Optimization of the production process in the detergent industry

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Abstract

The operation of industrial plants requires the study and development of products, assessing their quality and safety for consumers, as well as its stability, progressing into industrial production. This work aimed the optimization of the production process in the detergent industry, and encompassed several topics related to this theme: Revision and amendment of laboratory methods related to the determination of physical and chemical characteristics of the products; Statistical process control of different products; Statistical control of pre-packaged products; Stability tests of products throughout a short period of time, to ensure their quality; Improvement of the manual dishwashing detergent; Development of an abrasive hand cleaning gel; Study on competitive products. The revision of the laboratory methods improved the quality control performed on products, regarding the determination of viscosity and density. The statistical control of pre-packaged products enabled the determination of the main criteria to improve the filling systems of the company. With the study on competitive products, quantification of the ingredients present in these products was assessed. Thus, one could better understand its functioning. The stability tests performed enabled the detection of instability in the pH values of the manual dishwashing detergent. This problem was solved by adding chelating agents to the formulation. Finally, it was possible to develop an abrasive hand cleaning gel for use in industrial fields and workshops.

Keywords: Quality, Statistical Control, Stability; Improvement of products, detergents.

1. The Group

The group represents a holding company from a group of Portuguese companies operating in the Business Services, covering the following areas: Social and public Services, food marketing and logistics, cleaning services, pest control, vending machines, among other complementary services.

Their services are designed to companies and institutions, such as, government, hospitals, schools and armed forces. The company operates with the highest standards of food safety and hygiene, using the most modern techniques, applied by all employees and supervised by permanent teams of inspectors and quality technicians[7]. To ensure the trust and loyalty of consumers, it is necessary to serve them with quality products and brands. With the highest standards of quality, the group is able to do well at first, reducing waste and costs.

1.1. The company

The company is located in Carnaxide and aims to the production and packaging of detergents and cleaning products for industrial plants and institutions. Belonging to the group, is designed to ensure the efficiency and competitiveness of cleaning and hygiene products. The company

produces both liquid and powder detergents, with a product line called Sonaril.

Sells more than 40 products in diverse areas as shown in Table 1 (Brief Listing of products). The company started its activity in 2013 with an annual production of 1,500 tons (monthly average of 125 tons). The production is carried out discontinuously, where each batch corresponds to a single product made[1].

Class	Product	Description
Personal Cleansing	A	Hand sanitizer with alcohol
	B	Bactericide liquid soap
Manual Dishwashing Detergent	C	Liquid detergente for manual dishwashing
	D	Powder alkaline detergent
Mechanical Dishwashing Detergent	E	Chlorinated dishwashing detergent
	F	Rinse aid
	G	Acid Descaler
Household Cleaners	I	Chlorine Bleach
	J	All-purpose ammoniacal
	L	All-purpose Detergent
	M	Glass cleaner
	N	Oven cleaner

Table 1 – List of some products that are available at the company.

2. Theoretical Introduction

2.1. Detergents

A detergent is a product created to improve detergency phenomenon. In general, it comprises a solvent, an active basic compound - surfactant - and additional components such as, additives, rheology regulators, perfumes, preservatives, among others.

The surfactants are amphipathic molecules that consist of a hydrophobic part (non-polar), usually a straight or branched hydrocarbon chain containing from 8 to 18 carbon atoms. This chain is linked to a hydrophilic ionic part (polar)[2].

The detergency is a process that involves the removal of an undesirable substance, such as, soil of a solid surface, by applying a mechanical action in the presence of a chemical substance. This chemical has the power to reduce the tension between the soil and the surface, namely surface tension. The detergency mechanism involves three phases (Figure 1). The first step consists in wetting the surface to be cleaned. The adsorption of the surfactant into the soil/ surface interface allows wetting of surfaces by water. The soil removal, the second step, is achieved by mechanical stirring action, enabling the surfactant to drag the soil particles into the washing bath. Finally, the particle of dirt can be stably maintained in the washing bath within the walls of a micelle formed by the surfactant molecules[4].

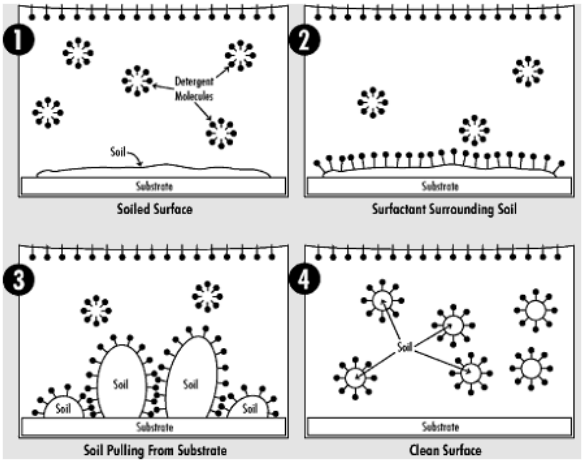

Figure 1 – Detergency mechanism[5].

2.2. Statistical Process Control

The Statistical Process Control is a control system that allows the actions to take to the process in a preventive manner. This study provides information on the number of elements that constitute the process, whether is the products, production stages, changes in materials, etc. The data from this study will identify the causes that affect the process and designate corrections to the production process or even on product specifications if necessary[3].

2.2.1. Control charts for variables

The control charts are a commonly used statistical technique, simple yet powerful.

Control charts are used to determine compliance with the specification limits. Process "under control" does not mean the product is within the specifications, as well as, process "out of control" does not mean the product is outside the specifications. The Charts X-R are the statistical control techniques used the most[3]. In order to construct these charts, is required the knowledge of the control parameters, such as, control limits, process mean and range of the data. These parameters should be based on, at least, 25 samples, where each sample consists of 4, 5 or 6 sub-samples[3]. The following equations represent the main parameters to be calculated to enable the construction of a chart X-R.

$$\bar{\bar{X}} = \frac{\overline{x_1}+\overline{x_2}+\cdots+\overline{x_m}}{m} \quad \text{Eq. 1}$$

$$\bar{R} = \frac{R_1+R_2+\cdots+R_m}{m} \quad \text{Eq. 2}$$

Where $\bar{\bar{X}}$ is the process mean and $\overline{\mathrm{R}}$ is the average range of the data.

$$UCL = \bar{\bar{X}} + A_2\bar{R} \quad \text{Eq. 3}$$

$$LCL = \bar{\bar{X}} - A_2\bar{R} \quad \text{Eq. 4}$$

Where UCL is the Upper Control Limit and LCL is the Lower Control Limit. A_2 is a constant.

2.2.2. Process Capability Studies

Once a process is in statistical control, it is necessary to assess whether the process is capable of meeting the specifications or not, using capability indicators. The indicators required to calculate the process capability are the process capability (Cp) and process capability index (Cp_k). These indicators are calculated according to Equations 5 and 6, respectively[3].

$$Cp = \frac{(USL-LSL)}{6\sigma_r} \quad \text{Eq. 5}$$

$$\mathrm{Cp}_k = Min\left(\frac{USL-\bar{\bar{X}}}{3\sigma_r}, \frac{\bar{\bar{X}}-LSL}{3\sigma_r}\right) \quad \text{Eq. 6}$$

Where USL is the Upper Specification Limit and LSL is the Lower Specification Limit.

The estimated value of the average is equal to $\bar{\bar{X}}$ and the standard deviation is calculated according to Equation 7.

$$\sigma_r = \left({}^{1}/_{d_2}\right) \times \bar{R} \quad \text{Eq. 7}$$

Where d_2 represents a constant.

3. Production Process

The company is able to produce liquid and powder detergents. The production of liquid detergents is carried out in reactors with different capacities.

The larger reactor in the facility has a capacity of $5m^3$ and is exclusively used for the production of the manual dishwashing detergent. This reactor has direct inlet of water and some main raw materials. The remaining materials are weighed in two industrial scales found in the production area. There is also a $2m^3$ reactor designed for the production of several liquid products, with both alkaline and neutral natures. The direct inlet to this reactor is exclusively for water (demineralized or network), with the remaining raw materials being weighed on the industrial scales of the production area.

3.1. Packaging Area

Adjacent to the production area is the area of packaging. The packaging of the products is mostly manual. Nevertheless, one can find two automatic filling machines in the facility. The products can be packaged in 500ml up to 20L, according to the monthly consumer needs. Packaged goods are stacked and protected with shrink film, as shown in Figure 2. Products packaged in 500mL, 750mL and 1L sizes are placed in cardboard boxes.

Figure 2 – 20L pallet with shrink film.

The packaging of product C is performed in an automatic Tormeca filling machine with two filling outputs. This product is commercialized in packs of 5L, 10L and 20L. The bactericidal liquid soap product Q is packaged in another automatic Tormeca filling machine with only one output. This product is sold in packs of 500ml.

4. Results and discussion

4.1. Analytical methods for quality control of detergents

4.1.1. pH Assessment

The pH determination is performed by the potentiometric method and is applied to all liquid and powder products manufactured. In liquids the reading is taken as is, and in powders, it is previously produced a 1% solution (w/w).

To assess the accuracy of the method assays were performed to different products by varying sampling conditions in the reactors. Samples were collected from two specific locations (top and bottom) for all the reactors, except for 1m³. Relatively to the 5m³ reactor, a single product was sampled, neutral. For the 2m³ reactor three types of products were sampled, one neutral and two alkaline with pH values between 12-13 and 13-14 , and finally for the 1m³ reactor only one product was sampled, neutral. From Table 2 one can see that the data for reactor 5m³ comprises deviation larger than the external laboratory (CTV) values. The method is less accurate for this product. Nevertheless taking the sample from the bottom produces a smaller standard deviation. Relatively to the neutral liquid from reactor 2m³, the deviation is low. In the case of alkaline liquids, the deviation increased, and readings of samples with pH values above 12 will have an associated error. Finally, for 1m³ reactor the results are very similar to the ones of the neutral products from 2m³ reactor. There is no risk of large errors associated with these pH readings.

Reactor	Sampling site	BSG	CTV	Deviation (%)
5m³	Top	6,8	-	-
	Bottom	6,7	**6,5**	**3,4**
2m³ Neutral	Top	6,6	-	-
	Bottom	6,7	**6,6**	**0,9**
2m³ pH:12-13	Top	12,7	**-**	**-**
	Bottom	12,7	**12,9**	**1,5**
2m³ pH:13-14	Top	13,4	-	-
	Bottom	13,3	**13,1**	**1,6**
1m³	Top	6,2	**6,2**	**1,1**

Table 2 – Data from the company (BSG) and the external laboratory (CTV) related to three types of reactors.

4.1.2. Specific gravity of liquid products

The determination of the specific gravity of all liquid products was performed by hydrometers. Samples sent to the external laboratory, showed that for viscous products, the density values were different compared to the company's values. Thus, tests were performed with a pycnometer for this type of products. In Figure 3 are represented the comparisons between the two methods from the company (pycnometer and hydrometer) and the results from the external laboratory (CTV). One can see that the data from the pycnometer and CTV are the closest. The hydrometer method displays values by excess, ie, higher than the data from both laboratories. The product C is a product of medium viscosity, in other words, fluid resistance to deformation occurs. Therefore using the pycnometer is a preferable alternative.

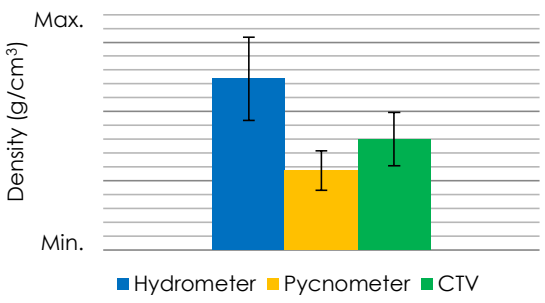

Figure 3 – Comparison of density values according to three different methods.

4.1.3. *Viscosity Assessment*

To assess whether the viscometer of the company was suitable for viscosity readings of the manufactured products, some tests were performed. It was concluded that another viscometer was required, more adequate to the product's viscosity. Thus, the company acquired a Brookfield LV viscometer.

Depending on the product, the spindle to use is chosen accordingly to Table 3. First the sample is placed in a 500mL container. This container will be used for all products and has a known diameter of 0,81cm. Then the spindle is immersed in the sample up to the reading mark. Finally the rotor rotation speed is defined according to Table 3. After stabilization of the temperature, readings can be taken.

Product	***Spindle***	***Velocity (rpm)***	***Temperature (ºC)***
C	S61	6	20
O	S63	30	20
B	S63	30	20
Q	S63	20	20
S	S61	4	20
A	S62	12	19

Table 3 – Parameters to determine the viscosity of products.

4.2. Statistical Process Control

4.2.1. *Product I*

This product is manufactured in 1m^3 reactors with manual entry of all raw materials. It is a chlorinated product with alkaline nature. Figure 4 shows the control chart related to average pH values. One can observe that the process is controlled with a stabilization trend around the process mean value which is supported by the decrease in the mean range. The values of the two process capability index are greater than 1.33, which means that this process is able to comply with the specifications and is also centered (Table 4). In Figure 5 is shown the chart relating to density readings from the hydrometer method. As can be seen, the process is quite controlled. The specification limits (USL/LSL) imposed by the company are correctly defined, since all data is within the control limits (UCL/LCL).

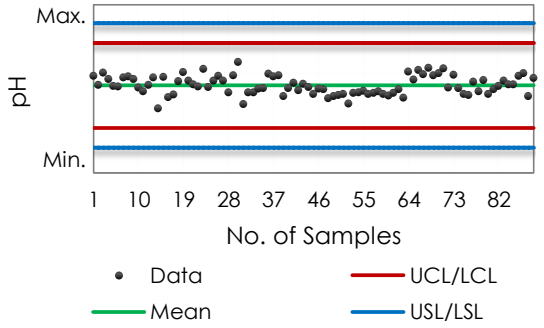

Figure 4 – Control Charts X / R of the mean pH values.

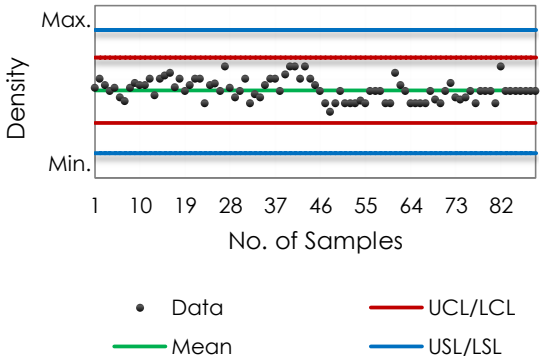

Figure 5 – Control Charts X / R of the mean density values.

4.2.2. *Product L*

This product is manufactured in the 2m^3 reactor. It is a neutral, multi-purpose product used to clean all surfaces. The major drawback of this product is the need to do a manual neutralization at the end of its production process. In Figure 6 depicts the control chart regarding the average values of pH. It can be seen a zone in the chart where the warning thresholds aren't displayed. After establishing the warning limits by the company, there was a stabilization of the process within these

values. Due to the large range between consecutive readings, the control process limits are rather larger than the warning. In order to set the existing warning limits as product specification, it is required to automate the process, or to review the pH value of neutralization tightening the acceptance levels. Thus, this process can be as stable as possible, avoiding high ranges between readings.

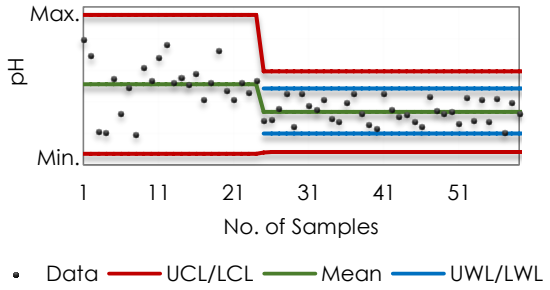

Figure 6 – Control Charts X / R of the mean pH values.

In Figure 7 it is shown the control chart relating to density values. It can be seen that although the control limits have a similar range as the warning limits, the values are not centered. This is due to the high value of the mean and to large ranges between consecutive readings, derived from reading errors of operators. The hydrometer method used to determine the density of products has a scaling limit with the same value as the midpoint of the warning threshold.

Nevertheless, it is a process that tends to stabilize for values below the process average, as shown by the most recent data presented in the chart control.

As shown in Table 4, Index capacity values for pH show that although the process is centered within the warning limits, this is not a capable process, once both values are below the unit. Thus, it will be necessary to extend these limits and continue to do a statistical process control. Relatively to density, the process has a value of Cp near the unit, indicating that the process is satisfactory, but is decentered.

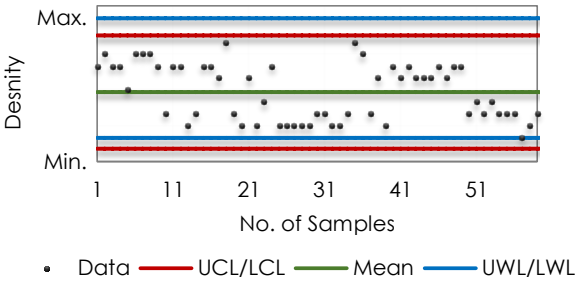

Figure 7 – Control Charts X / R of the mean density values.

Parameter	**Product I**		**Product L**	
	pH	Density	pH	Density
Cp	2,0	1,9	0,6	1,0
Cp_k	2,0	1,8	0,5	0,8

Table 4 – Parameters of statistical process control.

4.3. Statistical Control of Prepackaged

4.3.1. Automated process

Product Q is packed in an automatic filling machine, as described in Chapter 3. The product is sold in translucent and durable packs. Figure 8 represents the control chart for the average weights. One can see that it is quite a controlled process. Although there are variations in the amplitude of the weights, these are of maximum 0,015. The process is slightly above the nominal quantity, without exceeding the specification limits imposed by the company. The data capacity index shown at Table 5, indicate that the process is capable, which is within the specification limits and is able to comply with them, as both the capacity index, as are operating above 1,3.

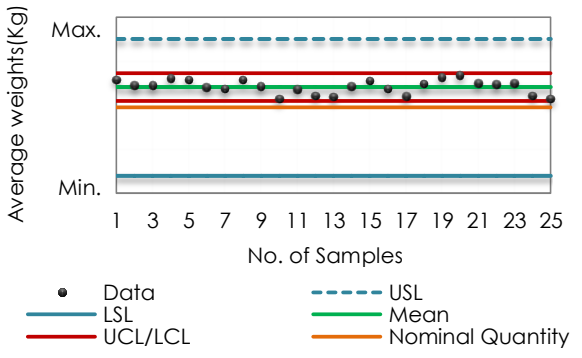

Figure 8 – Control Charts X / R of the average weight values.

4.3.2. *Manual process*

Product I is an example of one product packaged manually. Figure 10 represents the control charts for the filling of 5L format. It can be observed that the process was below the LSL imposed by law (samples 1 to 6). Thus, as shown in Figure 9, was found an auxiliary mark on the package which could help the manual filling. The nominal quantity necessary in the container must be above the labeled black arrows. After awareness of this procedure, a process weight average contiguous with the nominal quantity was obtained. The process is considered stable with a low range. However, looking at the values in Table 5, one can find process capacity values equal to 1. In this case, the range of the natural process and the specification limits are identical: it is said that the process is able to marginally meet specification limits. Neverthless, the process is centred.

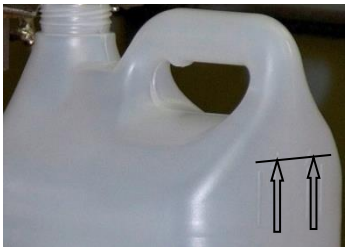

Figure 9 – Auxiliary mark for manual filling.

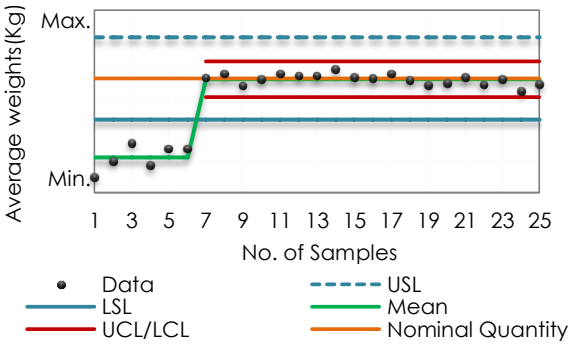

Figure 10 – Control Charts X / R of the average weight values.

Parameter	Automated Process	Manual Process
Cp	1,4	1,0
Cp_k	1,4	1,0

Table 5 – Parameters of statistical control of prepackaged.

4.4. Study of the product's stability

The study of the product's stability was periodic testing various types of products in order to simulate the environment in which products can be stored. One of the products selected for the implementation of these tests was product C, for being a well commercialized product. Chlorinated products were chosen for presenting volatility of their active ingredient, sodium hypochlorite. Finally, a product in development was chosen to verify its stability over time prior to begin commercializing.

The tests were conducted under several conditions, namely:

* Fridge at 6ºC;
* Room temperature;
* Heat at 40ºC;
* Sunlight.

The tests were conducted for 13 weeks and the organoleptic and chemical product changes were recorded (if any). Figure 11 shows the evolution of pH values over the 13 weeks for product C. It can be seen that in the heat and cold conditions, the pH remains constant over time, yet at room temperature, the pH decreases, which results in significant instability of the product. In terms of organoleptic properties, the product turns cloudy in cold conditions, unlike its crystalline form at room temperature. The use of hydrotropes increases the solubility of the surfactant in water, lowering the cloud point[2].

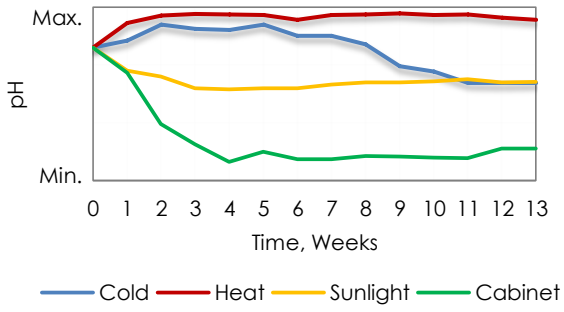

Figure 11 – Evolution of pH during 13 weeks for different storage conditions for product C.

4.4.1. *Improvement of product C*

During the stability studies, it was found that the product lowered its pH value, over time. It became known that it was the addition of the anionic surfactant that triggered instability due to the fact that the total hardness of water reacts with the surfactant releasing H^+ ions to the medium. Some quelating agents were selected for stability treatments. Stability tests were performed using phosphoric acid, citric acid, demineralized water and finally two different concentrations of EDTA. It can be seen in Figure 12, that using EDTA presented the desired effect and stabilized the pH throughout the testing period. Relatively to the two acids used, a reduction in pH values was still observed. Finally, the use of demineralized water didn't show any positive results.

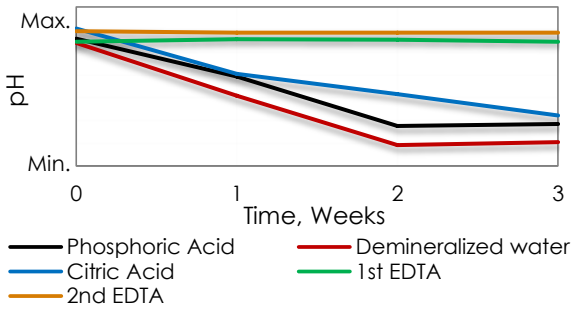

Figure 12 – Evolution of pH during 3 weeks to different types of stability treatments.

4.4.2. *Chlorinated products*

Relatively to chlorinated products was determined the chlorine loss over time to establish an estimated shelf life for the product. As mentioned above, solutions of sodium hypochlorite have limited storage stability. The decomposition is due to the following two reactions[6]:

$$3\ NaOCl \rightarrow 2\ NaCl + NaClO_3$$

$$2\ NaOCl \rightarrow 2\ NaCl + O_2$$

As shown in Figure 13, when the products were exposed to normal storage conditions, ie, stored in a cabinet at room temperature (16ºC) protected from light, the results show a chlorine loss in the order of 5% (Product E-red line). The most stable product is the product I (Blue line), with a maximum loss of 2%. For the product T (Yellow line) and the new product under development (Green line) the losses are similarly. Thus, if storage is performed under these circumstances for 3 months, the product loses between 2-5% active chlorine, still guaranteeing a full effectiveness.

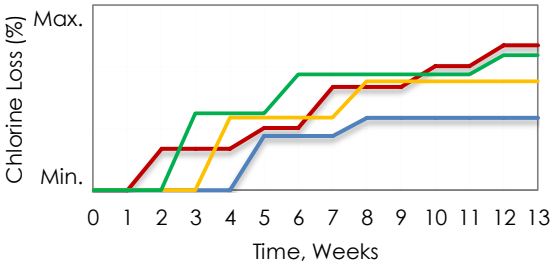

Figure 13 - Evolution of chlorine loss (%) of different products over 13 weeks in room temperature.

4.5. Development of an abrasive soap

To enhance and develop the company's market, a new product was designed to be used in heavy industry. The first formulation of this product was based on the addition to the already produced soap gel, two distinct abrasive agents: calcium carbonate and sawdust. This first formulation showed some drawbacks, including sedimentation of the two abrasives used (Figure 14). The second step was focused on changing the abrasives used, having been decided to use low density polyethylene, nutshell and pumice stone. In order to avoid the settling of these new abrasive, a new material was incorporated: a polysaccharide named Xanthan Gum. This Gum functions as a stabilizer by preventing the various constituents of a solution from separating. The maximum concentration of this polysaccharide in the soap formulation was obtained and the results were as expected. Finally the organoleptic characteristics of the product also requested attention and was chosen to use an orange color with matching orange essence. The

concentration of essence used was based on the recommend values. A higher concentration could cause the disruption of the gum and make the product less viscous. Thus, after hand washing, a nice orange flavoring lasts.

Figure 14 - Sedimentation of the two abrasive used in the formulation of the new product.

4.6. Analysis of competitive dishwashing detergents

In order to get an overview of the surrounding market, a study was carried out to some products of manual dishwashing. This study assessed the quantitative and qualitative composition of the products, and was aimed to determine various parameters, including: pH, density, viscosity, dry matter, anionic active matter and foam formation. The determination of all parameters except foam formation was made according to the analytical methods described above. For the determination of foaming, the following method was used: Use 5g of product to be analyzed and transferred to a 1000 ml volumetric flask. The solution is then measured into a 25 mL graduated 100ml cylinder. Stir five times, tilting the cylinder up and down. Finally readings at 30 seconds, 3minutes, 5minutes, must be performed to assess foam stability.

Table 6 shows the result of the study. As can be seen each one of the analyzed products has different characteristics and the company's products fall into the range of their variations. One can conclude that for products with higher content of anionic active matter, a greater foam formation is observed. Accordingly, foam is directly proportional to the amount of surfactants presented in a dishwashing detergent. On the contrary, it can't be confirmed that a product which presents a higher viscosity, has necessarily higher content of anionic matter. A thicker product may contain electrolytes. Finally, the differences between the values obtained by the dry extract and content of anionic matter have two distinct types of justification:

1. Relatively to product 1 the existence of non-ionic surfactants that are not accounted in the determination of anionic matter.

2. The presence of other raw materials, such as salts, preservatives, among others, which are not volatile.

Parameters	***1***	***2***	***Product C***	***Product P***
pH	8,5	8,8	6,5	6,5
Density (g/cm³)	1,018	1,050	1,022	1,026
Viscosity (cP)	830	575	520	1075
Dry extract (%)	25,1	13	6,8	13,5
Anionic Active matter (%)	14,3	8,3	4,8	12,3
Foam formation (30'')	58	42	36	43
Foam formation (5')	56	41	36	42

Table 6 - Analysis of the different parameters accordingly to competitive dishwashing products.

5. Conclusions

This master thesis covered different topics related to the company where it was performed, and the conclusions include several topics.

A review of the analytical method of pH revealed that the device shows different accuracies depending on the type of product read. A review of the viscosity method revealed that the Krebs viscometer, available at the company, was not the most appropriate viscometer, having been acquired a Brookfield LV which showed to be more precise for the manufactured

products. The revision of the density method showed that for products with medium and high viscosity, using the hydrometer becomes unviable and requires the use of a pycnometer instead. The analysis of process capability by control charts X/R and the assessment of the capacity index for different products, enabled to examine the manufacturing process. The introduction of prepackaged statistical control corrected some of the procedures that were used. In automated packaging, it was the adjustment of viscosity values of products and for the manual filling, the use of an auxiliary mark on the container. The stability study enabled the assessment of how the storage conditions influence the characteristics of the products. It allowed setting time limits for the use of chlorinated products with negligible chlorine loss. The study carried out at competitive products allowed quantifying the foam formation. It follows that product 1, has a higher foam volume. Products manufactured at the company, C and P differ in anionic matter and this is seen in the quantity and quality of foam formation. Finally, the development of a new product was started yet not completed. It was possible to make changes in the soap formulation, so, to ensure better product stability.

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