 17 mL	% air = 0.72
6 000 rpm	2 droplets	h = 14 mL	% air = 0.77
8 000 rpm	2 droplets	h = 10 mL	% air = 0.65
10 000 rpm	2 droplets	h = 10 mL	% air = 0.65

The results for the defoaming test were as good as the reference, but the antifoaming and the deaeration tests once again did not respect the performance requirements.

Table 26 - Antifoaming tests results for sample PD-985-13 with the Ultra-Turrax at 50°C

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 1.54
Reference	2 droplets	h = 5 mL	% air = 0.54
1 000 rpm	3 droplets	h = 10 mL	% air = 0.52
4 000 rpm	3 droplets	h = 8 mL	% air = 0.74
6 000 rpm	3 droplets	h = 12 mL	% air = 0.72
8 000 rpm	3 droplets	h = 10 mL	% air = 0.59
10 000 rpm	3 droplets	h = 11 mL	% air = 0.56

The defoaming test for the samples prepared at 50 °C was worse and the results for the antifoaming test were unsatisfactory. This means that those samples are not good enough for the objectives of the project.

For the samples prepared at 40 °C it was only tested the antifoaming capacity and the results were unsatisfactory, so the other characteristics were not even tested as one requirement was not met.

At this point only the samples made in the Ultra-Turrax® at 70 °C had acceptable results, so it was decided to verify if the formulation was dependent on this temperature to be successful. As a result, a higher temperature, namely 80 °C was tried. The antifoaming test did not result so this experiment did not go further.

The sample prepared in the Ultra-Turrax® at 70 °C was tried again with new flotation samples to check the consistency of the results. In this respect, the antifoaming test failed.

The reason for this incoherence might have to do with the degradation of the used flotation samples. As a matter of fact, the ideal procedure would be to work with fresh samples of pulp and flotation. However, not being possible to bring those samples from the paper industry with better frequency, the measurements presented so far were performed using the same pulp and flotation samples (including the first sample made with the Ultra-Turrax® at 70 °C).

As a result, it is obvious that none of the samples made by the Ultra-Turrax® worked, although it is not clear the nature of the failure.

The use of the homogenizer did not lead to better results, as can be seen in Table 27 and Table 28.

Table 27 - Antifoaming tests results for sample PD-985-13 with the Homogenizer at 70°C

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 2.75
Reference	3 droplets	h = 9 mL	% air = 0.71
30 bar	4 droplets	h = 16 mL	% air = 0.82
50 bar	3 droplets	h = 16 mL	% air = 1.23
100 bar	3 droplets	h = 15 mL	% air = 1.05
200 bar	3 droplets	h = 15 mL	% air = 0.82

The defoaming test had reasonable results for the samples made in the homogenizer at 70 °C as well as the deaeration test for the samples made at 30 and 200 bar. As the success was partial, none of the samples could be considered globally as a good option.

Table 28 - Antifoaming tests results for sample PD-985-13 with the Homogenizer at 50°C

Sample	Defoaming	Antifoaming	Deaeration
Blank			% air = 3.18
Reference	2 droplets	h = 11 mL	% air = 0.93
30 bar	3 droplets	h = 15 mL	% air = 1.26
50 bar	2 droplets	h = 15 mL	% air = 1.08
100 bar	2 droplets	h = 13 mL	% air = 0.89
200 bar	3 droplets	h = 15 mL	% air = 1.10

Once again the defoaming test worked for all samples made in the homogenizer at 50 °C but the antifoaming and the deaeration tests only had satisfactory results for the sample at 100 bar. Thus, new tests were made for this sample, although the results were still not adequate.

Hence those samples did not work, the other emulsions made in the homogenizer at different temperatures were not tested.

According to the results it is perceptible that this formulation (PD-985-13) does not work, so that new formulations were prepared.

The emulsions made previously were not very stable, so this can be the reason of their failure. In this respect, the new formulations are similar to the previous one but with more stabilizers in the composition.

It is crucial that emulsions are stable (do not spilt in layers, are not creamy or have particles) for the future application. For the formulations PD-985-101 until PD-985-116, only the emulsions below were stable:

- PD-985-102 at 150 bar
- PD-985-103 at 150 bar
- PD-985-104 at 150 bar
- PD-985-105 at 100 and 150 bar
- PD-985-106 at 150 bar
- PD-985-112 at 100 and 150 bar

GOVI seeks mainly an effective deaerator to apply in the industry. That is the reason why I will focus on the deaeration test from now on. According to this, the deaeration test was made for the emulsions listed above and the results are showed in Figure 9.

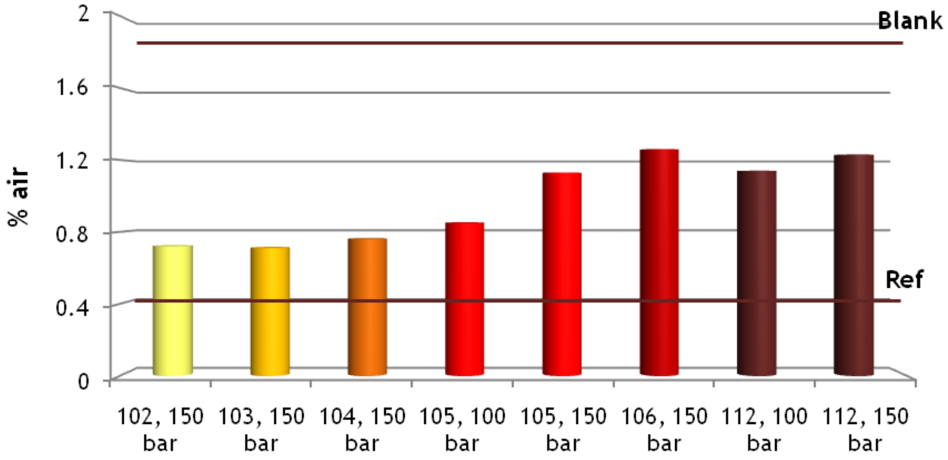

Figure 9 - Deaeration test results

Although none of the samples had a performance comparable to the reference, some of them are close to the reference what is to say that they have a considerable deaeration effect.

It is known that in an industrial application the antifoam shall work during a period of time. For this reason, a new experiment was performed aiming to evaluate the efficiency of the emulsions in time. It was decided to test the evolution of the deaeration in time with the emulsion that led to better results comparing to the reference.

The first three emulsions had similar results, nevertheless PD-855-102 was not so stable like the others. Moreover, the main difference between PD-985-103 and PD-985-104 is the amount of *FA 2*. For that reason, PD-985-103 was chosen since is economically more attractive.

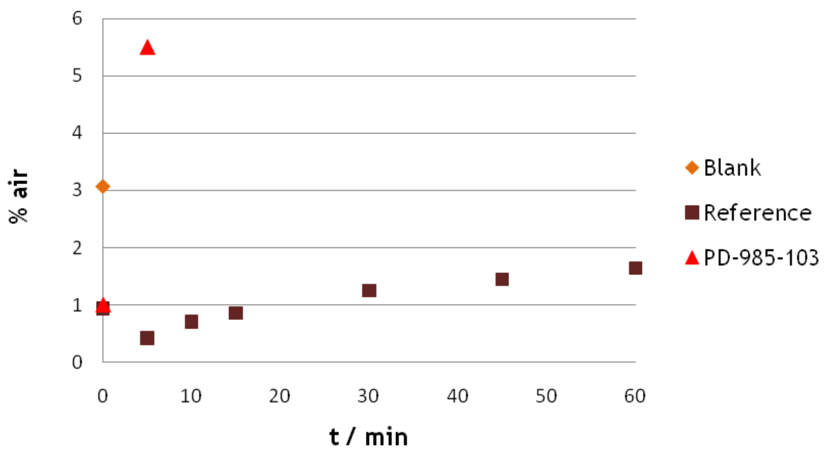

Figure 10 - Evolution of the deaeration effect in time

The tested emulsion (PD-983-103) has an unacceptable behavior after 5 min, thus the test did not proceed, even though the results obtained for the reference are quite interesting. Observing Figure 10 we can see that the reference has an optimum after 5 min and then the percentage of air increases with time, which means that it loses its effect in the course of time.

Surprisingly, it was observed that the emulsions PD-985-117 – PD-985-119 were not stable and for this reason they were temporarily disregarded.

Observing emulsions PD-985-120 – PD-985-126 it was concluded that only the following samples were stable: PD-985-120 (all pressures), PD-985-123 (all pressures) and PD-985-124 at 100 and 150 bar.

In Figure 11 are shown the results for the deaeration test.

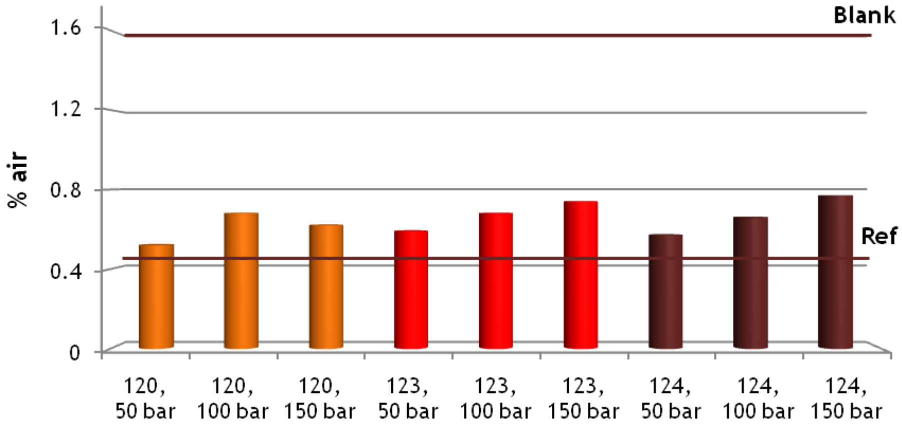

Figure 11 - Deaeration test results for emulsions PD-985-120, PD-985-123 and PD-985-124

All the samples made at 50 bar have better results. To prove their efficiency in time an analysis was made and it is possible to see the results in Figure 12.

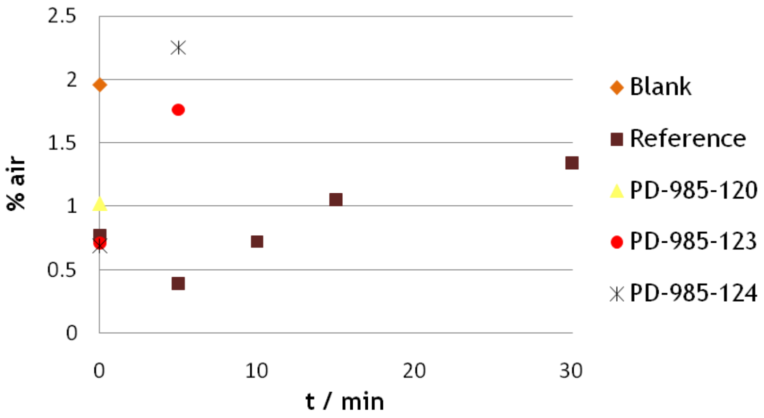

Figure 12 - Evolution of the deaeration effect in time

After five minutes it is possible to verify that the emulsions do not work. Nonetheless it is possible to see that the performance of the reference is similar to the previous behavior (Figure 10).

Regarding to emulsions PD-985-127 to PD-985-132, the deaeration test was made only for the emulsions present in Figure 13 since emulsions PD-985-128 and PD-985-132 at all pressures and emulsion PD-985-129 at 50 bar were not stable.

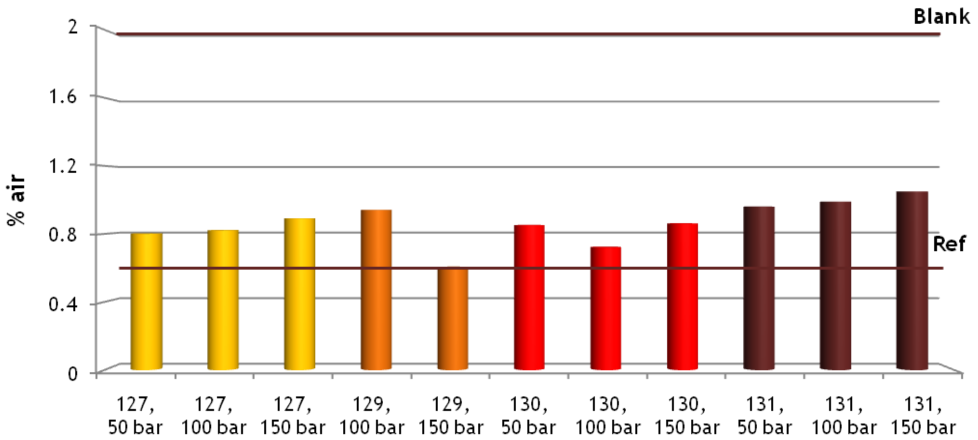

Figure 13 - Deaeration test results for emulsions PD-985-127 and PD-985-129 to PD-985-131

Emulsion PD-985-129 made at 150 bar had a percentage of air similar to the reference, however, when tested after 5 min, the value was already too high (% air = 1.59). Analyzing Figure 13 it is possible to conclude that the formulations PD-985-127 to PD-985-131 had all worse deaeration performances than the reference.

Emulsions PD-985-133 and PD-985-134 were not stable (agglomerated particles appeared in the surface and they were very viscous) and that is the reason why they were not tested. The deaeration tests results for the emulsions PD-985-135 and PD-985-136 are shown in Figure 14.

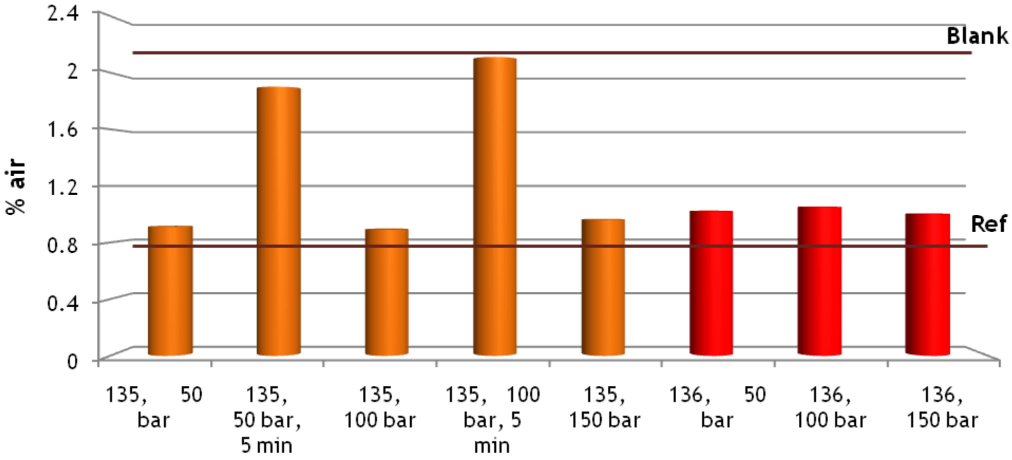

Figure 14 - Deaeration tests results for emulsions PD-985-135 and PD-985-136

Emulsions PD-985-135 initially had a percentage of air nearly to the reference, but after five minutes it was already too high, close to the blank value. As s result, the formulations are not good enough and there is not a big difference in the results whether *PVA 1* is included in the formulation or not.

Figure 15 shows the deaeration test results for PD-985-137 and PD-985-138 at different pressures.

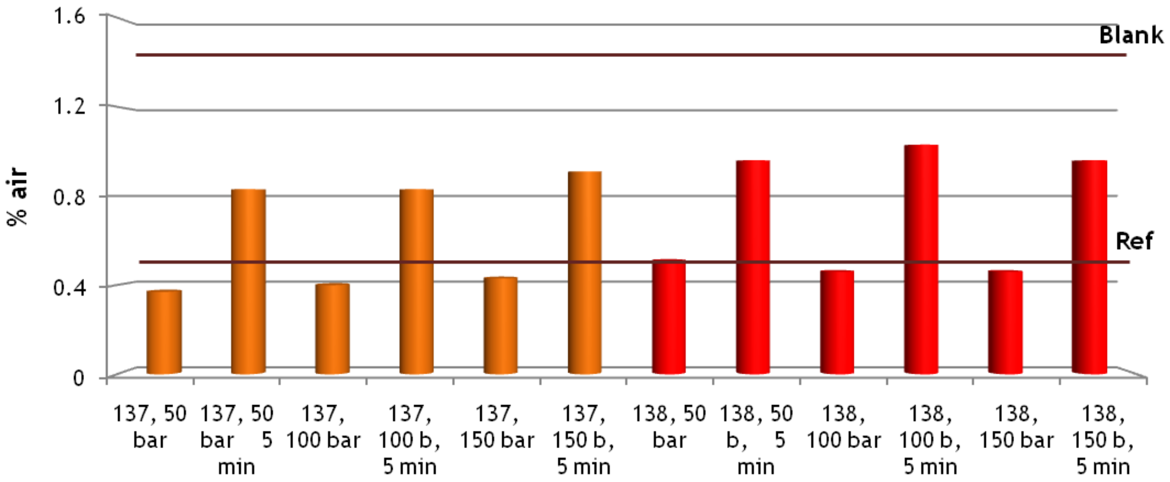

Figure 15 - Deaeration tests results for emulsions PD-985-137 and PD-985-138

All the emulsions show good results in the beginning and some are even better than the reference. Although after five minutes the result are not the desired since at least they should be as good as at time zero. This means that the formulations are not satisfying, but it is also possible to verify that the *PVA 4* (present in PD-985-137) gave better results than *PVA 3* (present in PD-985-138).

The obtained results for emulsions PD-985-139 to PD-985-141 and for PD-985-143 are showed in Figure 16. Emulsion PD-985-142 is present ahead because it led to interesting results.

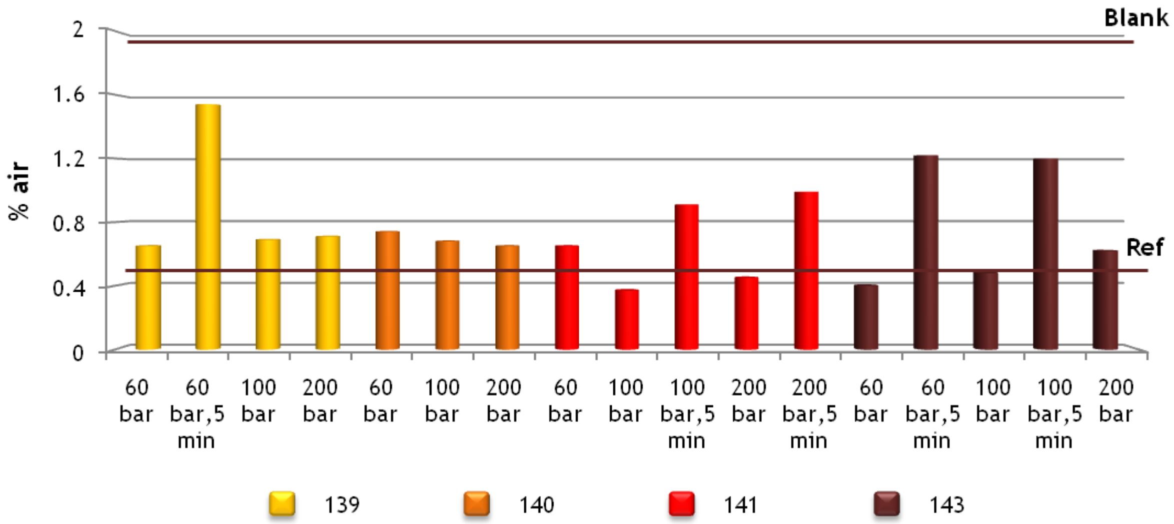

Figure 16 - Deaeration tests results for emulsions PD-985-139 to PD-985-141 and PD-985-143

As it is possible to see, the emulsions had satisfactory results in the beginning, especially PD-985-141 at 100 bar and at 200 bar and also the emulsion PD-985-143 at 60 bar. However, after five minutes the values were not adequate. It is also possible to conclude that the *PVA 5* (present in PD-985-141) was the best polymer of this series.

At this point the best dispersing agents were *PVA 4* (present in PD-985-137, PD-985-142 and in PD-985-143) and *PVA 5*. The emulsions containing the former polymer shown to perform well either having an organic phase composed of *White Oil* and *Solvent*, *Oleic Acid* and Solvent or just *Oleic Acid*. For this reason *PVA 4 was* the chosen dispersing agent for the following formulations.

Emulsion PD-985-142 had good results in the deaeration test and as a result an analysis in time was made to check the performance during a maximum period of time of one hour as it is shown in Figure 17.

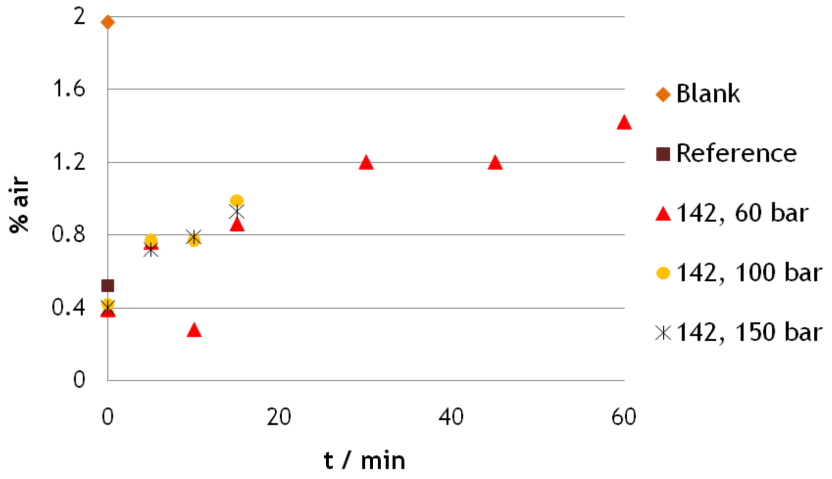

Figure 17 - Evolution of the deaeration effect in time for PD-985-142

Observing Figure 17 it is possible to notice that formulation PD-985-142 worked very well as a deaerator, particularly the sample made at 60 bar. The percentage of air of the latter, after 10 minutes, was even lower than for time zero and after one hour the same percentage was still lower than the blank value. This means that in the course of time the emulsion lost activity despite working for some time.

To confirm the efficiency of the previous formulation, the deaeration test was repeated three days later but the results were not successful. As the reason for this failure could be the instability of the emulsion (it was made some days before), the emulsion was made again three days after, six days after the first measurement. These results are presented in Figure 18.

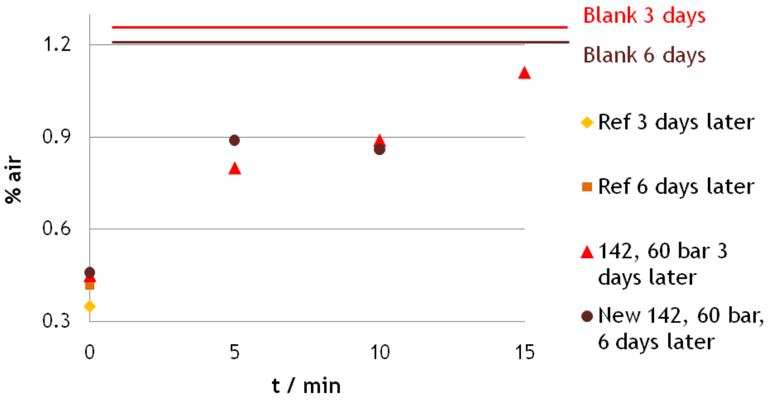

Figure 18 - Evolution of the deaeration effect in time for PD-985-142 at 60 bar after 3 and 6 days

Analyzing Figure 18 it is possible to see that the behavior of the emulsion PD-985-142 in time was not the desired one. In fact, after 15 minutes the percentage of air was already close to the blank. This means that the good results obtained before (Figure 17) are not reproducible.

In Figure 19 are presented the results for the deaeration test made for emulsions PD-985-144 and PD-985-145.

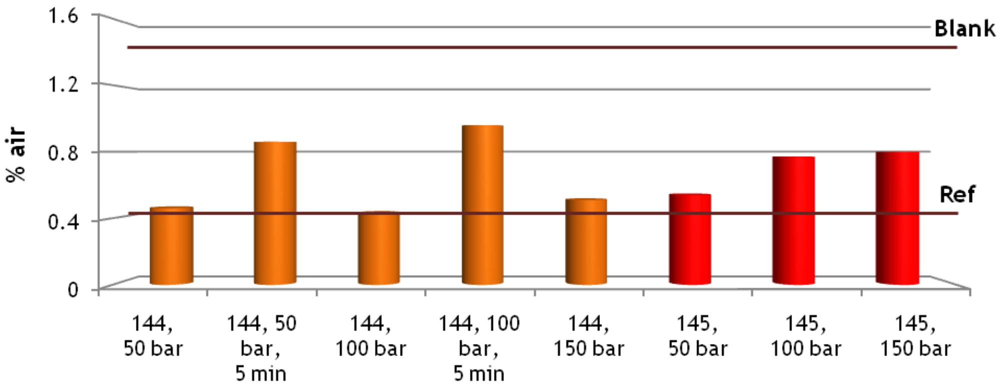

Figure 19 - Deaeration tests results for emulsions PD-985-144 and PD-985-145

It is possible to verify in Figure 19 that emulsions PD-985-144 made at 50 and 100 bar had a percentage of air close to the reference, however after five minutes the value was already too high and as a result none of the emulsions had satisfactory results.

The deaeration test results obtained for emulsions PD-985-146 to PD-985-148 are shown in Figure 20.

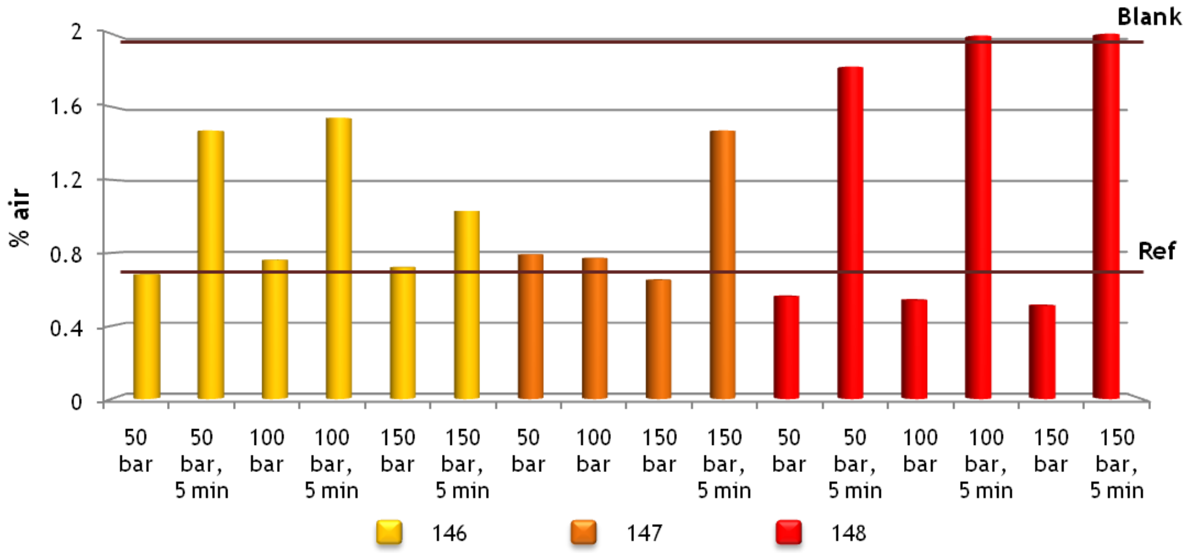

Figure 20 - Deaeration tests results for emulsions PD-985-146 to PD-985-148

All the emulsions presented in Figure 20 had a percentage of air close to the reference at time zero, especially emulsion PD-985-148. However, after five minutes de value was not acceptable, that is why it is possible to conclude that those formulations are not as good as intended.

To the best of GOVI knowledge the particle size and shape of the solid particles present in the antifoams formulations, affects their efficiency. The aim of using different pressures in the homogenizer is to obtain different particles sizes. By the experience, GOVI employees know that at higher pressure usually the emulsions are more stable but usually they are more effective at lower pressures.

To clarify the consistence of the aforementioned predictions, it was made a particle size distribution analysis for two formulations, respectively PD-985-142 and PD-985-146.

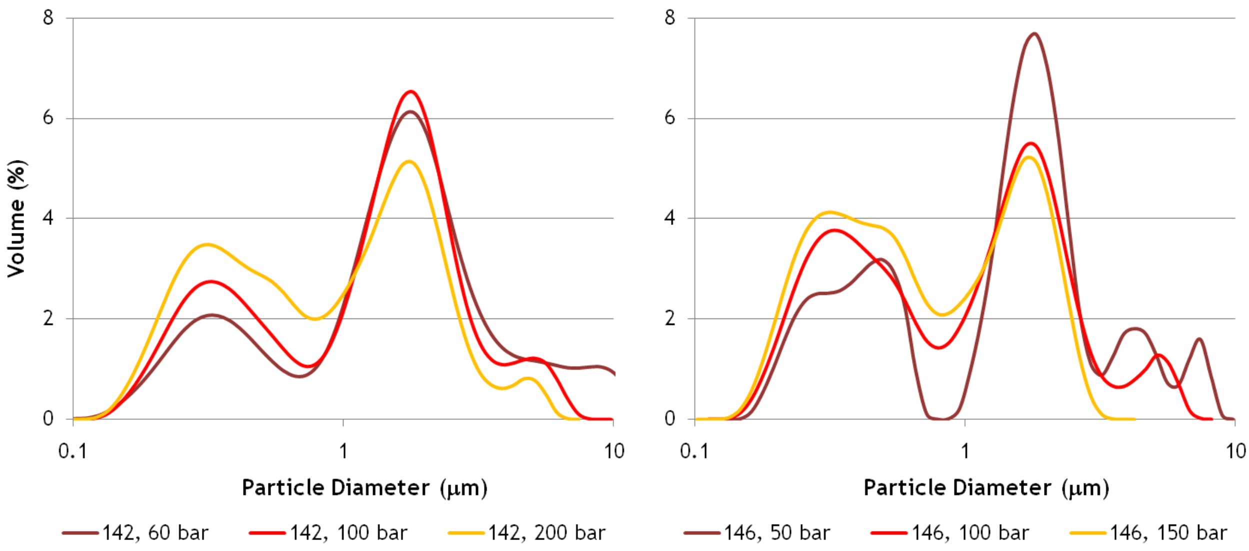

Figure 21 - Particle size distribution for PD-985-142 and PD-985-146

Observing Figure 21 it is possible to verify that the effect of the pressure in the emulsions is not very pronounced. In fact, all the particles have small sizes comprised in two principal ranges.

To date it was seen that the different pressures used in the preparation of the emulsions did not change very much the results of the antifoaming tests. Actually there was no linear tendency between the imposed pressure and the obtained results on the tests, for instance emulsions PD-985-120 and PD-985-145 had better results at 50 bar, while emulsions PD-985-130 and PD-985-141 gave better results at 100 bar and finally emulsions PD-985-129 and PD-985-147 were better at 150 bar.

As it was concluded above, the particle size is not very affected by the pressure also and for this reason from now on only one pressure for the emulsions, the medium pressure, 100 bar will be tested.

With regard to the particles size an analysis was also made to compare the particle size distribution of some emulsions that gave better results in the deaeration tests, likewise the reference.

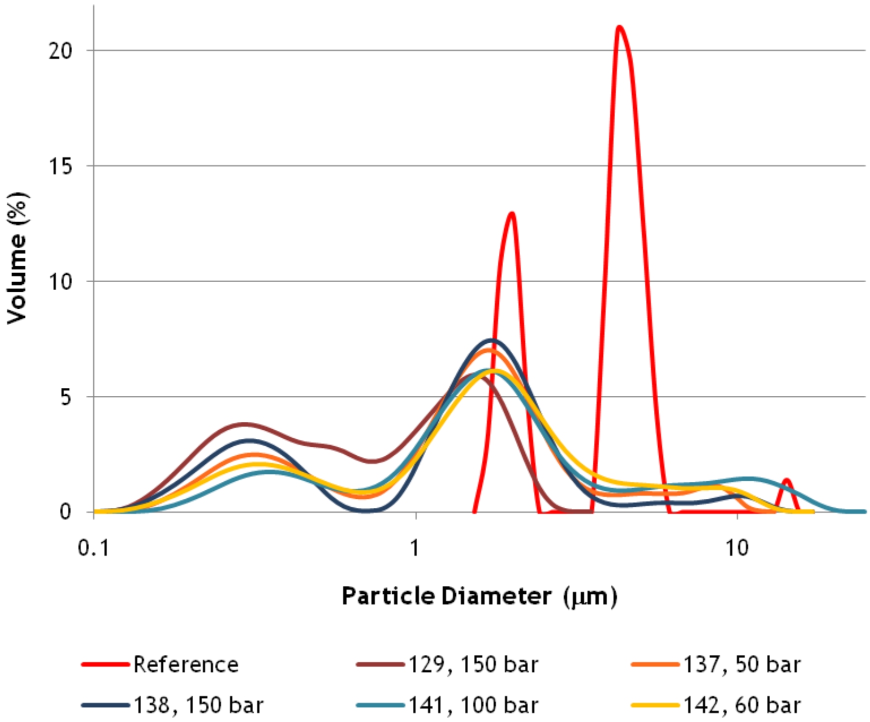

Figure 22 - Particle size distribution of emulsions with good deaearation capacity as well as the reference

Analyzing Figure 22 is it possible to notice that all the tested emulsions have a similar particle size distribution and that the sizes are comprised in two principal ranges as it happened with emulsions PD-985-142 and PD-985-146 at different pressures (Figure 21). All the emulsions were made in the homogenizer and for this reason it was probable that the sizes would be similar.

However, the particle size distribution of the reference is quite different from those emulsions. It presents two distinct peaks: the size of the particles is bigger than the size of the particles of the emulsions made in the homogenizer.

As the particle size distribution of different emulsions made in the homogenizer were quite different from the reference, it is possible to conclude that the equipment used by the competitor to make the reference product is different from ours.

Consequently, an emulsion was made using different equipments to check the particle size distribution. **Error! Reference source not found.** illustrates de obtained results for the emulsion PD-985-142 made using different equipments, such as a toothed blade mixer, the homogenizer with and without the cooling system and using the Ultra-Turrax® at two different speeds, namely 4000 rpm and 8000 rpm.

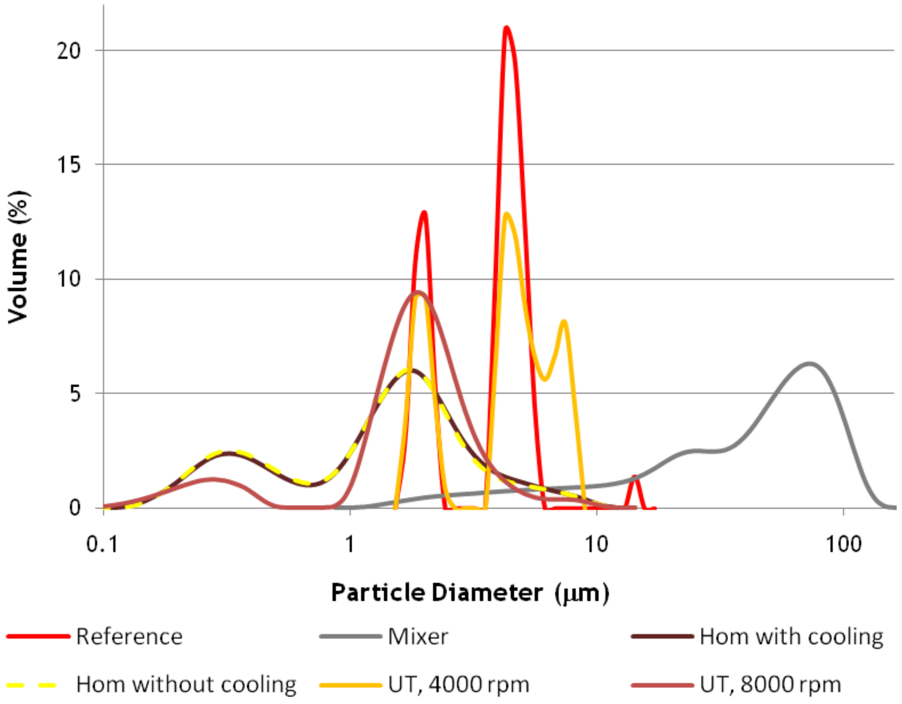

Figure 23 - Particle size distribution of PD-985-142 made by using different equipments

As it was assumed in the beginning of the project, the sizes of the particles made in the homogenizer practically are not affected by the use of the cooling system since the curves illustrated in **Error! Reference source not found.** are almost coincident. This also let know that the homogenizer with the cooling system is not a good alternative to make the emulsions.

It is also visible in **Error! Reference source not found.** that the sample made only with the mixer had particles with sizes extremely big. For this reason, this technique is not appropriated to make the emulsions.

Regarding to the distribution of the particle sizes of the emulsions made in the Ultra-Turrax® it is noticeable that they are more similar to the reference, especially at lower stirring speeds (lower stirring speeds implies bigger particles). In fact the emulsion made at 4000 rpm has two peaks in the same range as the reference. The main difference between them is the intensity of the peaks in those ranges and the higher value of sizes. These results showed that the Ultra-Turrax® probably is a good technique to adopt to make the emulsions.

According to this conclusion, emulsion PS-985-142 was made with the Ultra-Turrax® at one velocity above 4000 rpm, 5000 rpm, and the other below, 3000 rpm. An analysis of the particle size distribution was also made and was compared to the reference and to the previous emulsions made at 4000 rpm and 8000 rpm. These results are illustrated in Figure 24.

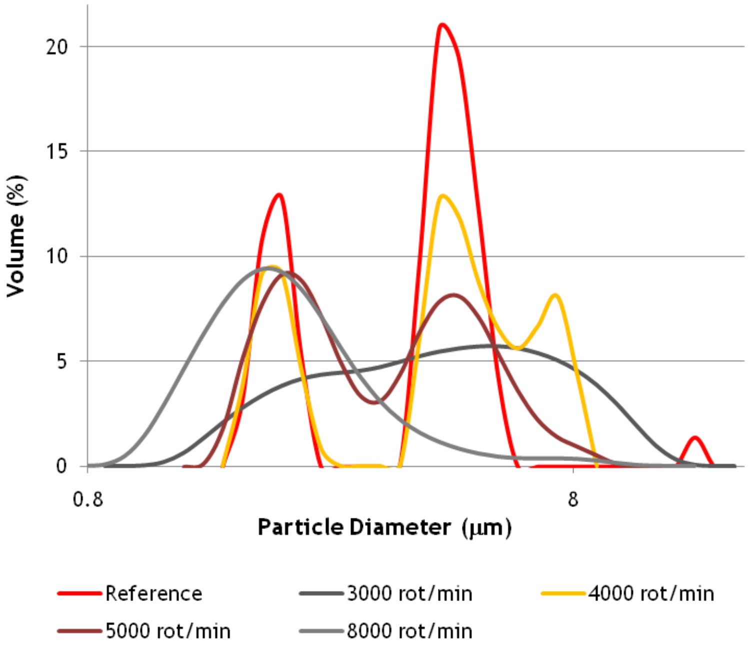

Figure 24 - Particle size distribution of PD-985-142 made in the Ultra-Turrax® at different velocities

Analyzing Figure 24 it is possible to conclude that the stirring speeds that led to a particle size distribution more similar to the reference are the 4000 and 5000 rpm. This probably means that these emulsions will led to better results in the antifoaming/deaeration tests.

To prove this hypothesis the deaeration test was made for these emulsions and results are illustrated in Figure 25.

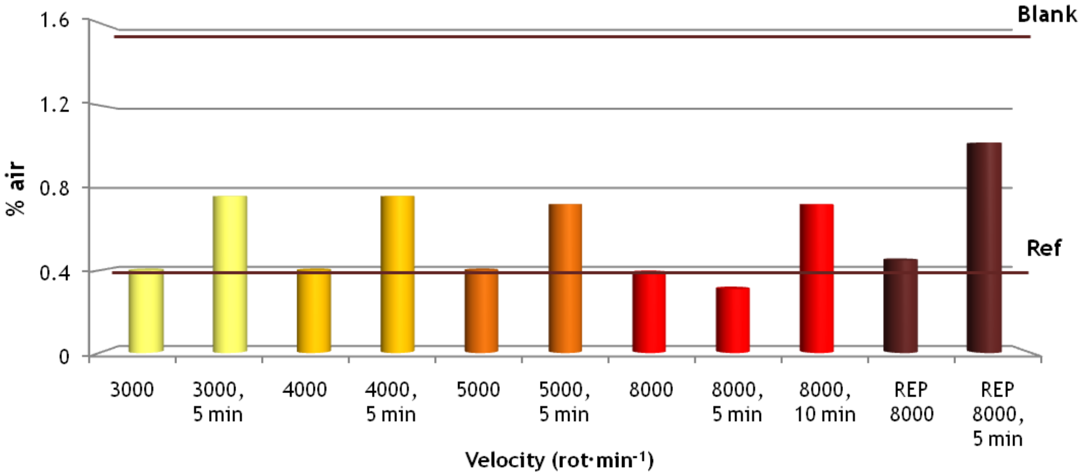

Figure 25 - Deaeration test results for PD-985-142 made in the Ultra-Turrax® at different velocities

All the emulsions had similar behavior excepting the emulsion made at 8000 rpm, because as it is noteworthy after five minutes the percentage of air was lower. To reinforce this observation, the emulsion was tested again and the results were similar to the other emulsions, in fact, after five minutes the percentage of air was the higher obtained.

As a consequence of this incoherence, the tests were repeated (for ten minutes this time) and the results are depicted in Figure 26.

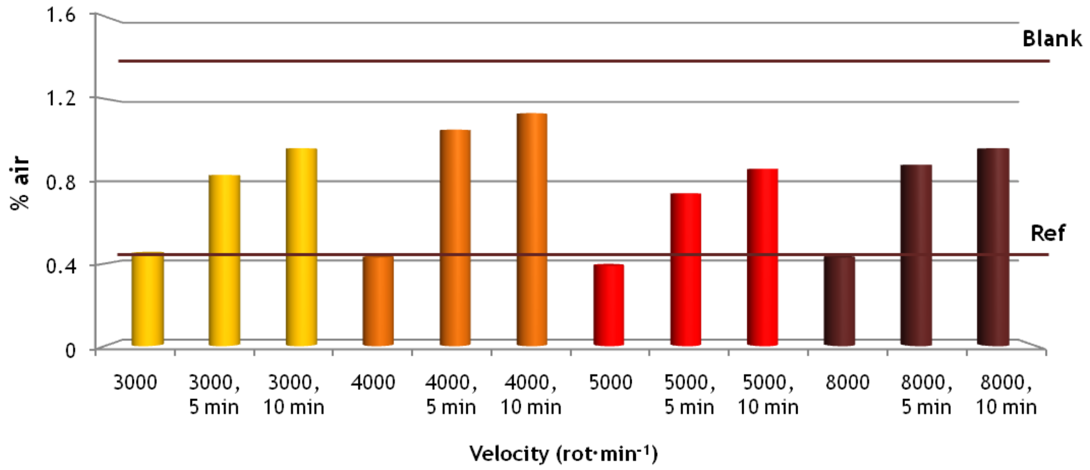

Figure 26 - Deaeration test results for PD-985-142 made in the Ultra-Turrax® at different velocities (repetition)

Once again, in the beginning, all the emulsions led to good results, though after five minutes the percentage of air was already increasing and continued to increase in the course of time.

It is also observable in Figure 26 that despite all the emulsions had similar results, the emulsion made at 5000 rpm gave the best result. As a result, this stirring speed was selected to make the following emulsions.

Emulsions PD-985-150, PD-985-151, PD-985-152 and PD-985-155 were not stable and for this reason the deaeration test could not be done for these emulsions.

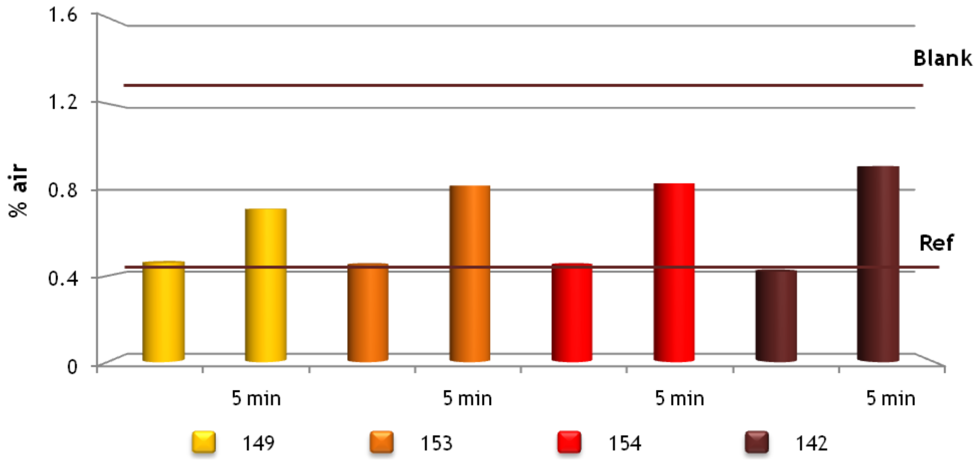

Figure 27 - Deaeration test results for PD-985-149, PD-985-153, PD-985-154 and PD-985-142

All the emulsions present in Figure 27 had equivalent results. Emulsion PD-985-149 had the lower percentage of air after five minutes and for this reason the next step was a trial to improve this formulation. Therefore the following formulations were similar to this one, but testing different PVAs.

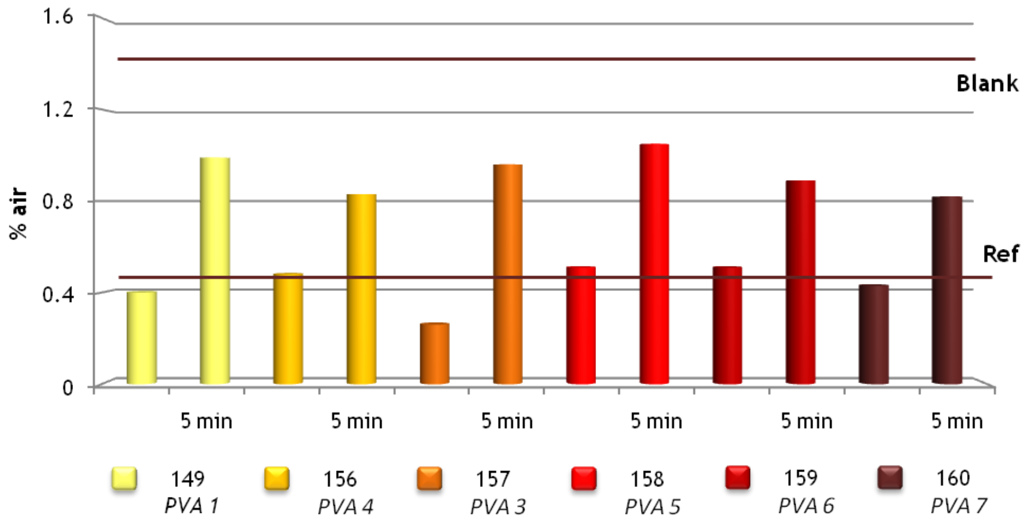

Figure 28 - Deaeration test results for PD-985-156 to PD-985-160

Observing the results, all the emulsions had good results at time zero. In fact all of them had a percentage of air below or equal to the reference. Nonetheless, after 5 min the percentage of air was already too high what means that these emulsions did not solve the problem of keeping their performance in the course of time.

Interpreting Figure 28 it is possible to conclude that the best polymer, at time zero, seems to be the *PVA 3* (present in PD-985-157). However, after 5 min the *PVA 4* (present in PD-985-156) and the *PVA 7* (present in PD-985-160) performances overcame *PVA 3*.

By establishing a comparison between this study and the previous one presented in Figure 16, where *PVA 1* and *PVA 3* were not present, the only common conclusion was found to be the good performance of *PVA 4*.

According to the accomplish studies on the influence of the polymer in emulsions performances, the results obtained in samples containing *PVA 3* revealed to perform better at initial time. After 5 minutes of testing, none of the different PVA polymer types had performances below the reference.

To conclude this project the antifoaming tests were repeated for the emulsions that had better results. Although there were formulations with similar results (for example the series showed in Figure 28), only a few were selected. The defoaming and the antifoaming tests results are shown in Table 29 and the deaeration tests results are illustrated in Figure 29.

Table 29 – Antifoaming tests results for the best formulations

Sample	Defoaming	Antifoaming
Blank		h = 20 mL
Reference	2 droplets	h = 14 mL
PD-985-137, 50 bar	2 droplets	h = 18 mL
PD-985-141, 100 bar	2 droplets	h = 17 mL
PD-985-142, 5 000 rpm	2 droplets	h = 14 mL
PD-985-157, 5 000 rpm	2 droplets	h = 16 mL
PD-985-160, 5 000 rpm	2 droplets	h = 15 mL

According to Table 29 all the emulsions have functioned as defoamers, while only emulsions PD-985-142 and PD-985-160 performed well as antifoams. It is especially noteworthy that emulsion PD-985-142 had a result equal to the reference.

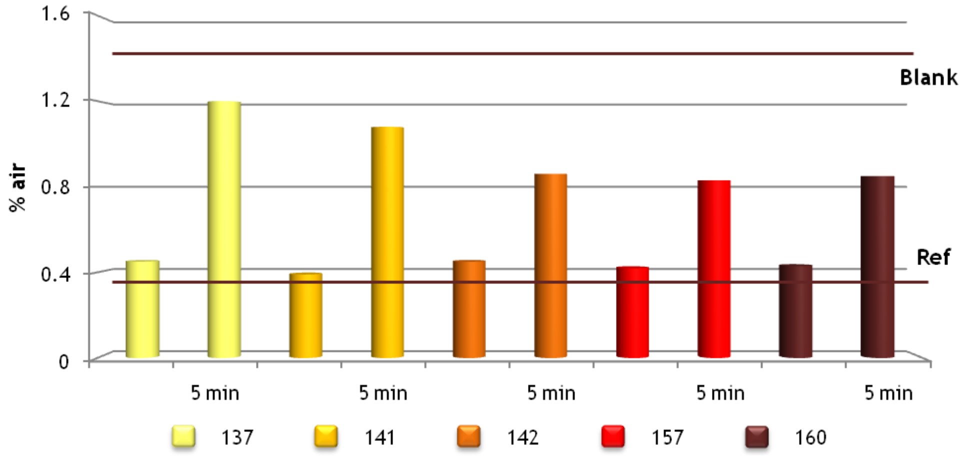

Figure 29 - Deaeration tests results for the best emulsions

With regard to the deaeration test, Figure 29 shows that all the emulsions at time zero had a percentage of air close to the reference and below 0.5 which means that they are good deaerators. However, after five minutes, the percentage of air is already too high so that they do not work in the course of time.

4 Conclusions

The emulsion PD-985-142, composed of *Solvent*, *Fatty Ester 2*, *Oleic Acid* and *PVA 4*, is the best tested emulsion in general terms. It led to the best results in the antifoam test, in which it was as good as the reference. The same emulsion had also one of the best performances regarding the deaeration test.

The emulsions PD-985-157 and PD-985-160, mutually composed of the *Solvent*, *Fatty Ester 2*, *Isost Acid 1,* and individually composed of *PVA 3* and *PVA 7,* respectively, also led to good results.

The previous conclusions allowed to conclude that the emulsions containing *Fatty Ester 2* as solid particles performed better than the other waxes, organic and inorganic particles also tested.

The methods used in the three antifoaming tests revealed to be subjective and thus inaccurate. Future work should aim to improve the methods and confirm the aforementioned conclusions.

The study of PVA polymers impact in the emulsions behavior has shown that *PVA 3* has a positive effect in the deaeration test at initial time. However, none of the studied polymers decreased the deaeration performances significantly after 5 minutes of testing.

Emulsions prepared using the Ultra-Turrax® revealed to have particle size distributions close to the reference product when processed at 4 000 rpm. When using the homogenizer, it was not possible to make emulsions with particle sizes in the range of the reference product, even by changing the working pressures. Future work should focus in the Ultra-Turrax®.

An accomplished study of deaeration performance in time of the reference product, showed an optimum percentage of air after 5 min and then a soft and asymptotic increase during 60 minutes. None of the emulsions considered in the same study had a similar behavior.

Future work should focus in the behavior of the emulsions in time, to check the reason of their failure in the course of time.

An overall conclusion of the accomplished project is that the results were not satisfactorily reproducible. It was not possible for me to identify the root of this behavior. Due to the low frequency at which fresh pulp samples were available, effort should be put in a future studying of the pulp properties and its degradation with time.

5 Evaluation of the Accomplished Work

5.1 Achievements

The main objective of this project was to find an antifoam product to apply in the paper industry. This product must be a defoamer, which means that it should destroy existing foam; moreover it must be a deaerator, as it has to lead the bubbles to coalescence so that they can cream faster to the surface and it must also be an antifoam, as it should prevent the foam formed naturally or upon agitation.

This objective was fulfilled for emulsion PD-985-142, composed of *Solvent*, *Fatty Ester 2*, *Oleic Acid* and *PVA 4*. This emulsion led to the best results in the antifoam test, in which it was as good as the reference, and also it had one of the best performances regarding the deaeration test.

During the project a concern was identified and it had to do with the behavior of the product in the course of time. It was thought that for the product to be efficient it should work for a period of time. For this reason, a study of deaeration performance in time was accomplished for the reference product, and it showed an optimum percentage of air after 5 min and then a soft and asymptotic increase during 60 minutes. Conversely, none of the emulsions considered in the same study had a similar behavior, including the aforementioned emulsion PD-985-142.

5.2 Limitations and Future Work

During the project, it was found that the results were not reproducible, since emulsions had different behaviors when tested at different times. It was impossible to identify the reason of this behavior, but it might have to do with the pulp samples used for the tests. As follows they were always different since it was not possible to collect pulp with higher frequency.

This fact implied that the experiments were carried out using pulp samples that were not always fresh and that may have suffered, thus, some degree of chemical or biological degradation. Apart from this, it was not possible to verify the quality of the pulp samples obtained from the paper industry costumer, which means that eventual variations in the pulp properties of each sample were not taken into account in the results. Therefore, future work should include a study of the pulp properties and its degradation with time.

As the emulsions prepared using the Ultra-Turrax® revealed to have particle size distributions close to the reference product when processed at 4 000 rpm, a feature that was not possible to reach using the homogenizer (not even by changing the working pressures), future work should focus in the Ultra-Turrax®.

None of the tested emulsions functioned for a period of time equivalent to the reference product activity.

Given that emulsion PD-985-142 led to results as good as the reference product at time zero, future work should aim to improve this formulation so that it can function in time, rather than trying to test new structural raw materials in new formulations.

It would be helpful to understand the source behind the instantaneous activity of emulsion PD-985-142, which can lay in the stability of the emulsion. If the emulsion is not stable when applied in the pulp, it will have a tendency to break and lose its antifoaming features.

5.3 Final Considerations

I do feel very satisfied with the accomplishment of this project, which answered successfully to the initial goals.

The project was very challenging and innovative, since this is an area scarce in information and where my *a priori* knowledge was low. In five months I had the opportunity to acquire useful know-how regarding colloidal systems, particularly in terms of emulsion formulations and emulsifying technologies. The contact and work with paper industry, which was not new for me, allowed to get better knowledge on a specific type of paper process, namely the recycling of used paper.

Apart from that I also had the opportunity to develop my final Master degree project in a company that successfully worked as a bridge between my studies at the university and the world of chemical industry and business. It was a great chance to adapt to this new environment.

The final balance is highly favorable and personally I do feel this internship and this project a worthwhile experience both from professional and academic points of view.

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Annex 1: EGT

The Entrained Gas Tester (EGT) is a measurement equipment that uses Boyles' Law for gases (P1*V1 = P2*V2) to determine the amount of air in a sample. At 1 atm pressure (about 15 psi) is applied to the sample in the EGT by turning a *Knob*. A trapped air bubble in the *Pressure Indicator* indicates the pressure and one atmosphere is reached when the bubble is reduced in size by one half. At this time, it is compressing the volume of all the air in the sample by one half. Since the total volume of the sample chamber is a known constant, there is just a simple percentage of air constant factor for each full revolution of the Knob.

Simply stated, after 1 atm is reached, all one has to do is count the number of revolutions it takes to get the Knob all the way back out. Then subtract the Correction Factor and multiply by the Percentage of Air Factor to get the final answer in percentage of air.

The EGT existing in the lab has 5 cm diameter and 0.6 cm wall. It is made of clear cast acrylic tube and has a sample volume of approximately 700 mL.

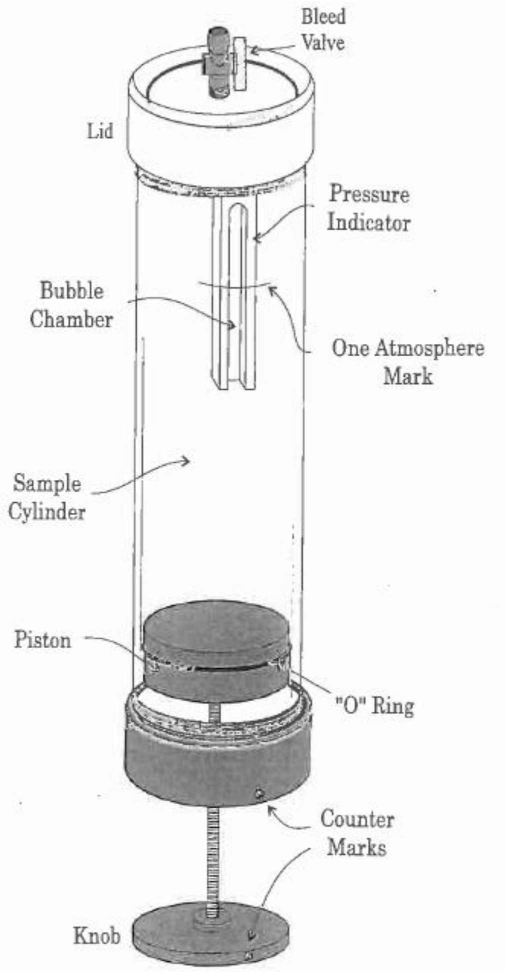

Figure 1.1 – Scheme of the EGT

Annex 2: Equipments

Mixer

	**EUROSTAR power basic** Powerful laboratory stirrer for tasks up to the "high viscosity" range • Speed range: 50 – 2 000 rpm • Motor rating input/output: 130/110 W

Big Mixer (Ultra-Turrax®)

	**IKA ULTRA-TURRAX® T 50 basic** Used in combination with an S 50 series dispersion tool, the ULTRA-TURRAX® T 50 basic unit is a high-speed dispersing and emulsifying unit capable of handling freeflowing and liquid media in batches. • Speed range: 1000 – 10 000 rpm • Power consumption 1100 W • Power output 700 W • Frequency: 50/60 Hz

Sonicator

	**BRANSON Ultrasonic Cleaner** **Model 1510** • Digital Control Plus Heat & Timer • Mechanical Timer Plus Heat • Mechanical Timer • Tank Size: 6" x 5.5" x 4" • Frequency: 40 kHz

Homogenizer

	**APV-1000 Homogenizer** Ideal for a wide variety of emulsions and dispersions • Operating pressure up to 1000 bar / 14 500 psi • Nominal capacities of 22 l/h / 6 gph

Viscometer

	**BROOKFIELD Digital Viscometer** **Model RVDV-E** • Direct reading of viscosity in cP or mPa.s • Accuracy: +/-1.0% of range

Moisture Analyzer (Dry Matter Percentage)

	**Mettler Toledo HR73 Moisture Analyzer** • Maximum sample weight: 71 g • Minimum sample weight: 0.1 g • Readability: 1 mg • Technology: Halogen • Temperature range: 50 – 200 ˚C

Particle Size Distribution

	**BECKMAN COULTER Laser Diffraction Particle Size Analyzer** • Particle size range for Single-Wavelength: 0.4µm - 2000µm • Particle size range for Multi-Wavelength: 0.017µm - 2000µm • One of the highest submicron resolutions, using the Polarization Intensity Differential Scattering (PIDS) technology

Annex 3: Deaeration test results

Table 3.1 – Deaeration test results for emulsions PD-985-102 to PD-985-106 and PD-985-112

Sample	Deaeration
Blank	% air = 1.91
Reference	% air = 0.40
PD-985-102 at 150 bar	% air = 0.72
PD-985-103 at 150 bar	% air = 0.71
PD-985-104 at 150 bar	% air = 0.76
PD-985-105 at 100 bar	% air = 0.85
PD-985-105 at 150 bar	% air = 1.13
PD-985-106 at 150 bar	% air = 1.26
PD-985-112 at 100 bar	% air = 1.14
PD-985-112 at 150 bar	% air = 1.23

Table 3.2 – Deaeration test results for emulsions PD-985-120, PD-985-123 and PD-985-124

Sample	Deaeration
Blank	% air = 1.60
Reference	% air = 0.45
PD-985-120 at 50 bar	% air = 0.52
PD-985-120 at 100 bar	% air = 0.68
PD-985-120 at 150 bar	% air = 0.62
PD-985-123 at 50 bar	% air = 0.59
PD-985-123 at 100 bar	% air = 0.68
PD-985-123 at 150 bar	% air = 0.74
PD-985-124 at 50 bar	% air = 0.57
PD-985-124 at 100 bar	% air = 0.66
PD-985-124 at 150 bar	% air = 0.77

Table 3.3 - Deaeration test results for emulsions PD-985-127 and PD-985-129

Sample	Deaeration
Blank	% air = 2.22
Reference	% air = 0.62
PD-985-127 at 50 bar	% air = 0.80
PD-985-127 at 100 bar	% air = 0.82
PD-985-127 at 150 bar	% air = 0.89
PD-985-129 at 100 bar	% air = 0.94
PD-985-129 at 150 bar	% air = 0.60
PD-985-129 at 150 bar, after 5 min	% air = 1.59

Table 3.4 - Deaeration test results for emulsions PD-985-130 and PD-985-131

Sample	Deaeration
Blank	% air = 1.91
Reference	% air = 0.59
PD-985-130 at 50 bar	% air = 0.85
PD-985-130 at 100 bar	% air = 0.72
PD-985-130 at 150 bar	% air = 0.86
PD-985-131 at 50 bar	% air = 0.96
PD-985-131 at 100 bar	% air = 0.99
PD-985-131 at 150 bar	% air = 1.05

Table 3.5 - Deaeration test results for emulsions PD-985-135 and PD-985-136

Sample	Time (min)	Deaeration
Blank	0	% air = 2.19
Reference	0	% air = 0.76
PD-985-135 at 50 bar	0	% air = 0.91
PD-985-135 at 50 bar	5	% air = 1.90
PD-985-135 at 100 bar	0	% air = 0.89
PD-985-135 at 100 bar	5	% air = 2.11
PD-985-135 at 150 bar	0	% air = 0.96
PD-985-136 at 50 bar	0	% air = 1.02
PD-985-136 at 100 bar	0	% air = 1.05
PD-985-136 at 150 bar	0	% air = 1.00

Table 3.6 - Deaeration test results for emulsions PD-985-137 and PD-985-138

Sample	Time (min)	Deaeration
Blank	0	% air = 1.45
Reference	0	% air = 0.49
PD-985-137 at 50 bar	0	% air = 0.37
PD-985-137 at 50 bar	5	% air = 0.83
PD-985-137 at 100 bar	0	% air = 0.40
PD-985-137 at 100 bar	5	% air = 0.83
PD-985-137 at 150 bar	0	% air = 0.43
PD-985-137 at 150 bar	5	% air = 0.91
PD-985-138 at 50 bar	0	% air = 0.51
PD-985-138 at 50 bar	5	% air = 0.96
PD-985-138 at 100 bar	0	% air = 0.46
PD-985-138 at 100 bar	5	% air =1.03
PD-985-138 at 150 bar	0	% air = 0.46
PD-985-138 at 150 bar	5	% air = 0.96

Table 3.7 - Deaeration test results for emulsions PD-985-139 to PD-985-143

Sample	Time (min)	Deaeration
Blank	0	% air = 1.97
Reference	0	% air = 0.52
PD-985-139 at 60 bar	0	% air = 0.65
PD-985-139 at 60 bar	5	% air = 1.54
PD-985-139 at 100 bar	0	% air = 0.69
PD-985-139 at 200 bar	0	% air = 0.71
PD-985-140 at 60 bar	0	% air = 0.74
PD-985-140 at 100 bar	0	% air = 0.68
PD-985-140 at 200 bar	0	% air = 0.65
PD-985-141 at 60 bar	0	% air = 0.65
PD-985-141 at 100 bar	0	% air =0.37
PD-985-141 at 100 bar	5	% air = 0.91
PD-985-141 at 200 bar	0	% air = 0.45
PD-985-141 at 200 bar	5	% air = 0.99
PD-985-142 at 60 bar	0	% air = 0.39
PD-985-142 at 60 bar	5	% air = 0.76
PD-985-142 at 60 bar	10	% air = 0.28
PD-985-142 at 60 bar	15	% air = 0.86
PD-985-142 at 60 bar	30	% air = 1.20
PD-985-142 at 60 bar	45	% air = 1.20
PD-985-142 at 60 bar	60	% air = 1.42
PD-985-142 at 100 bar	0	% air = 0.42
PD-985-142 at 100 bar	5	% air = 0.77
PD-985-142 at 100 bar	10	% air = 0.77
PD-985-142 at 100 bar	15	% air = 0.99

PD-985-142 at 200 bar	0	% air = 0.40
PD-985-142 at 200 bar	5	% air = 0.72
PD-985-142 at 200 bar	10	% air = 0.79
PD-985-142 at 100 bar	15	% air = 0.93
PD-985-143 at 60 bar	0	% air = 0.40
PD-985-143 at 60 bar	5	% air = 1.22
PD-985-143 at 100 bar	0	% air = 0.48
PD-985-143 at 100 bar	5	% air = 1.20
PD-985-143 at 200 bar	0	% air = 0.62

Table 3.8 - Deaeration test results for emulsions PD-985-144 and PD-985-145

Sample	**Time (min)**	**Deaeration**
Blank	0	% air = 1.48
Reference	0	% air = 0.40
PD-985-144 at 50 bar	0	% air = 0.46
PD-985-144 at 50 bar	5	% air = 0.86
PD-985-144 at 100 bar	0	% air = 0.43
PD-985-144 at 100 bar	5	% air = 0.96
PD-985-144 at 150 bar	0	% air = 0.51
PD-985-145 at 50 bar	0	% air = 0.54
PD-985-145 at 100 bar	0	% air = 0.77
PD-985-145 at 150 bar	5	% air = 0.80

Table 3.9 - Deaeration test results for emulsions PD-985-146 to PD-985-148

Sample	Time (min)	Deaeration
Blank	0	% air = 1.96
Reference	0	% air = 0.71
PD-985-146 at 50 bar	0	% air = 0.68
PD-985-146 at 50 bar	5	% air = 1.47
PD-985-146 at 100 bar	0	% air = 0.76
PD-985-146 at 100 bar	5	% air = 1.54
PD-985-146 at 150 bar	0	% air = 0.72
PD-985-146 at 150 bar	5	% air = 1.03
PD-985-147 at 50 bar	0	% air = 0.79
PD-985-147 at 100 bar	0	% air = 0.77
PD-985-147 at 150 bar	0	% air = 0.65
PD-985-147 at 150 bar	5	% air = 1.47
PD-985-148 at 50 bar	0	% air = 0.56
PD-985-148 at 50 bar	5	% air = 1.82
PD-985-148 at 100 bar	0	% air = 0.54
PD-985-148 at 100 bar	5	% air = 1.99
PD-985-148 at 150 bar	0	% air = 0.51
PD-985-148 at 150 bar	5	% air = 2.13