



M 2023

STUDY OF DIFFERENT DIPPING PROCESS CHARACTERISTICS IN FOAM FORMATION

ANA BEATRIZ DE CARVALHO MARQUES
MASTER THESIS IN CHEMICAL ENGINEERING
PRESENTED TO THE FACULTY OF ENGINEERING
OF THE UNIVERSITY OF PORTO

Master in Chemical Engineering

***Study of different dipping process
characteristics in foam formation***

Master dissertation

by

Ana Beatriz de Carvalho Marques

Developed within the course of dissertation

held in

Continental - Indústria Têxtil do Ave, S. A.



Supervisor at FEUP: Prof. Margarida Bastos

Joint supervisor at FEUP: Prof. Joana Peres

Coordinator at Continental - ITA: Eng. Cátia Costa



February 2023

Acknowledgment

I would like to thank Continental - Indústria Têxtil do Ave, S.A, and Faculdade de Engenharia da Universidade do Porto for providing me with the opportunity to work in one of Portugal's most famous industries. This opportunity provided me with a wealth of knowledge.

To Eng. Magda Dias, Eng. Pedro Costa and Eng. Nuno Drumond for all of their assistance when I needed it. Special thanks to Eng. Cátia Costa for all of her help and supervision throughout the project.

To Professor Margarida Bastos and Professor Joana Peres, for all of your guidance and assistance during this journey, as well as the sharing of ideas to produce this dissertation.

To TUNAFE, my university family, the people that have helped develop my skills. Thank you for all the laughs, cries and fears, for helping me grow, and for all the love. An special thank you to Joana Martins for all the advice and hard work on making me a better person.

To Cumperativa, to those who taught me what academic life means, thank you for teaching me to always have fun and seize every moment. Thank you for all the studding days, and great times, I am grateful for your friendship.

To my boyfriend Luís Cruz, for all the great moments and all the support during these years. Without you it would not be the same.

A special thank you to the most important people in my life, my mother Sandra Carvalho, my father Luís Marques, my brother Luís Pedro and to my grandparents, for believing in me and supporting all of my aspirations. Thank you for never letting me give up and always pushing me to be the best version of myself.

Professor Margarida Bastos and Joana Peres, supervisor and co-supervisor of this dissertation, are integrated members of LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, financially supported by LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC).

Abstract

This thesis exposes a study about the foaming problem that occurs in the cord impregnation manufacturing process of the company. This is a final and essential process in the company's production circuit because it is during this process that the textile acquires a sufficient and fundamental adhesion surface for the next phase, which consists in the adhesion of the textile to the rubber that surrounds the tire. This adhesion capacity is achieved because the textile material comes into contact with a dipping solution studied for this purpose, in a process called impregnation. With the formation of foam in the impregnation dipping bath, the cord does not fully penetrate the immersion solution, which generates a productivity deficit and a reduction in the quality of the final product.

Based on this, the first phase of this study consisted in evaluating, at a laboratory scale, the impact of certain parameters/characteristics of the process on foam formation, namely the components of the dipping solution, the variation of the dipping solution temperature and its storage time. Laboratory scale trials were then performed to study the application of an anti-foaming agent to the dipping solution and study its impact on reducing the amount of foam. In the second phase of this project, it was also possible to evaluate at the production scale, the impact of other factors on foaming, namely the impact of the formulation and storage tanks of the dipping solutions. With the commissioning of new tanks designed to minimize the problem, it was possible to evaluate the impact of the storage time of the prepared dipping solutions on the foaming problem and finally to evaluate the impact of the different machines, structurally and functionally.

The laboratory tests results led to the conclusion that the dipping solution formulated with vinyl pyridine (VP) Latex C, performs the best in a laboratory environment. The storage time of the dipping solution between 0 to 24 hours should have no influence on foam formation in the production process and there is also no apparent relationship between the dipping solution formulation temperature and foam volume. Finally, for VP Latex C, the dipping solution with tap water and well water originates less foam than demineralized water. In order to minimize the possibility of the anti-foam impact on the quality of the final product, it was concluded that it is ideal to add the lowest possible concentration of antifoam A (AF), this being 0.06 %. Regarding the production tests, when analyzing the set of tests, the reason for the results may have to do with the speed of the machine.

Keywords: Foam, dipping solution, antifoams, tires, textile reinforcements

Resumo

Esta tese expõe um estudo acerca da problemática de formação de espuma que ocorre no processo de impregnação de corda da empresa. Este é um processo final e essencial no circuito produtivo da empresa, pois é durante o mesmo que o têxtil adquire uma superfície de aderência suficiente e fundamental para a fase seguinte, que consiste na adesão do têxtil à borracha que envolve o pneu. Essa capacidade de adesão é conseguida porque o material têxtil entra em contacto com uma solução de imersão estudada para o efeito, num processo denominado de impregnação. Com a formação de espuma na tina de impregnação, a corda poderá não passar totalmente na solução de imersão, o que gera um défice de produtividade e uma redução da qualidade do produto final.

Com base nisto, a primeira fase deste estudo consistiu em avaliar à escala laboratorial o impacto de certos parâmetros/características do processo na formação de espuma. Em seguida, foram realizados ensaios à escala laboratorial para estudo da aplicação de um anti espuma na solução de imersão, e estudar o seu o impacto na redução da quantidade de espuma.

Na segunda fase deste projeto, foi ainda possível avaliar à escala produtiva, o impacto de outros fatores na formação de espuma, nomeadamente o impacto dos tanques de formulação e armazenamento das soluções de imersão. Com a colocação em funcionamento de novos tanques projetados para minimização da problemática, foi possível, avaliar o impacto do tempo de armazenamento das soluções de imersão preparadas na formação de espuma e por fim avaliar o impacto da diferença de máquinas, estruturalmente e funcionalmente.

Os resultados dos ensaios laboratoriais permitiram concluir que a solução de imersão formulada com VP látex C, tem o melhor desempenho em ambiente de laboratório, uma vez que levou a um menor volume de espuma. o tempo de armazenamento da solução de imersão entre 0 e 24 horas não deve ter qualquer influência na formação de espuma no processo de produção e também não existe qualquer relação aparente entre a temperatura de formulação da solução de imersão e o volume de espuma. Finalmente, para o VP látex C, a solução de imersão com água da torneira e água do poço origina menos espuma do que a água desmineralizada. A fim de minimizar a possibilidade do impacto do anti espuma na qualidade do produto final, é ideal adicionar a menor concentração possível de AF, sendo esta 0,06%. Relativamente aos testes na produção, ao analisar o conjunto de testes, a razão dos resultados pode ter a ver com a velocidade da máquina.

Palavras-chave: Espuma, solução de impregnação, anti espumas, pneus, reforço têxtil

Declaration

I hereby declare, under word of honor, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

Porto, 2 of February of 2023

Ana Beatriz de Carvalho Marques

(Ana Beatriz de Carvalho Marques)

Index

Acknowledgment.....	iv
Abstract.....	v
Resumo	vi
Index	i
List of Figures	v
List of Tables	ix
Notation and Glossary.....	xi
1 Introduction.....	1
1.1 Presentation of the Company.....	1
1.2 Contribution of the author to the work	2
1.3 Organization of the dissertation	2
2 Context and State of the art.....	3
2.1 Tires	3
2.2 Textiles in the Tire Construction	6
2.3 Textile Reinforcements Processing.....	7
2.3.1 Cord design - Twisting.....	7
2.3.2 Dipping Process.....	8
2.4 Foam impact in the dipping process	12
2.4.1 Foam formation	12
2.4.2 Characterization of the equipments in productive environment.....	13
2.5 Antifoaming Agents	15
2.5.1 Antifoaming agent composition.....	15
2.5.2 Antifoam Mechanism	17
3 Materials and Methods	22
3.1 Materials	22
3.2 Methodology	23
3.2.1 Dipping solution preparation	23

3.2.2	Foam volume evaluation	24
3.3	Dipping process parameters influence in foaming.....	24
3.3.1	VP Latex influence	25
3.3.2	Dipping solution storage time influence	25
3.3.3	Influence of the water quality	25
3.3.4	Storage temperature influence	26
3.4	Antifoaming agent influence in foaming.....	26
3.5	Statistical Analysis	27
3.6	Storage conditions influence on foaming in production process.....	27
4	Results and discussion	29
4.1	Dipping process parameters influence in foaming.....	29
4.1.1	VP latex influence	29
4.1.2	Dipping solution storage time influence	30
4.1.3	Influence of the water quality	31
4.1.4	Storage temperature influence	34
4.2	Antifoam concentration influence in foaming.....	36
4.3	Storage conditions influence	40
5	Conclusion.....	42
6	Assessment of the work done	43
6.1	Objectives Achieved.....	43
6.2	Final Assessment	43
7	References	44
Annex A - Adhesion Mechanism		49
Annex B - Study of Dip content in the tire textile reinforcements		50
B.1	Wet-Chemical Method.....	50
B.2	Weighing Method.....	51
B.3	Time Domain-Nuclear Magnetic Resonance (TD-NMR)	51
Appendix A - Schemes		53
A.1	SEC II	53

A.2	New storage tanks	54
Appendix B	- Laboratory Results.....	55
B.1	Dipping process parameters	55
B.2	Antifoam concentration	62
Appendix C	- Statistical Analysis	65

List of Figures

Figure 1 - Components of a modern tires and its amount (Continental Internal Information, 2013).	3
Figure 2 - Tire components from a radial tire of Continental.	4
Figure 3 - Diagonal bias, radial, and belted bias tires, respectively (Santos, 2018).....	5
Figure 4 - "Z" and "S" twisting directions (Santos, 2018).....	7
Figure 5 - Adhesion interchange mechanism between fibers and rubber (Drumond, 2013).	8
Figure 6 - Schematic plant of Single-end equipment (Adapted from Martins, 2013).	10
Figure 7 - Proposed RFL morphology linked to rubber (Costa, 2017).	11
Figure 8 - Schematic presentation of the main physicochemical processes which define the foam volume upon foaming (Petkova et al., 2020).	13
Figure 9 - (a) Entry and spreading of oil droplet at the air/solution interface; for successful entry $E_c = \gamma_w/a + \gamma_w/o - \gamma_o/a > 0$ and (b) for successful spreading of oil droplet $S_c = \gamma_w/a - \gamma_w/o - \gamma_o/a > 0$ (R. Pugh, 2016).	19
Figure 10 - Schematic representation of the different antifoam mechanisms (Denkov et al., 2014). ..	20
Figure 11- Examples of foam volume measure: for $t = 0$ s the foam volume is 0 mL and for $t = 60$ s the foam volume is 310 mL.....	24
Figure 12 - Scheme of the dipping solution path during dipping process.	28
Figure 13 - Evolution of foam volume over time, in a dipping solution formulated with VP latex from different suppliers.....	29
Figure 14 - Statistical analysis of VP Latex influence: a) Mean foam volume vs VP Latex type for each time; b) Tukey Simultaneous 95% Confidence intervals of the dipping solution with different VP Latex.	30
Figure 15 - Evolution of foam volume over time, for different dipping solution storage times for a dipping solution with VP Latex C.	31
Figure 16 - Evolution of foam volume over time, in dipping solution formulated with VP latex B different types of water.....	32
Figure 17 - Statistical analysis of type of water influence in dipping solution with VP Latex B: a) Mean foam volume vs water type; b) Tukey Simultaneous 95% Confidence intervals of the dipping solution with VP Latex B and different types of water.	33
Figure 18 - Evolution of foam volume over time, in dipping solution formulated with VP latex C different types of water.....	33

Figure 19 - Statistical analysis of type of water influence in dipping solution with VP Latex C: a) Mean foam volume vs water type for each time; b) Tukey Simultaneous 95 % Confidence intervals of the dipping solution with VP Latex C and different types of water.	34
Figure 20 - Evolution of foam volume over time, in different dipping solution storage temperature.	35
Figure 21 - Statistical analysis of storage temperature influence in dipping solution with VP Latex C: a) Mean foam volume vs storage temperature; b) Tukey Simultaneous 95 % Confidence intervals of the dipping solution with VP Latex C at different storage temperatures.	36
Figure 22 - Evolution of foam volume over time, in dipping solution formulated with VP latex B at each concentration of AF.	37
Figure 23 - Evolution of foam volume over time, in dipping solution formulated with VP latex C at each concentration of AF.	37
Figure 24 - Mean of foam volume vs AF concentration for each VP Latex.	39
Figure 25 - Tukey Simultaneous 95% Confidence intervals of the dipping solution with each concentration of AF for both VP Latex.	39
Figure A.1 - Schematic approach to trimethylol resorcinol (RF resole) formation/ presence on precondensed resin (Drumond, 2013).	49
Figure A.2 - Greth and Hultzsch mechanism for adhesion chemistry on RFL - compound (Drumond, 2013).	49
Figure A.3 - van der Meer mechanism for adhesion chemistry on RFL - compound (Drumond, 2013)... ..	49
Figure B.1 - Example of a peel adhesion test results: showing a good result, on the left, and a bad one on the right (Rocha, 2019).	50
Figure B.3 1 - Hahn echo sequence representation (Adapted from Bruker, 2023).	52
Figure A.1.1 - SEC II dipping bath scheme.	53
Figure A.1.2 - SEC II dipping bath scheme side cut.	53
Figure A.2.4 - Alabnet axial propeller.	54
Figure A.2.2 - This simulation is indicative at the viscosity level and may not coincide with the viscosity of the product in the quotation.	54
Figure A.2.1 - Klopper top lid scheme.	54
Figure A.2.3 - This simulation is indicative at the viscosity level and may not coincide with the viscosity of the product in the quotation.	54
Figure A.2.2 - Upper atmospheric vertical agitator.	54
Figure B.1.1 - Water temperature for $T = 14.0\text{ }^{\circ}\text{C}$ trial.	59
Figure B.1.2 - Latex temperature for $T = 14.0\text{ }^{\circ}\text{C}$ trial.	59
Figure B.1.3 - Dipping solution temperature for $T = 14.0\text{ }^{\circ}\text{C}$ trial.	59

Figure B.1.4 - Water temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.	60
Figure B.1.5 - Latex temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.	60
Figure B.1.6 - Dipping solution temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.	60
Figure B.1.7 - Water temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.	61
Figure B.1.8 - Latex temperature for $T = 21.0\text{ }^{\circ}\text{C}$ trial.	61
Figure B.1.9 - Dipping solution temperature for $T = 21.0\text{ }^{\circ}\text{C}$ trial.	61
Figure C.1 - Statistical analysis of VP Latex influence: a) Normal probability plot of residuals; b) Standardized Residuals versus fitted values; c) Standardized Residuals versus order of data.	64
Figure C.2 - Statistical analysis of VP Latex influence: Standardized Residuals versus Time.	65
Figure C.3 - Main effect plot, mean of foam volume vs VP latex.	65
Figure C.4 - Tukey Simultaneous 95% Confidence intervals of the time of the dipping solution with each Time for both VP Latex.	66
Figure C.5 - Statistical analysis of water type influence in dipping solution with VP Latex B: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.	67
Figure C.6 - Statistical analysis of water type influence in dipping solution with VP Latex B: Standardized Residuals versus Time.	67
Figure C.7 - Tukey Simultaneous 95% Confidence intervals of the time of the dipping solution with VP Latex B with each type of water.	68
Figure C.8 - Statistical analysis of water type influence in dipping solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.	69
Figure C.9 - Statistical analysis of water type influence in dipping solution with VP Latex C: Standardized Residuals versus Time.	69
Figure C.10 - Main effect plot, mean of foam volume vs water type.	70
Figure C.11 - Tukey Simultaneous 95% Confidence intervals of the time of the dipping solution with VP Latex C with each type of water.	70
Figure C.12 - Statistical analysis of storage temperature influence in dipping solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.	71
Figure C.13 - Statistical analysis of storage temperature influence in dipping solution with VP Latex C: Standardized Residuals versus Time.	72
Figure C.14 - Statistical analysis of storage temperature influence in dipping solution with VP Latex C: Standardized Residuals versus Temperature.	72

<i>Figure C.15 - Tukey Simultaneous 95% Confidence intervals of time the dipping solution with VP Latex C for each storage temperature.</i>	<i>73</i>
<i>Figure C.16 - Statistical analysis of AF concentration influence in dipping solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.</i>	<i>73</i>
<i>Figure C.17 - Statistical analysis of AF concentration influence in dipping solution with VP Latex C: Standardized Residuals versus Time.</i>	<i>74</i>
<i>Figure C.18 - Statistical analysis of AF concentration influence in dipping solution with VP Latex C: Standardized Residuals versus AF concentratrion.....</i>	<i>74</i>
<i>Figure C.19 - Main effect plot, mean of foam volume vs AFconcentration and VP Latex.....</i>	<i>75</i>

List of Tables

<i>Table 1 - Storage tanks characterization.....</i>	<i>15</i>
<i>Table 2 - Antifoaming agents components (Nanjing Invelychem Co., 2020).</i>	<i>16</i>
<i>Table 3 - Types and applications of antifoaming agents.</i>	<i>17</i>
<i>Table 4 - Types of water and their properties.</i>	<i>22</i>
<i>Table 5 - VP latex from different suppliers composition.</i>	<i>23</i>
<i>Table 6 - Properties of AF</i>	<i>23</i>
<i>Table 7 - Tests characterization for VP latex parameter.</i>	<i>25</i>
<i>Table 8 - Tests characterization for each storage time.....</i>	<i>25</i>
<i>Table 9 - Tests characterization for each type of water.</i>	<i>26</i>
<i>Table 10 - Tests characterization for each temperature of the dipping solution.....</i>	<i>26</i>
<i>Table 11 - Tests characterization for antifoam study.</i>	<i>27</i>
<i>Table 12 - Tests characterization in productive environment.</i>	<i>28</i>
<i>Table 13 - Analysis of Variance.</i>	<i>38</i>
<i>Table 14 - Results of foam level, adhesion and DPU, for tests in SEC II.....</i>	<i>41</i>
<i>Table B.1.1 - Foam volume for VP Latex from different suppliers.</i>	<i>55</i>
<i>Table B.1.2 - Foam volume for different dipping solution storage times.</i>	<i>56</i>
<i>Table B.1.3 - Foam volume for dipping solution formulated with VP latex B and different types of water.</i>	<i>56</i>
<i>Table B.1.4 - Foam volume for dipping solution formulated with VP latex C and different types of water.</i>	<i>57</i>
<i>Table B.1.5 - Foam volume at different dipping solution temperature.</i>	<i>58</i>
<i>Table B.2.1 - Foam volume for each concentration of AF for dipping solution with VP latex B.</i>	<i>62</i>
<i>Table B.2.2 - Foam volume for each concentration of AF for dipping solution with VP latex C.</i>	<i>63</i>
<i>Table C.1 - Analysis of the variance for VP Latex influence.</i>	<i>65</i>
<i>Table C.2 - Analysis of the variance for water type influence in dipping solution with VP Latex B. ...</i>	<i>67</i>
<i>Table C.3 - Analysis of the variance for water type influence in dipping solution with VP Latex C. ...</i>	<i>69</i>
<i>Table C.4 - Analysis of the variance for storage temperature influence in dipping solution with VP Latex C.</i>	<i>72</i>

Notation and Glossary

B_c	Bridging coefficient	mN^2/m^2
DPU	Dip Pick-up Percentage of solid dip impregnated	%
E_c	Entering coefficient	mN/m
S_c	Spreading coefficient	mN/m
SC	Solid Content Percentage	%

Greek Letters

γ	Equilibrium interfacial tension
----------	---------------------------------

Indexes

a	Air
o	Oil
w	Aqueous phase

List of Acronyms

AF	Antifoam A
APEO	Alkylphenol ethoxylates
C-ITA	Continental - Indústria Têxtil do Ave, S.A.
Dtex	Decitex
F	Formaldehyde
FID	Free induction decay
F/R	Formaldehyde/Lates ratio
ITA	Indústria Têxtil do Ave, S.A.
L	Latex
NMR	Nuclear Magnetic Resonance
PET	Polyethylene terephthalate
R	Resorcinol
rf	Radio frequency
R&D	Research and development
RF resin	Resorcinol-Formaldehyde Resin
RFL	Resorcinol-formaldehyde-latex
SE	Single-end
SEC I	Single-end Cord I
SEC II	Single-end Cord II
TD - NMR	Time Domain - Nuclear Magnetic Resonance
VP	Vinyl pyridine

1 Introduction

Tires are the essential contact point between the car and the road. Rubber, steel, and textile reinforcements are just a few of the elements used to make pneumatic tires (Brewer, 2006; Continental, 2013).

Textiles do not properly adhere to rubber without treatment, because the two materials are incompatible. Therefore, textiles must undergo a dipping solution treatment, where a dipping solution is applied to these reinforcements to provide a sufficient bonding surface between the fiber and the surrounding rubber matrix in the tire. The physical properties are modified during this procedure by stretching and temperature, while the chemical characteristics are significantly modified by dipping solution and temperature. Resorcinol-formaldehyde-latex (RFL)-based dips are used in industry. The three primary components are resorcinol (R), formaldehyde (F), and latex (L), all dispersed in water (Santos, 2018).

Currently, some chemical dispersion solutions used in industrial environments have as their main problem, that needs to be overcome, the production of foam, which causes processing inefficiencies. As a result, there might be less dipping in the cords, which reduces their ability to adhesion to the rubber and, therefore, the quality of the final product. As such, it is intended with this project to study the use of anti-foam additives to minimize impacts on production. However, the use of these additives can, if not well optimized, cause loss of properties in the textile reinforcement. Given this background, it is crucial to study these phenomena in a lab setting and then transfer them to production through tests under real conditions.

1.1 Presentation of the Company

Continental is a leading automotive manufacturing company specialized in tires and a creator of the most secure tire in the world. It was founded in 1871 in Hanover, Germany, and initially focused on producing rubberized fabrics, solid tires for carriages and bicycles, as well as soft rubber goods. Indústria Têxtil do Ave, S.A. (ITA) was established in 1950 as a branch of Mabor in Lousado, Portugal, to create reinforcing textiles for tires. In 1987 it joined the Continental Group, but only in 1993 Continental totally acquired the Portuguese tire manufacturer Mabor and the textile cord manufacturer ITA. When ITA joined Continental, the company's name was changed to Continental - Indústria Têxtil do Ave, S.A. (C-ITA). Continental grows its presence throughout time in a number of nations while also growing production and developing specialized plant units. In the modern era, Continental has five powerful divisions: Chassis & Safety, Powertrain, Interior, Tires, and ContiTech. The Company is always growing to meet modern demands, developing new products and revolutionizing the automotive industry (Continental, 2022b; Santos, 2018).

C-ITA is today, for Continental, an internal partner in all Research and development (R&D) work for new processor solutions and products in the textile area, as well as an integrated supplier with a benchmark for this market. C-ITA is in charge of turning raw material (yarn) into cords and preparing those cords for their final use through their dipping process. In order to give the final product different performance, C-ITA uses various materials such as aramid, nylon, polyethylene terephthalate (PET), and rayon in textile tire reinforcement (Santos, 2018).

1.2 Contribution of the author to the work

This project is a continuation of other works in foam formation in the Single-end Cord II (SEC II), to provide better machine operation and increase productivity, because there would be no need to slow down to stop the foam formation. The application of an antifoam in the dipping solution was studied to provide a better view of the impact of adding the AF to the dipping solution, and its effect in reducing foaming.

In the first stage of this master thesis, different parameters that could influence the foam formation were studied to identify which one had more influence on the foam formation. Besides that, it was possible to study the use of anti-foam additives in minimizing impacts on the foam formation in dipping solutions. Also, application and validation of new dipping storage tanks was possible.

The work proceeds with the study of the application of antifoams in dipping baths, as well as understanding the parameters impact in the equipment operation and foaming.

1.3 Organization of the dissertation

This thesis is divided into 8 chapters plus Annexes and Appendixes, each of which is followed by a succinct summary.

Chapter 1 - Introduction. Continental presentation and a brief contextualization of the developed work.

Chapter 2 - Context and State of the art. Description of tire and textile reinforcements industry, the textile reinforcements processing and antifoaming agents.

Chapter 3 - Technical Description. Description of the methods and equipment used during the course of this project.

Chapter 4 - Results and Discussion. Analysis of the results obtained and statistical analysis.

Chapter 5 - Conclusion. Conclusion presentation of the project results.

Chapter 6 - Assessment of the work done. Global appreciation of the accomplished work.

References. List of the references used in this project.

Annex A - Some additional information can be found in this chapter.

Appendix A - Some additional schemes can be found in this chapter.

Appendix B - Some laboratory results can be found in this chapter.

2 Context and State of the art

2.1 Tires

Tires are the essential point of contact between the car and the road. Tires are primarily designed to protect the driver and passengers by being able to withstand the many conditions of the road, such as wet and slick pavement or roads with snow or ice (Santos, 2018).

As represented in Figure 1, tires are made up of 15 different rubber compounds and more than 20 different parts, and they go through several machines and processes before they are finished and prepared for sale. Thus, tires can be referred to as complex engineering items (Santos, 2018).

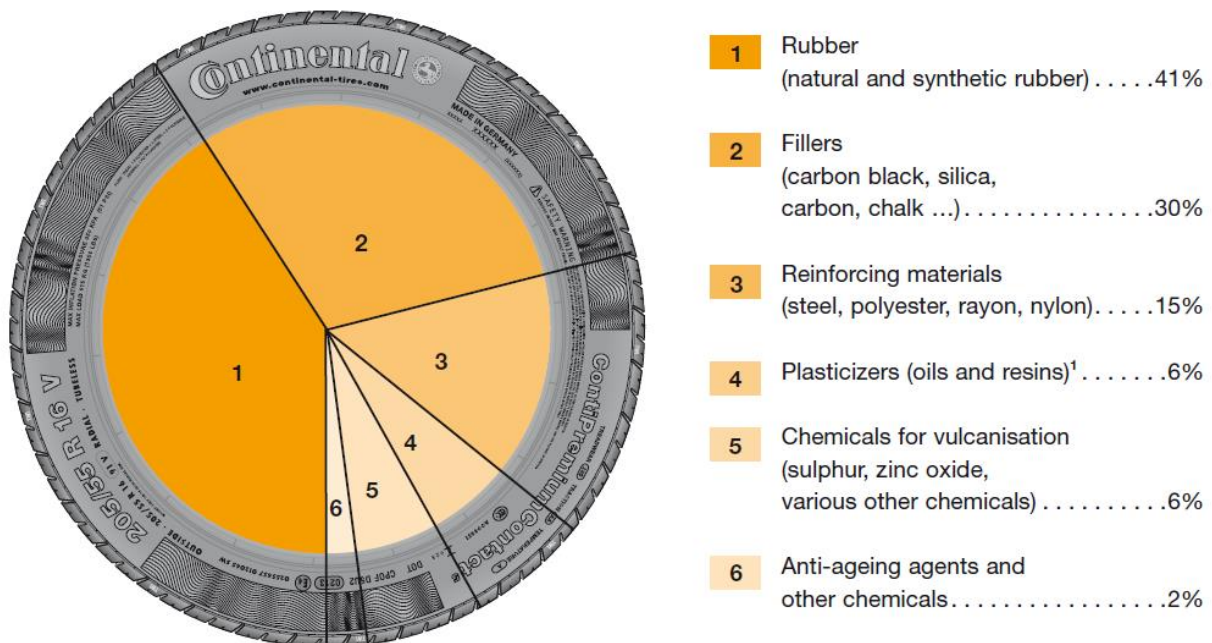


Figure 1 - Components of a modern tire and its amount (Continental, 2013).

During the 1800s, pneumatic tires with their small cross sections and high pressures were developed primarily for bicycles, which improved solid rubber tires. Belted bias tires were created in the 1960s, and tubeless tires with improved rim designs were produced in the 1950s. Diagonal bias, belted bias, and radial tires are now the three types of tires that differ from one another in the bias layer arrangement (Continental, 2022a).

The tread and belt assembly and the casing are the two major structural components of a tire. There are multiple layers to these components, as shown in Figure 2. Taking a closer look at each component, starting with the road surface and moving toward the tire's center (Continental, 2022a).

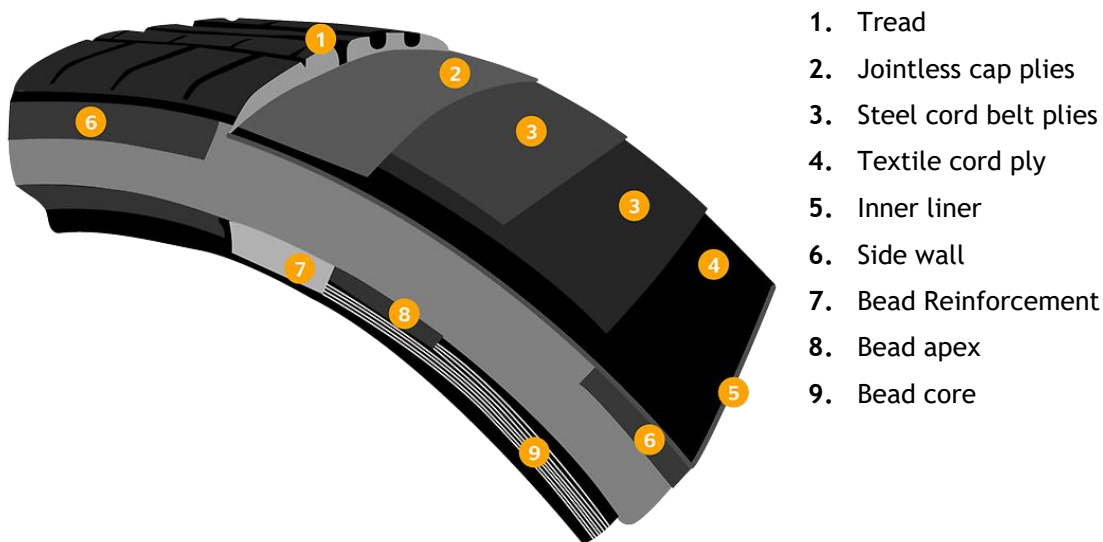


Figure 2 - Tire components from a radial tire of Continental (Continental, 2022a).

Beginning with the tire's outermost layers, which are the tread and belt (1 and 3). The casing is encased by this mostly rubber part, which offers low rolling resistance, excellent handling, a long lifespan, and exceptional gas mileage (Continental, 2022a).

The tread (1), which makes up the tire's outer layer and is made of both natural and synthetic rubber, strikes a balance between wear, traction, handling, and rolling resistance. The grip required for driving, stopping, and cornering is provided by the tread. In the end, all of this adds up to a tire that performs well under a variety of driving circumstances (such as on wet, dry, or snow-covered ground) while maintaining appropriate wear resistance, low noise, and a smooth ride (Brewer, 2006; Continental, 2013).

A textile layer called the cap-ply (2), which is typically made of nylon, is wrapped circumferentially on top of the belts to increase their ability to withstand centrifugal forces at high speeds. They are made out of a single, sturdy nylon cord that is embedded in rubber. From one side to the other, this cord loops around the tire's circumference without overlapping (Brewer, 2006; Continental, 2022a; Santos, 2018).

The belts' (3) primary purpose is to improve shape retention and directional stability, lower rolling resistance, and improve tire mileage performance. The belts are composed of carbon steel and have many layers with various characteristics. On top of the body plies, beneath the tread region, there are two steel belts that are positioned at diametrically opposed angles (Brewer, 2006; Continental, 2013, 2022a).

The carcass acts as an inner tube by containing air and cushioning the tire. The load is carried by the air, not by the tire itself. The textile cord ply (4) is a layer of fabric, specifically rubberized rayon or polyester, which regulates the tire's internal pressure and keeps it in shape (Continental, 2022).

In order to improve air retention in the internal part of tubeless tires, a thin layer of a specially developed substance called the inner line (5) is applied there. It enables the tire to be inflated properly. The carcass, which extends from bead to bead and is made of textile cord and rubber, acts as the main reinforcement material. The placement of these strands in a radial pattern gives them strength and a quality that prevents bending and straining while driving (Brewer, 2006; Continental, 2013).

Rubber tire sidewalls (6) serve to shield the body plies from damage from abrasion, impact, and flex fatigue. Some tires also contain reinforcements to enhance handling or stability (Brewer, 2006; Continental, 2013).

The tire bead component (7, 8 and 9), which is a part of the casing, contributes to the tire's edge's ability to adhere firmly to the wheel groove. Here, air pressure keeps the tire firmly attached to the wheel. There are three components to the bead. The nylon or aramid used for the bead reinforcement (7) is a type of strong, heat-resistant synthetic fiber, it is a fine cabling improves directional stability and makes it easier to respond precisely to steering inputs (Continental, 2022a).

Similar functions to those of the bead reinforcement are carried out by the Bead apex (8), a stabilizing wedge made of synthetic rubber that also adds to the comfort of steering. The steel wire that makes up the bead core (9) is finally covered in rubber. The core makes ensuring the tire is securely mounted to the wheel rim (Continental, 2022a).

As schematized in Figure 3, there are three different tire kinds (diagonal bias, belted bias, and radial) with various structures depending on how the body plies are arranged (Brewer, 2006).

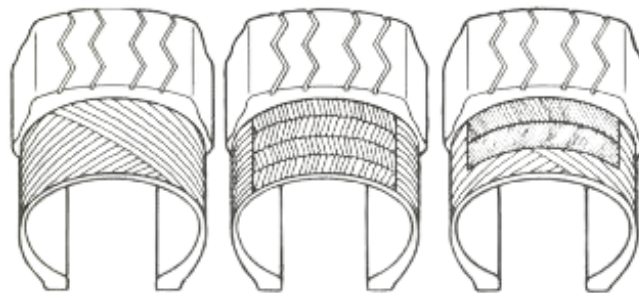


Figure 3 - Diagonal bias, radial, and belted bias tires, respectively (Santos, 2018).

In contrast to other types of tires, diagonal bias tires have a simple construction. From bead to bead, the body ply cords are positioned at angles that are significantly less than 90 degrees from the tread centerline. Bias tires with belts have a similar straightforward design to diagonal bias tires. The belts prevent the carcass from expanding, enhancing the strength and stability of the tread area (Brewer, 2006).

The structure of radial tires is more complex than that of conventional tires. From bead to bead, the body ply cords are arranged radially at a 90° angle to the tread's centerline. Belts

are laid diagonally in the tread area of the tire to increase tread stiffness, improve wear and handling, and strengthen and stabilize the tire. The emphasis of this thesis will be on the textile cord-based reinforcement materials for better tire performance (Brewer, 2006).

2.2 Textiles in the Tire Construction

A tire is made up of numerous layers, each of which has a variety of components and reinforcement materials, of which roughly 12 % are textile fibers. About 70 % of the textile reinforcements used on the carcass and cap-ply in Continental tire facilities in Europe are made by C-ITA. The design and functionality of the tire are influenced by textiles. They support the sidewall and tread and keep the air pressure in the tires in check (Santos, 2018).

The material is created to get the necessary tire qualities thanks to the well-known and unique capabilities that the textile reinforcements confer in accordance with their role. Currently, C-ITA uses four main types of raw materials: rayon, aramid, nylon, and PET (Santos, 2018).

Aramid is an aromatic polyamide, and it has exceptional thermal characteristics due of hydrogen bonding, chain rigidity (high glass transition temperatures), chain organization, and chain orientation. These mechanical characteristics offer excellent stiffness, strength, and little elongation. Despite its high cost, aramid can be utilized as a substitute for steel cord in the belts or in the overlay plies (Brewer, 2006; Lewin, 2006).

Nylon fibers are synthetic long-chain polymers. It possesses low moisture sensitivity, low modulus (stiffness), low glass transition temperature, and strong heat resistance and strength. These characteristics make nylon fibers suitable for use as a cap and overlay ply in radial tires (Brewer, 2006).

PET fibers are synthetic, long-chain polymers generated by melt spinning or continuous polymerization/spinning. This material has considerably high tensile strength, stiffness, good thermal stability, flame resistance, chemical resistance and at the same time a light weight and is less expensive. PET fibers are frequently utilized in belt plies and radial body plies (Brewer, 2006; Costa, 2017; Lewin, 2006).

Rayon is a fiber produced from cellulose. Due to its high tenacity, low shrink, high modulus, and strong adherence to rubber, this fiber is typically utilized in body ply cord or belt for tire reinforcement. This fiber is an expensive material that reacts strongly to moisture. C-ITA creates hybrid cords made of aramid and nylon, giving rise to a substance with distinctive behaviors and enhanced qualities (Brewer, 2006; Lewin, 2006).

2.3 Textile Reinforcements Processing

2.3.1 Cord design – Twisting

Before being used in the reinforcement of the tires, fibers can be organized into four levels of design: filament, yarn, cord and fabric, with filament serving as the simplest unit. A yarn is created by spinning a collection of filaments together. The yarn produces a cord after being twisted (either by itself or with additional yarns). Depending on the application, the cord can be weaved into fabric or not (Drumond, 2013).

Twisting can be used in either the "S" or "Z" direction. According to Figure 4, if the cord is wound clockwise, it is twisted in "S," and if it is wound counterclockwise, it is twisted in "Z." The yarns are often twisted in a "Z" shape, and they are twisted together in a "S" shape to make the cord. In addition to the fact that the material can change, hybrid cords can also be made from twisted single yarns or combinations of two or more yarns. The twist given to cords might be tighter or looser depending on the number of turns per meter of cord (Santos, 2018).

The composition of cords, the quantity of threads woven together, and their linear density all serve to define them. Decitex (Dtex), which is the weight in grams of a length of 10,000 meters, is the unit used to measure linear density. The construction of the cord is known as having all these characteristics. The cord will be a part of the tire's cap-ply. Weaving machines are utilized to create the fabric that will be used for the carcass (Santos, 2018).

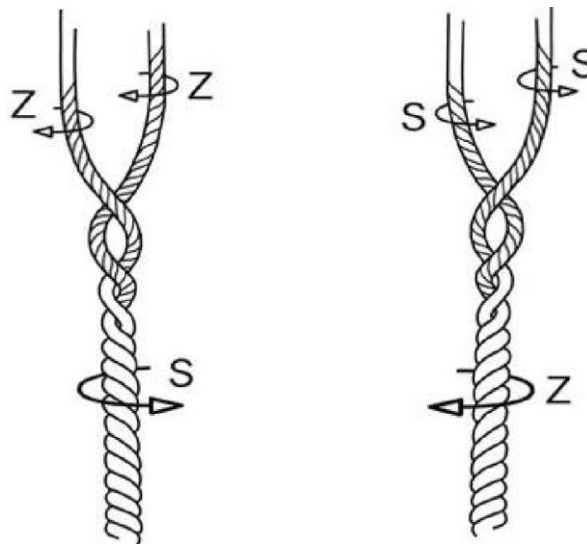


Figure 4 - "Z" and "S" twisting directions (Santos, 2018).

Twisting is the process of creating cords from PET, Nylon 6.6, Aramid, and Rayon yarns. To do this, twisting machines are employed to create the cords, which essentially consist of two or more strands twisted in a specific direction (turns per meter).

Twist rates play a crucial role in tire cord performance. Lower twists enable a cord to behave like a rod, maximizing strength, while higher twists allow a cord to behave like a spring that

will not open under compression. Twisting reduces tenacity, improves fatigue in compression (which is the main driver of higher twists), raises the cost of the cord per tire (since the cords get shorter as they are twisted), and raises shrinkage during processing and curing (Brewer, 2006).

With increasing twist, tenacity and fatigue resistance can occasionally decrease. The design of a tire should prevent any cords from opening, chafing, or fretting while it is in compression mode. When bending loads and strains are significant in tire sidewalls, cord fatigue in compression is a crucial concern (Brewer, 2006).

2.3.2 Dipping Process

After the textiles are created, they go through a process that involves inserting the cord in the rubber and then vulcanizing it. Polymeric cords, in general, have a smooth and inert surface as well as a polar property. As a result, interactions with non-polar rubber are poor. Due to the incompatibility of these two materials, textiles do not adhere to rubber properly without any treatment. To attain an ideal tire performance and durability, the adhesion between both phases - reinforcement and rubber - is vital as the interface quality is responsible for excellent or bad stress transmission from the matrix to the textile cord. Figure 5 depicts the adhesion interchange mechanism between fibers and rubber (Costa, 2017; Drumond, 2013; Louis & et al., 2016).

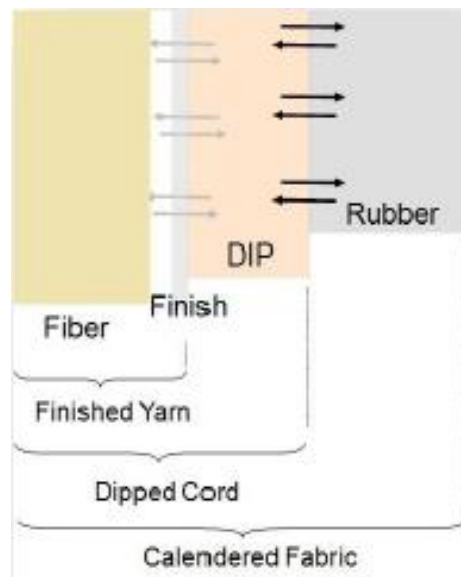


Figure 5 - Adhesion interchange mechanism between fibers and rubber (Drumond, 2013).

The procedure is dipping the cord in a solution to create an interface that enables the cord and rubber to bond together. According to the literature, the most common method for improving the adhesion of textile cord to rubber is the use of an RFL-dip based on an emulsion of a latex mixed with a water solution of resorcinol and formaldehyde. In addition to these components, the conventional dipping solution still has an alkaline solution such as ammonia or sodium

hydroxide. There are many benefits of using water rather than an organic solvent, including cost savings, ease of treatment, and lack of health risks. At C-ITA, all dipping solutions are water-based (Costa, 2017; Santos, 2018).

When latex is employed alone as an adhesive, a good adhesion between rubber and textile cannot be accomplished because latex lacks active groups and the adhesive coating film's tensile qualities are insufficient. Latex adheres to both the rubber and the resin providing the flexibility properties to the dipped cord (Drumond, 2013).

In addition to creating linkages at the composite's interface, this adhesive helps to decrease the disparity in characteristics between the two materials (for example the high-polarity polymers in cords versus low polarity of rubber and high modulus in cords versus low modulus of rubber). By reducing changes at the interface, the durability of composites is increased because the interfacial tensions are reduced (Costa, 2017).

The resin in the referred dipping solution is composed of resorcinol and formaldehyde, which are responsible for creating polarity in the dip layer and reacting with the polar groups present on the fiber surface. In the adhesive formulation for fiber-rubber composite applications, due to its water solubility and improved reactivity with formaldehyde at room temperature, resorcinol has been selected as the preferred phenolic molecule in the adhesive formulation of fiber-rubber composite applications. At C-ITA, resorcinol and formaldehyde can be added to latex after being partially condensed in a diluted aqueous alkali solution thanks to the use of a precondensed resin (Costa, 2017; Drumond, 2013).

Resorcinol "trimers" with methylol groups (referred to as resoles) along with some mono and dimers of resorcinol are present in the precondensed resin dispersion. Three resorcinol molecules are referred to as a trimer when they are joined by a methylene (-CH₂) bridge. View Figure A.1 for an approach to trimethylol resorcinol (RF resole) formation/ presence on precondensed resin (Drumond, 2013).

This type of resin prevents ammonia from interacting with formaldehyde during RFL-dip preparation, preventing the creation of hexamethylenetetramine, which may interfere with the resin's formation by restricting its extent. It could potentially be the cause of latex colloidal instability. Increasing the formaldehyde concentration in RFL solution at low temperature (ideally room temperature or lower) and alkaline conditions will stimulate the production of methylol groups in the resin structure. Formaldehyde will act as a crosslinking promoter. The synthesis and stability of methylol derivatives of resorcinol and Resorcinol-Formaldehyde Resins (RF resins) are critical for developing and strengthening the binding between the fibers and RFL adhesives (Drumond, 2013).

Ammonia is essential to maintain an alkaline pH (of about 9 to 10). Working with polymeric substances such as latexes and resins requires tight pH control, otherwise, partially condensed reaction products would arise, affecting the desired direction of the chemical reaction (Drumond, 2013).

Contrarily, the latex component, in addition to forming the matrix in the RFL-dip and providing the necessary flexibility, also provides good bonding to the rubber by crosslinking the two phases together during vulcanization, facilitating the interaction of the materials and promoting the rubber and fiber's adherence as a result of vulcanization. In some situations, more ammonia is added to the solution to enhance the latex's stability and increases the rubber's adhesion to cord (Costa, 2017; Santos, 2018).

An equipment called Single-end (SE), shown schematically in Figure 6, is used to dip the cords in C-ITA. This equipment is named for its arrangement, the greige cord is unwinding on the same side that the dipped cord is winding, hence the name (left side). A roll unit and vacuum unit are used to remove surplus dipping solution after the greige cord has been dipped in the dipping bath, some schemes are presented in Figures A.1.1 and A.1.2 in Appendix A. Then, the cord is pulled through tensioning rollers that provide the required stretching. The cord enters the first oven where the dip is dried, then enters in the second oven where the cord is hot stretched, getting its final properties. The cord is wound up in bobbins and supplied to clients after all the stages have been finished (Martins, 2013).

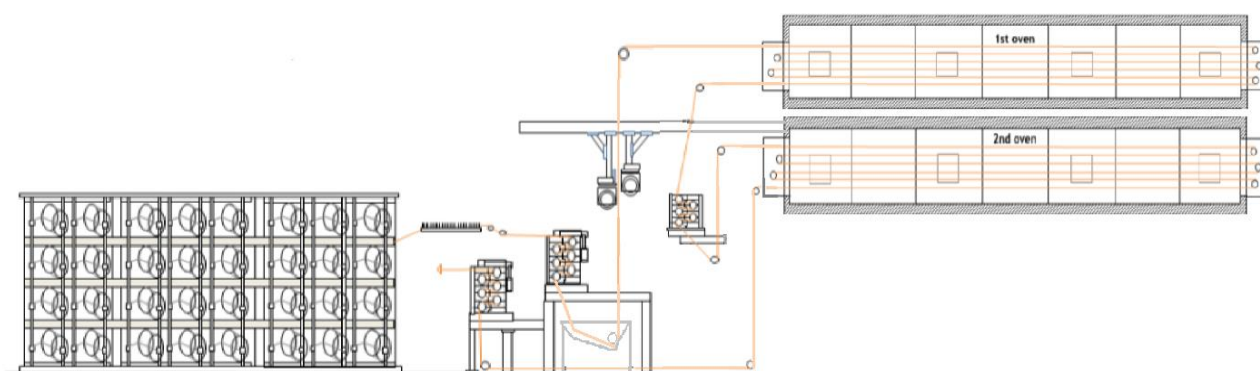


Figure 6 - Schematic plant of Single-end equipment (Adapted from Martins, 2013).

The dipping conditions, such as the oven temperatures, velocity, stretch, and Solid Content Percentage (SC) (%), depend on the cord to be impregnated. Temperature and exposure time will both have an impact on the curative process of the dip on fibers. Temperature performs three functions: promoting the drying of the fiber and the curing process of RFL-dip, as well as, together with stretching, conferring the final mechanical qualities. All dipping process parameters must be optimized for each type of reinforcing fiber, RFL, and rubber to adhere to (Drumond, 2013; Santos, 2018).

The amount of dip in the cord is quantified in C-ITA for safety reasons: if it has a small amount of dip, the cord may not have proper adhesion to the rubber and the tire may not be safe for driving conditions; if it has a large amount of dip, it will be a waste of material, increase costs, and be unfriendly to the environment. The final product is expected to retain the mechanical, physical, and chemical properties required for driving conditions while remaining intact (Santos, 2018).

Certain materials necessitate a pre-dip process in order for the cord to connect to the dipping solution. Some suppliers ship the yarn after it has been oil finished, eliminating the need for a pre-dip (Santos, 2018).

Various forms of bonding are typically created between the components after the reinforcement is processed and vulcanized alongside the rubber matrix. The primary (covalent bonds with oxygen and hydrogen) and hydrogen bonding that take place inside resorcinol-formaldehyde and the textile are primarily responsible for the relationship between the cord and the RF resin. In contrast, the bond between rubber and latex is primarily created by the co-vulcanization of the two aforementioned phases as well as its interaction with the rubber's dispersion forces. Figure 7 depicts the dipping solution structure connected to rubber in order to better understand the morphology of the RFL-dip (Costa, 2017).

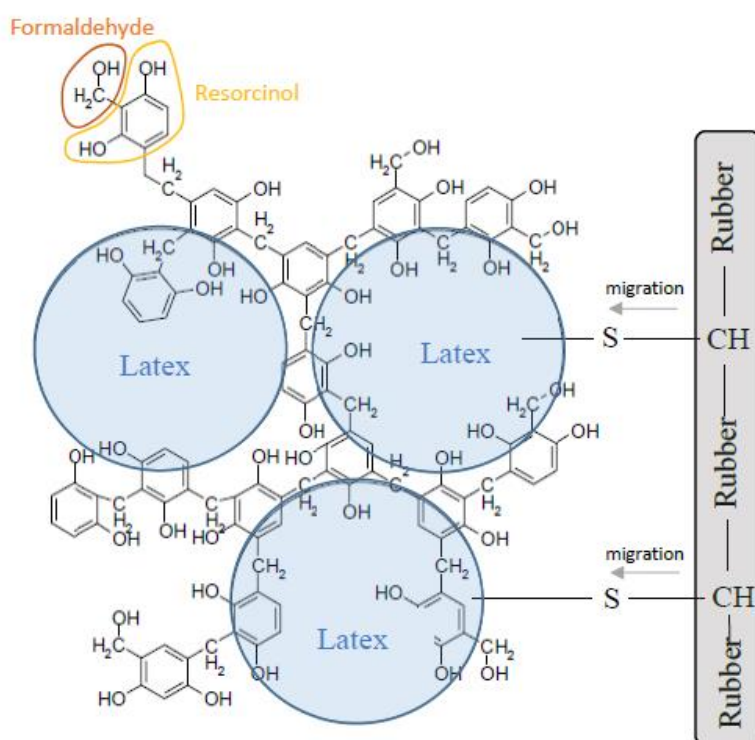


Figure 7 - Proposed RFL morphology linked to rubber (Costa, 2017).

As previously stated, formaldehyde interacts with resorcinol resin to create methylol derivatives. Condensation results in methylol derivatives, which contain four to five resorcinol nuclei linked together by methylene-CH₂ and methylene ether-CH₂-O-CH₂ bonds. The ratio of

formaldehyde to resin (F/R) raises both the degree of condensation and the degree of branching. The rate of condensation is affected by the concentration, maturation time, and temperature of the resin solution, as well as the curing time and temperature of the RFL-dip (Drumond, 2013).

There have also been other viewpoints expressed regarding the rubber-RFL bond, including interdiffusion between RFL and rubber, co-vulcanization of carbon-carbon double bonds in RFL with rubber, ionic interaction, and chemical reaction between RF resin and rubber (Drumond, 2013).

These postulated mechanisms are diverse, and they are based on assumptions rather than rigorous evidence. Co-vulcanization of the RFL-rubber contact is one of the hypothesized mechanisms. Only a few authors empirically confirmed this by studying the RFL-rubber interaction in depth. Greth proposed that phenol formaldehyde resin combines with the double bond in the isoprene unit of natural rubber to create chromanes, and that the bond between resorcinol formaldehyde resin and rubber is the same as other phenolic resin rubber linkage. Van der Meer recommended that methylene quinone intermediates be generated and subsequently reacted at the methylene group close to the unsaturated carbon in natural rubber. In Figure A.2 and A.3, are presented Dip Pick-up (DPU) schemes of mechanism for adhesion chemistry on RFL (Drumond, 2013; Wennekes, 2008).

2.4 Foam impact in the dipping process

The cords are dipped in a SE equipment, as previously seen in 2.3.2. For this purpose, C-ITA has two separate machines: Single-end Cord I (SEC I) and SEC II. There are some aspects of these two machines that are different, which will be covered further. The foam formation in SEC II, with higher incidence at certain times of the year, is currently the main problem, that needs to be overcome, in several chemical dispersion solutions used in equipments. Foaming results in processing inefficiencies because the cord may pass through the foam instead of the dipping solution. As a result, there may be less dipping in the cords, which can reduce their ability to stick to the rubber and, consequently, the quality of the final product. In addition, when there is a lot of foaming, it is necessary to reduce the machine's velocity and sometimes stop it.

2.4.1 Foam formation

Thousands of small bubbles of mechanical or chemical origin make up a foam, which is produced within a liquid. Figure 8 illustrates two processes that have opposing impacts on foam volume: air entrapment and bubble coalescence. When newly entrapped air through mechanical agitation or gas incorporation (by bubbling or chemical reaction) is unable to coalesce with the huge air-water contact, the foam volume increases. The coalescence between entrapped air

bubbles and this wide contact, on the other hand, eliminates the trapped air and maintains the foam volume low. In turn, bubble coalescence is determined by the conflict between the rate of surfactant adsorption on the bubble surfaces and the drainage time of the foam films generated between the air bubbles and the vast air-water interface (Petkova & et al., 2020; Vardar-Sukan, 1998).

The interaction of the air entrapment and bubble coalescence processes with the substantial air-water interface determines the foam volume. The competition between the rates of surfactant adsorption and foam film thinning to the critical thickness of film rupture, in turn, is what drives coalescence (Petkova & et al., 2020).

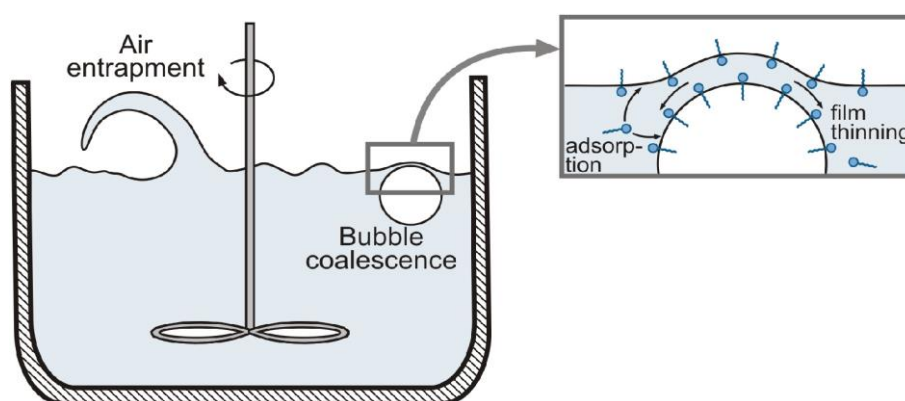


Figure 8 - Schematic presentation of the main physicochemical processes which define the foam volume upon foaming (Petkova & et al., 2020).

2.4.2 Characterization of the equipments in productive environment

There might be various factors that might influence the foam formation. After observation and analysis of the equipment it was possible to outline some of the parameters related to the equipment processing that may influence foaming. Some of these parameters are related to the differences between the SEC I and SEC II machines. As previously described, there is foam formation in SEC II, with higher incidence at certain times of the year. Considering this, the aspect that will have, presumably, the greatest influence on foam formation is the temperature. Besides, the conventional storage tanks are made of iron which, through C-ITA's experience, is a problem, because iron destabilizes latex.

Considering the cord Dtex, using a thinner cord does not have as much impact as using a thicker one. This might be related to the raw material conditions, because it is not known if the yarns, used to make a cord, come pure and there might be differences in the batches, or in the transportation. The processing of this yarn can bring a spin finish, that is a liquid or solid composition that is applied to the surfaces of man-made fibers in order to improve the processing of such fibers in short-staple or long-staple spinning, this compost can react with the dipping solution (Elhawary, 2010).

Focusing on the RFL solution used in SEC II, the dipping solution pumping and components like the supplier of VP Latex used or the type of water (tap, well or demineralized - which have different constituents), and even dipping solution storage time, may be also important factors for creating more or less foam.

The differences between the SEC I and SEC II machines, like the operating speed (with SEC II working at a higher speed than SEC I), dipping bath construction and size (SECI has a larger bath than SEC II, wider and deeper; it also has a plate that SEC II does not) and the number of rolls in the dipping bath (because the more rollers, the greater the bath agitation), may have influence in foaming.

Other aspects occurring during the process that may influence foaming, such as during the equipment washing process, some detergent may be left on by mistake and create more foam. Also, the equipment start up, if it is not gradual, and agitation of the dipping solutions in the storage tanks can also be important for foam formation.

Also, previous studies demonstrate that to reduce the foam volume, it can be used a water sprinkler. These are sprinkler cones with a very small droplet, and the effect is surface tension lowering, eliminating the foam. Nonetheless, the water used might dilute the dipping solution.

As mentioned before, the seasonality of the foam formation is also important. According to previous investigations in C-ITA in the winter and colder months, bath formulation temperature (temperature at which constituents are) or room temperature and storage conditions of those components can contribute to foaming. So, previous projects were able to develop new dipping solution storage tanks, with different characteristics. The new dipping solution storage tanks are AISI 304 stainless steel vertical cylindrical tanks, insulated with rockwool and coated in AISI 304 stainless steel. Upper atmospheric vertical agitator, Alabnet axial, which is an axial-radial flow propeller for homogenizing, holding in suspension, mixing and heat exchange functions for low and medium viscosity products.

Regarding the material, the conventional tanks are made of iron which, through C-ITA's experience, is a problem because iron destabilizes latex. So stainless steel prevents latex destabilization by iron. Also, the type of propeller was chosen so the dipping solution flow goes above the propeller, preventing foam formation when agitation is on, maintaining a good homogenization. Dipping solution enters the tank by an anti-waterfall mechanism, here the dipping solution goes against the tank wall and descends to the bottom, preventing bubbles formation. Finally, the new tank has a klopper type lid, that helps maintain the concentration of the ammonia in the dipping solution as it does not let it escape from the tank. Ammonia is important for stabilizing the latex. Some schemes of these new storage tanks are presented Figure A.2.1, A.2.2, A.2.3 and A.2.4 in Appendix A.2. In Table 1, the differences between conventional and new storage tanks are summarized.

Table 1 - Storage tanks characterization.

	Conventional Tanks	New Tanks
<i>Material</i>	Iron	AISI 304
<i>Isolation</i>	None	Rockwool
<i>Propeller</i>	Angle bracket	Alabnet axial
<i>Stirring speed</i>	25-50 Hz	25-50 Hz
<i>Inlet</i>	Direct	Anti-waterfall
<i>Lid</i>	Straight with opening	Klopper
<i>Bulkheads</i>	Four	None
<i>Volume Measurement</i>	Load cell	Load cell
<i>Transfers</i>	Spindle pump and Double diaphragm pump	Double diaphragm pump

2.5 Antifoaming Agents

Defoamers were added to eliminate stable foams that already existed (produce low foam stability) through a shock effect, whereas antifoam were initially defined as chemicals or materials that were pre-dispersed in the liquid phase prior to processing to prevent foam formation (produce low foamability). The majority of chemical additives nowadays, however, perform numerous tasks, and their nomenclature differs depending on the industry in which they are utilized, making it challenging to draw the distinction between defoamers and antifoam. They are also referred to as air release agents, foam suppressants, foam inhibitors, and foam control agents (Butt H. & et al, 2013; Gochev & et al., 2016; R. Pugh, 2016).

2.5.1 Antifoaming agent composition

A carrier fluid like silicone, mineral oil, esters, or polyols, as well as hydrophobic solids like waxes, fatty alcohols, fatty acids, or modified silica, make up most antifoams. Other functional elements that support dispersion, spreading, stability, compatibility, wetting, etc, may also be present in antifoams. The different antifoaming components are presented in Table 2. Typically hydrophobic, finely dispersed, and insoluble substances are used as antifoams in aqueous systems. As a result, many commercial antifoams for aqueous solutions are made of hydrophobic oil matrix and hydrophobic particle dispersion (Crucible Chemical Company, 2023; Gochev & et al., 2016).

Table 2 - Antifoaming agents components (Nanjing Invelychem Co., 2020).

	<i>Function</i>	<i>Examples</i>
Active Ingredients	Breaking foam, defoaming, and lowering surface tension	Hydrophobic silica, polyethers, higher alcohols, mineral oils, vegetable oils
Surfactant	Disperse the active ingredient into small particles that are easily dispersed in water, resulting in improved defoaming and foam suppression.	Nonylphenol ethoxylate, soap salt and similar compounds
Carrier	It aids in the combination of the carrier and the foaming system, as it is easily dispersed into the foaming system and combines the two, and its surface tension is low, which aids in the suppression of foaming.	Mineral oil (aliphatic or aromatic), solvent mixture, water (for pre-emulsified defoamer), silicone, esters, or polyols
Other	Improve the emulsification effect	

Considering the type of carrier fluid, there are two primary types of antifoam.

Silicone Antifoam: The most efficient antifoam substances are liquid silicones, particularly linear and cyclic polydimethylsiloxanes, which can be used in concentrations as low as 1 to 100 mg/kg. To guarantee stable dispersion, silicones are often pre-dissolved in aromatic solvents. Comparatively to other additives, silicone defoamers have the drawback of being particularly quickly removed from the lubricant due to their insolubility and strong affinity for polar metal surfaces (Mang & et al., 2011).

Silicone-Free Defoamers: are being employed in more applications, especially in metalworking operations. Cutting fluids and hydraulic fluids must be silicone-free to ensure the subsequent application of paints or lacquers on the workpieces. The most prevalent types of silicone-free defoamers are special poly (ethylene glycols) and other organic copolymers (Mang & et al., 2011).

It is frequently possible to prevent foaming or get rid of existing foams because foams are produced across a wide range of industries and cause a variety of problems with industrial operations. Chemicals known as foam inhibitors and antifoaming agents work to eradicate foams by thwarting the many factors that promote foam stability. A slight concentration of them is utilized to achieve this. The types and uses of antifoaming agents are shown in Table 3 (Chang, 2016; Owen, 2001).

Table 3 - Types and applications of antifoaming agents.

Type	Name	Application
Mineral oil	Liquid paraffin	Papermaking
Oil	Animal oil, sunflower seed oil, colza oil, sesame oil	Food processing, fermentation
Aliphatic ester	Glycol distearate, sorbitol laurate, divinyl diethanol laurate, natural wax, glycerol ricinate	Paper pulp, adhesion agent, painting, fermentation, petroleum refining, dyeing, boiler water, food processing
Alcohol	Octanol, hexyl alcohol, glycol, diisobutyl carbinol, cyclohexanol	Papermaking, dyeing, painting, fermentation
Amide	Ethanediamine distearyl, storage amine distearyl, ethylene diamine dipalmitoyl	Boiler water, papermaking
Phosphate	Tributyl phosphate, trioctyl phosphate	Casein, fiber
Metallic soap	Aluminum stearate, calcium dioleate, potassium oleate	Lubricating oil, fiber, papermaking
Organosilicon	Dimethicone, silicon grease, modified polysiloxane, fluorosilicon oil	Food processing, fermentation, lubricating oil, papermaking, painting, adhesion agent, petroleum industry, chemical industry

2.5.2 Antifoam Mechanism

When antifoam is added, a solution or dispersion becomes more complicated. Understanding an antifoam mechanism necessitates considering a dispersion because both the antifoam and the foam are dispersion of gas bubbles in a liquid (the antifoam scattered in the liquid to be foamed) (Gochev & et al., 2016).

Due to the wide range of activities that antifoaming chemicals are utilized in, it is not surprising that a variety of alternate explanations for how they work have been put out. Additionally, comprehensive experimental research addressing the fundamental mechanisms of antifoam action have been documented. In actuality, the situation is much more complicated, and in some systems, multiple mechanisms may be active at once. Contrarily, the primary purpose of the antifoam is to replace or decrease the quantity of surfactant present at the interface with something that produces a less stable foam film. The chemical must also be resistant to chemicals but insoluble in the foaming medium. (R. Pugh, 2016).

Due to their high surface activity, foam breakers displace the foaming agent and carry some of the underlying liquid with them, increasing the surface pressure over small areas of liquid layers. As a result, small regions of the film become thinner and lose their resistance to rupture. The liquid film will break as a result of this low-surface-tension zone expanding all around it and losing its flexibility and capacity for self-repair. The liquid's elasticity at the surface and

surface-active chemicals' propensity to balance out cause the foam to break. The stability characteristic can be eliminated by antifoaming chemicals by increasing drainage and gas diffusion velocity, lowering film viscosity, and reducing film surface viscosity (Chang, 2016).

The oil drop enters the air/water interface where it spreads over the foam layer and ruptures it, according to a generally established mechanism for antifoaming activity. The introduction of an entering coefficient (E_c) and a spreading coefficient (S_c), both of which are defined in terms of the change in free energy when an oil droplet enters the interface or spreads at the surface, was found to be convenient based on this method. The following is a list of these:

$$E_c = \gamma_{w/a} + \gamma_{w/o} - \gamma_{o/a} \quad (1)$$

$$S_c = \gamma_{w/a} - \gamma_{w/o} - \gamma_{o/a} \quad (2)$$

where $\gamma_{w/a}$, $\gamma_{o/a}$ and $\gamma_{w/o}$ are, respectively, the equilibrium interfacial tensions of the aqueous phase (w) / air (a) interface, oil (o) / air (a) interface and aqueous phase (w) / oil (o) interface. It is crucial to remember that the entering and spreading coefficients, which are thermodynamic features independent of the process kinetics present in the draining film, are what determine whether the precise structure of the oil droplet is energetically advantageous. In reality, higher positive values don't always represent faster entering or spreading; instead, they signify the final thermodynamic state. Because silicones have a higher surface activity, silicone foam control materials entering the air/water interface are almost always positive (lower surface tension than the foaming liquid) (R. Pugh, 2016).

At first, it was believed that as soon as the oil drop entered the air/water interface, it would spread out to cover both sides of the original film as a duplex film. As a result, the initial liquid film is driven away, leaving an oil film that might liquefy and separate. Given that the mechanism is only workable under specific vital circumstances, two crucial procedures must undoubtedly be considered $E_c > 0$ (where the oil enters the air/water interface) and $S_c > 0$ (when the oil spreads on the duplex film on both sides of the original film) are the definitions for these. This circumstance is shown in Figure 9 by the balancing of the relevant surface tension and spreading coefficient. (R. Pugh, 2016).

Additionally, it was initially thought that the aqueous foam film would only break due to the spreading liquid's mechanical action, and that as the lens slid over the liquid below, the shearing stress would be transferred to a depth of several microns. As a result, the surrounding liquid moves in the same direction, thins out, and raises the risk of rupture. However, despite the fact that these equations and quantifications of E_c and S_c are helpful in that they offer a general overview of antifoaming activity, they are generally regarded as inadequate (R. Pugh, 2016).

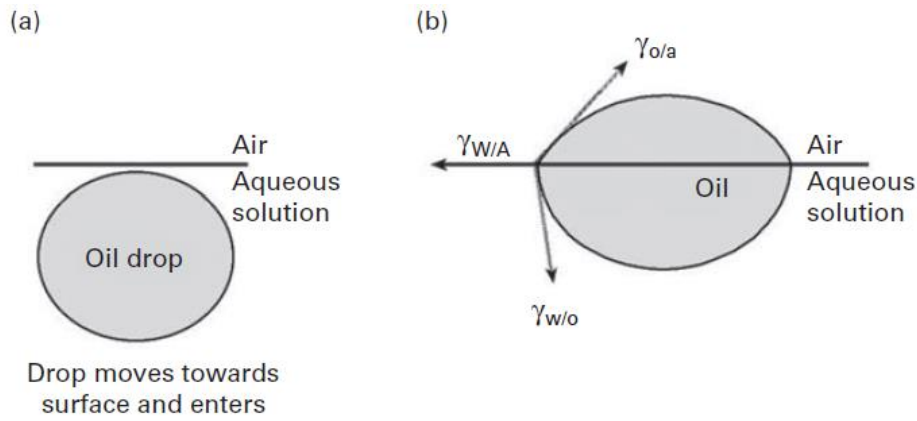


Figure 9 - (a) Entry and spreading of oil droplet at the air/solution interface; for successful entry $E_c = \gamma_{w/a} + \gamma_{w/o} - \gamma_{o/a} > 0$ and (b) for successful spreading of oil droplet

$$S_c = \gamma_{w/a} - \gamma_{w/o} - \gamma_{o/a} > 0 \text{ (R. Pugh, 2016).}$$

Another reason for the unreliability of these spreading equations is that there is a magnitude difference between the initial entry coefficient (where the components are pure) and the equilibrium values. In fact, they do not consider the geometry of the system or the interactions of thin film forces (where contamination often occurs) (R. Pugh, 2016)

Furthermore, whether the condensed approach, the oil escapes from the interface to form a lens without contaminating the w/a interface, is yet unclear, and two other scenarios have also been considered. The first includes the spread of oil at the w/a surface, which causes an unstable film to separate and leave oil lenses that pollute the interface (pseudo-partial wetting). Alternately, the oil may spread to create a duplex film that is so thick that its w/a and o/a surface tensions are identical to the bulk phase values and has no lenses (complete wetting). In any of these three scenarios, the equilibrium spreading pressure can only be zero or negative, causing the oil drop to bridge both sides of the aqueous film, which leads to instability and rupture (R. Pugh, 2016).

Only later was it proposed that the oil lens might shatter the thin foam film through a bridging mechanism. Early work focused on the importance of the development of the oil lens (but not necessarily the spreading) in the mechanism of antifoaming. The wettability of the bridging particle is the primary determinant of bridge stability, and the bridging/dewetting mechanism is typically stated in terms of the bridging coefficient, B_c , which is connected to the interfacial energy by the equation (3) (R. Pugh, 2016).

$$B_c = \gamma_{w/a}^2 + \gamma_{w/o}^2 - \gamma_{o/a}^2 \quad (3)$$

Film rupture with droplets has been explained by a number of potential methods, as depicted in Figure 10. Any of the bridging mechanisms begins with the oil drop joining that creates a

"bridge" between two film surfaces. Next, there are two conceivable possibilities for film destabilization (Denkov & et al., 2014).

According to theoretical research, positive values of B_c are associated with bridge dewetting, which is connected to the particles' capacity to span foam layers. For the particle to act as an antifoam, it must be positive. $E_c > 0$ is present in all of these processes, and the antifoam oil spreads quickly over the thin film lamella surfaces, possibly resulting in a Marangoni-driven flow of liquid in the foam film. This stage is then followed by a fluid entrainment or bridging process (fluid entrainment) (R. Pugh, 2016).

The requirements of the laws of capillarity, including the curvature of the various interfaces ensuring capillary pressure balance (Laplace law) and the appropriate three-phase contact angles satisfying the vectorial balance of the interfacial tensions at the three-phase contact lines, cause the oil bridge to deform in the storage-stretching mechanism (Figure 10 C-D) (Neumann triangle). At some point, the oil bridge becomes a biconcave shape, with the center section being the thinnest. This bridge is unstable due to uncompensated capillary pressure at the w/o and o/a interfaces, and stretching happens in a radial direction. The laws of capillarity cannot be satisfied for such an oil bridge if the bridging coefficient $B_c > 0$ (see Equation (3) for a definition of B_c), and it stretches radially until it ruptures in the bridge center. Deformable antifoam globules often activate the bridge stretching mechanism as opposed to a large concentration of solid or polymerized gel particles (Denkov & et al., 2014; R. Pugh, 2016).

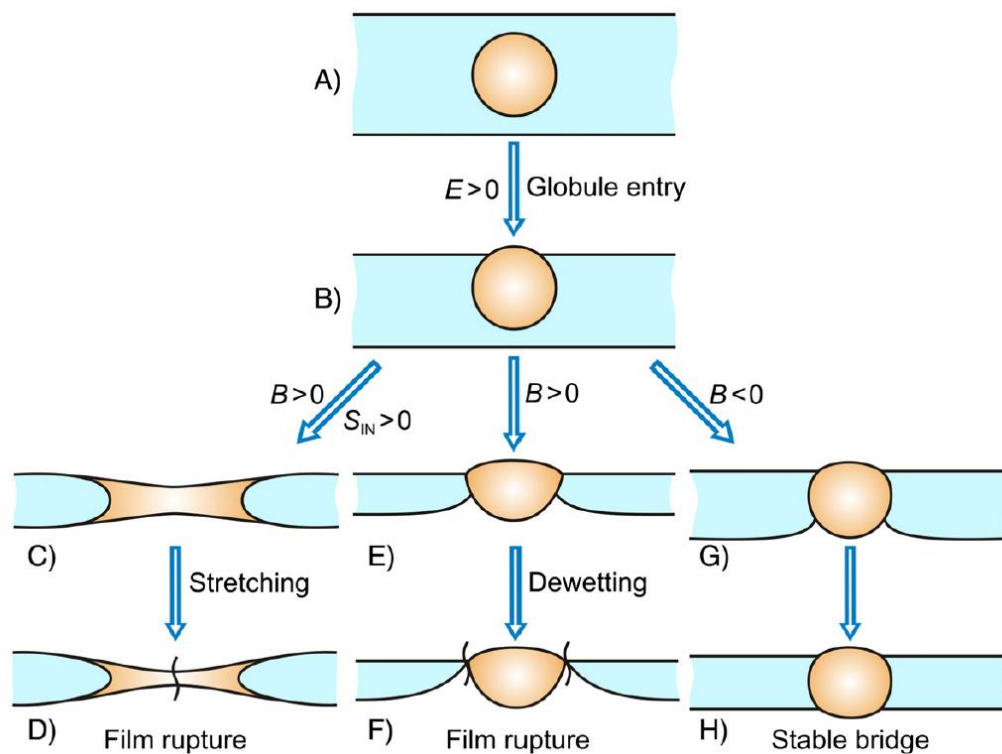


Figure 10 - Schematic representation of the different antifoam mechanisms (Denkov & et al., 2014).

In the bridging-dewetting mechanism (Figure 10 E-F), the oil bridge cannot deform because the foam film surfaces are dewetting the oil drop surface and causing film rupture at the oil bridge's edge. Figure 10 G-H shows an example of a foam film that has a stable oil bridge forming without rupturing (Denkov & et al., 2014).

Antifoams can be problematic even though they are helpful for transporting dispersion and preventing severe foam formation during application. Antifoams can lessen the wetting characteristics of succeeding processes, like the wetting of an impregnated and dried fiber or the binding strength of a polymer-coated nonwoven, when they are added to impregnation pools containing polymer dispersions. They may encourage the removal of either dry or wet soil. Antifoams can aggregate with polymer dispersions, resulting in the separation of oily particles, the production of deposits on rolls, and the non-uniform distribution of an antifoam. Additionally, antifoams stop foam from forming, which is important for textile applications. However, this can be avoided by employing a foaming agent in a higher concentration (surfactant) (Fischer, 2011).

3 Materials and Methods

This chapter describes the studies performed in this project as well as the methods applied to evaluate the foam formation capability of some dipping solutions and to determine the efficiency of a certain antifoam product. The first phase of this project was to study how certain components of the dipping solution can influence foaming during the production process and to investigate how an anti-foaming additive can be used to reduce production-related effects. To this end, several studies were carried out at the laboratory level. In the second phase was possible to replace the dipping solution conventional storage tanks, putting into operation the new dipping solution storage tanks. In order to validate these new tanks, it was necessary to evaluate if they have an impact on foam production.

In order to be able to delineate which parameters could influence the foam formation, it was first necessary to analyze the machine and its operation. This was done by watching the start-ups on different days, with different shifts. Applying the parameters in laboratory scale, several trials in laboratory, only manipulating one variable at a time, were performed. Concerning the solute formulation, dipping solution was formulated with VP latexes from different suppliers and different types of water. In addition, the dipping solution storage time was tested to see if it had influence on foam formation. To test the seasonality, some tests with cold water or cold VP latex were performed.

3.1 Materials

The dipping solution used in this study is composed of water, VP Latex, ammonia, RF-resin and formaldehyde. Currently, C-ITA uses different types of water and has different suppliers of VP latex for the dipping solution. Regarding the types of water, C-ITA uses 3 types: demineralized water, tap water and well water. The conductivity was obtained through a Conductimeter Crison GLP 31, the ions concentration was determined using a Thermo Scientific iCAP7000. The values of these properties are presented in Table 4:

Table 4 - Types of water and their properties.

Type	Conductivity ($\mu\text{S}/\text{cm}$)	$[\text{Ca}^{2+}]$ (mg/L)	$[\text{Mg}^{2+}]$ (mg/L)	$[\text{Na}^+]$ (mg/L)
Demineralized	13.48	<0.05	<0.005	1.57
Tap	109.50	17.31	0.68	4.22
Well	273.00	15.30	4.13	25.77

With regard to vinyl pyridine (VP) Latex, all the VP latexes are from different suppliers, and are a ter-polymer of styrene, butadiene and 2-VP, with different ratios. VP Latex form supplier

A has a 15:75:10 ratio and is manufactured by emulsion polymerization method containing an emulsifying system of the synthetic anionic type. On the other hand, VP latex from supplier B has a 15:70:15 ratio, respectively. VP latex from supplier C has high VP content. Henceforth, we will designate VP latex from supplier A, VP latex from supplier B and VP latex from supplier C by VP latex A, VP latex B and VP latex C, respectively.

Table 5 - VP latex from different suppliers composition.

VP Latex	Composition/Information on Ingredients	SC (%)	pH
A	Pyridine, 2-ethenyl-, polymer with 1,3-butadiene and ethynylbenzene, 15:75:10 ratio	41	11 ± 1
B	Pyridine, 2-ethenyl-, polymer with 1,3-butadiene and ethynylbenzene, 15:70:15 ratio	30 - 40	10 - 12
	Water, distilled, conductivity or of similar purity	50 - 60	
	Residuals	< 0.3	
C	Pyridine, 2-ethenyl-, polymer with 1,3-butadiene and ethynylbenzene	41	10 - 12
	Ammonia, anhydrous		
	Resin acids and Rosin acids, potassium salts		

The antifoam used for this study, was antifoam A (AF), an oil based, that is a silicone and Alkylphenol ethoxylates (APEO) free defoamer widely used in all synthetic latex systems. It is a blend of liquid hydrocarbons and modified nonionic compounds. This antifoam was made available from a C-ITA supplier, with whom C-ITA partnered for further testing and, therefore, the only homologated by C-ITA. In Table 6, some information about the properties of AF are presented.

Table 6 - Properties of AF

Viscosity at 25 °C (cSt)	Nitrogen mass fraction (%)
3000	0.4

3.2 Methodology

3.2.1 Dipping solution preparation

The dipping solution preparation resulted from mixing three previously independently prepared solutions: aqueous latex VP dispersion, aqueous alkaline RF-resin and aqueous formaldehyde solution. First, add the VP latex under study to water, previously weighted on a laboratory scale (VWR LPG-6501 with precision ± 0.1 g) . The mixture was homogenized on a magnetic stir plate

(VWR VMS-A), obtaining mixture 1. Separately, water was weighed, and an amount of ammonia was added, followed by a quantity of RF-resin, forming mixture 2. Next, this mixture is added to the previously made, mixture 1 and homogenized resulting in mixture 3. Finally, water is again weighed out and an amount of formaldehyde is added, forming mixture 4 which is added to mixture 3, obtaining the final dipping solution.

3.2.2 Foam volume evaluation

To evaluate the amount of foam formed during the impregnation process a laboratory assay was performed, using an internal method that is an adaptation of Bikerman's method (R. J. Pugh, 2016).

In a graduate cylinder of 1000 mL, 100 mL (± 5 mL) of the dipping solution under study was measured at the specified temperature, and air is blown into the graduate cylinder using a glass frit. After switching on the diaphragm pump of maximum 100 kPa (VWR PM20404-820.3) the glass frit is immersed in the dipping solution. Video recordings were made of all tests, and the volume of foam formed at different bubbling times was determined by the difference between the initial volume of the solution and the volume reached by the foam at the time of measurement. In Figure 11, it is illustrate the value measured example.

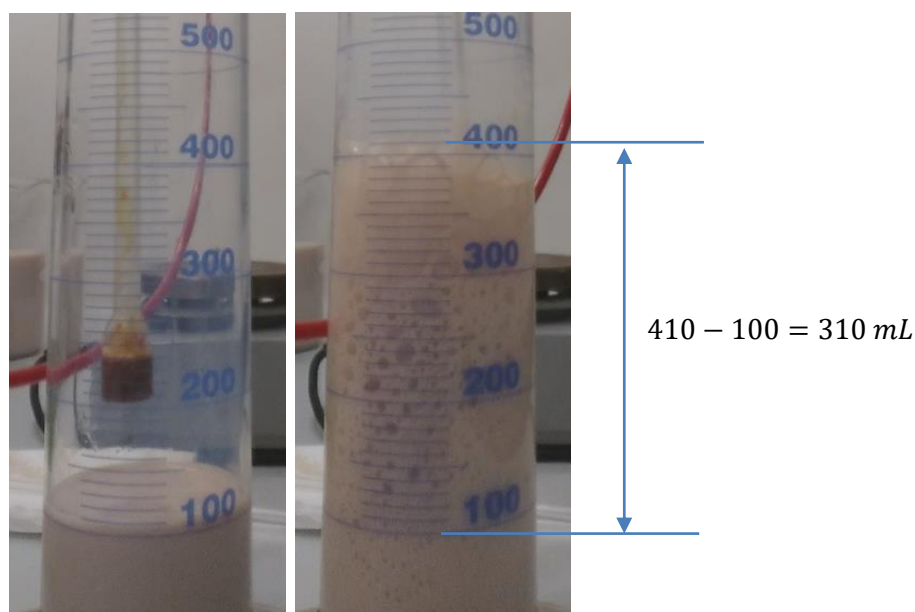


Figure 11- Examples of foam volume measure: for $t = 0$ s the foam volume is 0 mL and for $t = 60$ s the foam volume is 310 mL

3.3 Dipping process parameters influence on foaming

The first phase of this project was to study how certain components of the dipping solution can influence foaming during the production process.

3.3.1 VP Latex influence

Three tests were done to evaluate the impact of the VP latex in foaming. Dipping solution was formulated with VP latexes A, B or C. In Table 7, the dipping solutions for each test and number of trials are presented. The tests were performed as described in 3.2.2, and the results will correspond to the average of the respective number of trials and the standard deviations were calculated.

Table 7 - Tests characterization for VP latex parameter.

Test	VP Latex	Water	Number of trials
1	A	Tap	6
2	B	Tap	6
3	C	Tap	6

3.3.2 Dipping solution storage time influence

Proceeding to study the dipping solution storage time, the dipping solution has been formulated with VP latex B and tested 0 hours later, 5 hours later and 24 hours later. In Table 8, it is presented the dipping solution formulation for each test and the number of trials are presented. The tests were performed as described in 3.2.2, the results correspond to the average of the respective number of trials, and the standard deviations were calculated.

Table 8 - Tests characterization for each storage time.

Test	Storage time (h)	VP Latex	Water	Number of trials
4	0	B	Tap	3
5	5	B	Tap	3
6	24	B	Tap	3

3.3.3 Influence of the water quality

The impact of the water used to formulate dipping solution was studied, by formulating the dipping solution with different types of water (Demineralized, Tap and Well). In Table 9, is presented the dipping solution formulation for each test and number of trials. The tests were performed as described in 3.2.2, the results correspond to the average of the respective number of trials, and the standard deviations were calculated.

Table 9 - Tests characterization for each type of water.

Test	VP Latex	Water	Number of trials
7	B	Demineralized	12
8	B	Tap	6
9	B	Well	6
10	C	Demineralized	12
11	C	Tap	6
12	C	Well	6

3.3.4 Storage temperature influence

To test how temperature might influence foaming, the temperature of the dipping solution was manipulated. VP latex C was refrigerated once, water, on the other hand, was refrigerated twice. This cooling resulted in components between 3°C and 8°C, that were then used to formulate the dipping solution. After the dipping solution formulation, the dipping solutions temperature was measured using compact thermal imaging camera (FLIR Cx-Series), and the images obtained are shown in Appendix B. The temperatures considered were the average between the black and blue points. In Table 10, it is shown the dipping solution formulation for each test and number of temperatures of each component and temperature of the dipping solution. The tests were performed as described in 3.2.2, the results correspond to the average of the respective number of trials, with standard deviations calculated.

Table 10 - Tests characterization for each temperature of the dipping solution.

Test	Dipping solution temperature	VP Latex	Number of trials
13	14 °C	B	6
14	19 °C	B	6
15	21 °C	B	6

3.4 Antifoaming agent influence in foaming

After the dipping solution was formulated with VP Latex B and VP Latex C, the antifoam concentration influence in foaming was studied. For this purpose, 150 mL the respective dipping solution was measured into a 150 mL beaker and the respective volumes of AF were added using micropipettes of appropriate capacity (10 and up to 1000 µL, VWR Ultra High-Performance), stirring with a glass rod for 20 seconds. In Table 11, it is listed the amount of AF for 150 mL for each concentration of AF used (%). The tests were performed as described in 3.2.2, the results correspond to the average of the respective number of trials, with the corresponding standard deviations calculated.

Table 11 - Tests characterization for antifoam study.

<i>Test</i>	<i>AF (%)</i>	<i>AF volume (μL)</i>	<i>VP Latex</i>	<i>Water</i>	<i>Number of trials</i>
16	0.00	0.0	B	Tap	5
17	0.06	10.0	B	Tap	5
18	0.08	13.3	B	Tap	5
19	0.10	16.7	B	Tap	5
20	0.25	41.7	B	Tap	5
21	0.50	83.3	B	Tap	5
22	1.00	16.0	B	Tap	5
23	0.00	0.0	C	Tap	5
24	0.06	10.0	C	Tap	5
25	0.08	13.3	C	Tap	5
26	0.10	16.7	C	Tap	5
27	0.25	41.7	C	Tap	5

3.5 Statistical Analysis

A statistical analysis was performed, using Minitab 18 software, on the data obtained in order to determine whether two population means are equal or nearly identical, using General Linear Model ANOVA. Also, the examination of residual plots aids in determining if the ordinary least squares assumptions are being met. The model assumptions are normality, constant variance, and random error independence. If these criteria are met, ordinary least squares regression will yield unbiased coefficient estimates with the lowest possible variance. (Montgomery & et al., 2003)

3.6 Storage conditions influence on foaming in production process

As stated in 2.4, previous projects were able to develop new dipping solution storage tanks, with different characteristics. In order to validate these new tanks, it was necessary to evaluate if they have an impact on reducing foaming, so four tests were done, two in SEC II and in two SEC I.

1000 L of dipping solution were formulated, made with demineralized water and VP latex C (stored between 15 and 17 °C, temperature normally used for dipping solutions in production process). After formulated, it was necessary to test the dipping solution pH and SC of the dipping solution to validate its use. Then, the dipping solution was transferred into the new storage tanks from here the dipping solution was used in the respective equipment's dipping bath, where the cord was dipped. The dipping solution is not used immediately after

preparation in production and often might be stored for some days. In Figure 12, it is presented a scheme of the dipping solution path during dipping process.



Figure 12 - Scheme of the dipping solution path during dipping process.

In a weekly cleaning, all the components of the equipment were cleaned. The cleaning conditions of the SEC equipment for these tests are described in Table 12, furthermore, previously the dip tubes and the dipping bath are washed with water.

The machines, SECI and SECII, were turned on and the cords were run through the dipping bath. The speed of passing the cords through the dipping bath gradually increased. SECII worked at a higher speed than SECI, about 20% higher, and it was verified the absence or presence of foam in the dipping bath during the cords impregnation stage, at 15 minutes intervals for about 3 hours.

Table 12 - Tests characterization in productive environment.

<i>Test</i>	<i>Equipment</i>	<i>Storage (day)</i>	<i>Weekly cleaning</i>
28	SEC II	1	Before
29	SEC II	3	None
30	SEC I	0	None
31	SEC I	2	None

After the impregnation of the cords under the above-deROPrised conditions, the quality of the product was evaluated in the C-ITA Quality Control Laboratory, namely the amount of dipping solution in the impregnated cord was determined, i.e., the DPU per greige cord (%) was used to quantify the dipping solution in the cord, and one assay to ascertain the cord-rubber adhesion (peel adhesion test) were performed.

4 Results and discussion

4.1 Dipping process parameters influence in foaming

The first phase of this project was to study how certain components of the dipping solution can influence foaming during the production process. With that in mind, several trials, manipulating only one variable at a time, were carried out in a laboratory environment.

4.1.1 VP latex influence

At first, VP latex from different suppliers was used in the dipping solution formulation as it was the component which, presumably, would have the greater impact in foam formation. The foam volume for each VP latex A, B and C was measured and is shown in Table B.1.1 (Appendix B). Figure 13 shows the evolution of foam volume over time, in a dipping solution formulated with the different VP latexes. When foam volume exceeded 900 mL foam overflow was observed and the teste was interrupted.

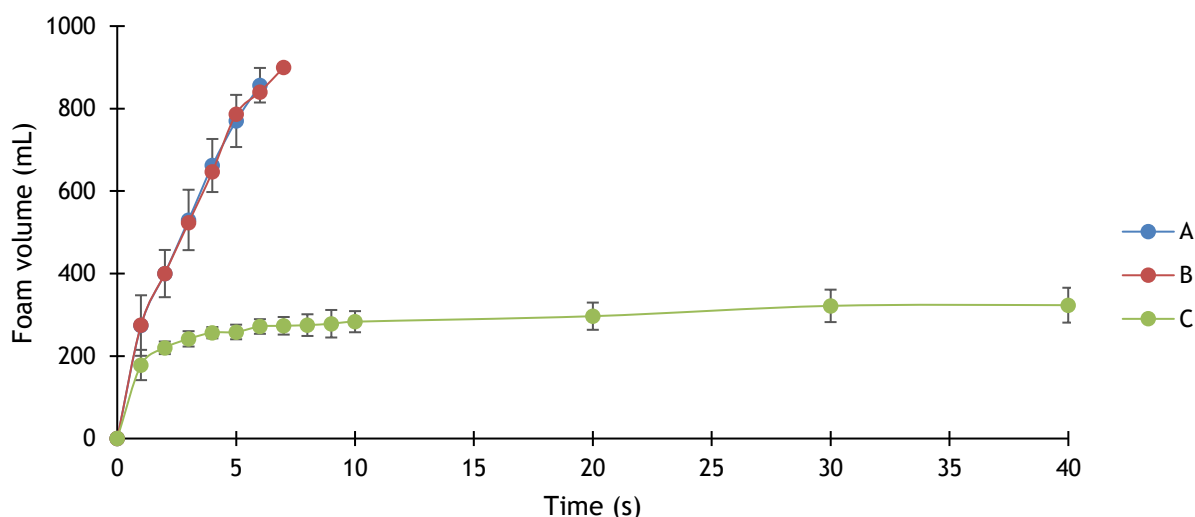


Figure 13 - Evolution of foam volume over time, in a dipping solution formulated with VP latex from different suppliers.

For the dipping solution with VP Latex A and with VP Latex B, the foam overflow was observed at 7 s and 8 s, respectively. For dipping solution with VP Latex C, even after 180 s, there is no foam overflow. These results allowed to conclude that the dipping solution formulated with VP latex C, has the better performance laboratory environment as it led to a lower foam volume.

However, this contradicts what happens in Production, because a dipping solution formulated with VP latex C originates more foam in the SEC equipment than the dipping solution with other VP latex.

After these results, it was thought to adapt the method in order to bring it closer to what happens in Production. However, it would not be advisable, as this was the method followed by one of the antifoam suppliers, thus allowing comparison of results.

An ANOVA test was performed to investigate the effect of VP Latex type and duration time on foam formation. In this analysis, it was only considered the time duration between 1 and 6 seconds. The results are summarized in Table B.1 (in Appendix C). It can be concluded that the main effects of VP Latex type (P -value $< 10^{-16}$) and time duration (P -value $< 10^{-16}$) affect foam formation. Furthermore, there is an indication of interaction between these factors (P -value $< 10^{-16}$). Figure 14 a) supports the interaction effect since, on average, the foam volume change depends on the VP Latex type for each time duration.

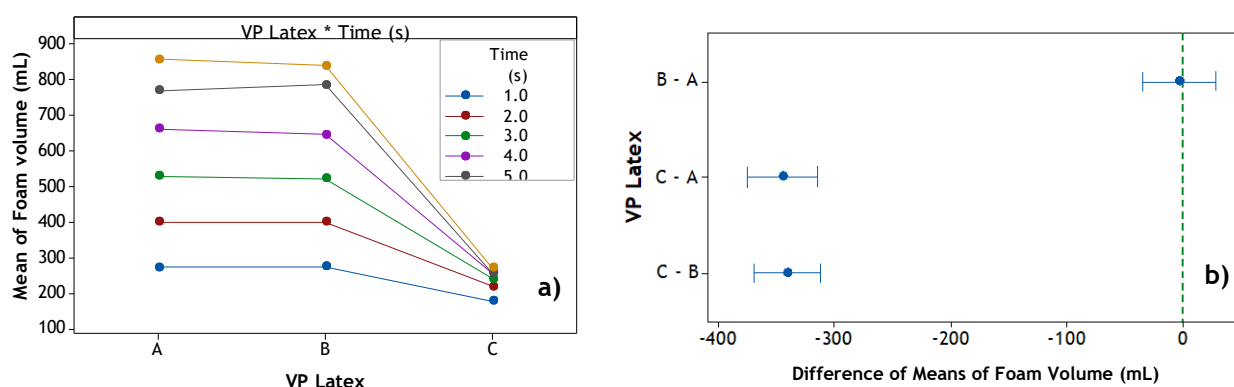


Figure 14 - Statistical analysis of VP Latex influence: a) Mean foam volume vs VP Latex type for each time; b) Tukey Simultaneous 95% Confidence intervals of the dipping solution with different VP Latex.

Tukey's multiple comparison method was used to compare individual means of foam volume of each VP Latex supplier. From Figure 14 b), it can be observed that the confidence intervals (CI) of mean volume foam differences between VP Latex C and VP Latex A and B exclude zero therefore, it can be concluded that the foam volume formation with VP Latex C is significantly different and less from VP Latex A and B. Furthermore, there are no significant differences between VP Latex A and B since CIs of mean volume foam differences between these two include zero.

4.1.2 Dipping solution storage time influence

The aging of the dipping solution was another parameter studied to find out if it would have any influence on the volume of foam formed during the process. This parameter is important in a production environment because there is no capacity to formulate fresh dipping solutions. So it is important to discover if the storage time has an impact in foaming.

The evolution of foam volume over time, for different dipping solution storage times for a dipping solution with VP Latex C is shown in Figure 15 and in Table B.1.2, Appendix B, the values of foam volume are presented.

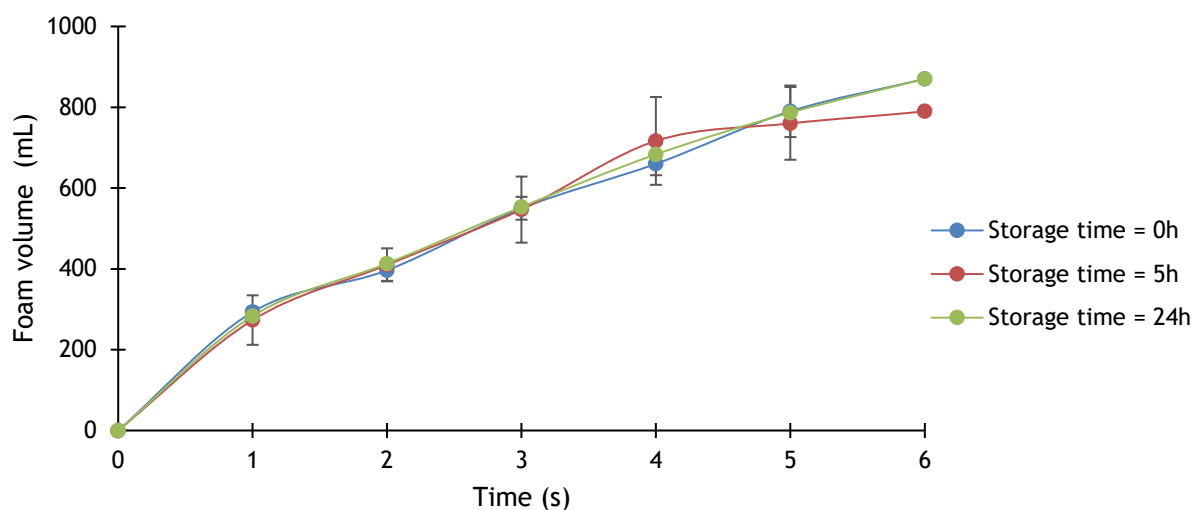


Figure 15 - Evolution of foam volume over time, for different dipping solution storage times for a dip solution with VP Latex B.

During these tests, foam overflows were observed at 7 s and 8s for the three dipping solution different storage times (0, 5 and 24 h). Analyzing the graph is possible to see that there is not a significant difference between foam formation for each dipping solution, so dipping solution storage time between 0 to 24 hours should not have any influence in foaming in the production process.

4.1.3 Influence of the water quality

In the production process, C-ITA uses different types of water depending on the time of year, and this has to do with the variation in the amount of water in the well. A water demineralization system is already in industrialization process. To follow up the dipping formulation solution in the production process, dipping solutions of VP Latex B and VP Latex C were formulated with different types of water (demineralized, tap and well).

The evolution of foam volume over time, in dipping solutions formulated with different types of water (demineralized, tap and well) for each VP latex from different suppliers (VP latex B and VP latex C) are presented in Figures 16 and 17, respectively. The values of foam volume are presented in Table B.1.3 and Table B.1.4 (Appendix B).

Figure 16 shows that, for VP latex B, there is no apparent relation between dipping solution formulated with the different types of water and foam volume. The foam overflow was

observed in time 6 s, 7 s and 8 s for dipping solutions prepared with demineralized, tap and well water, respectively.

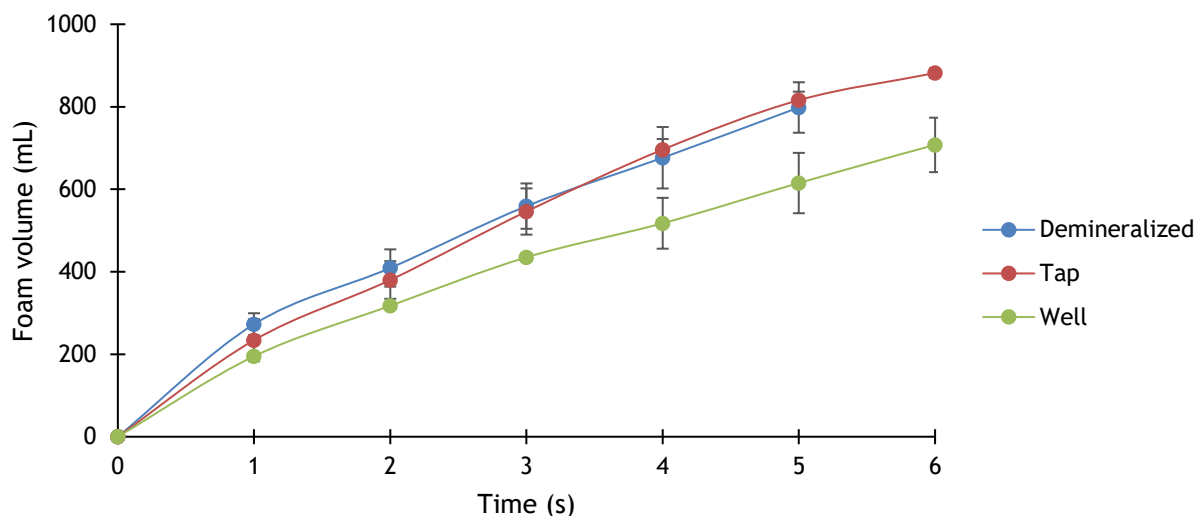


Figure 16 - Evolution of foam volume over time, in dipping solution formulated with VP latex B different types of water.

An ANOVA test was performed to investigate the effect of water type and duration time on foam formation. In this analysis, it was only considered the time duration between 1 and 5 s. The results are summarized in Table B.2 (in Appendix C). It can be concluded that the main effects of water type (P -value $< 10^{-16}$) and time duration (P -value $< 10^{-16}$) affect foam formation. Furthermore, there is no indication of interaction between these factors (P -value = 0.055). The primary effect plot's interesting factors, in this case the type of water factor, is shown in Figure 19 a). The type of water factor is significant for a dipping solution with VP Latex B, meaning that the mean of foam volume varies throughout the levels of type of water.

Tukey's multiple comparison method was used to compare individual means of foam volume of each VP Latex supplier. From Figure 17 b), it can be observed that the CI of mean volume foam differences between demineralized and well water and well and tap water exclude zero therefore, it can be concluded that the foam volume formation with well water is significantly different and less from tap and demineralized. Furthermore, there are no significant differences between these latest types of water since CIs of mean volume foam differences between demineralized and tap water include zero.

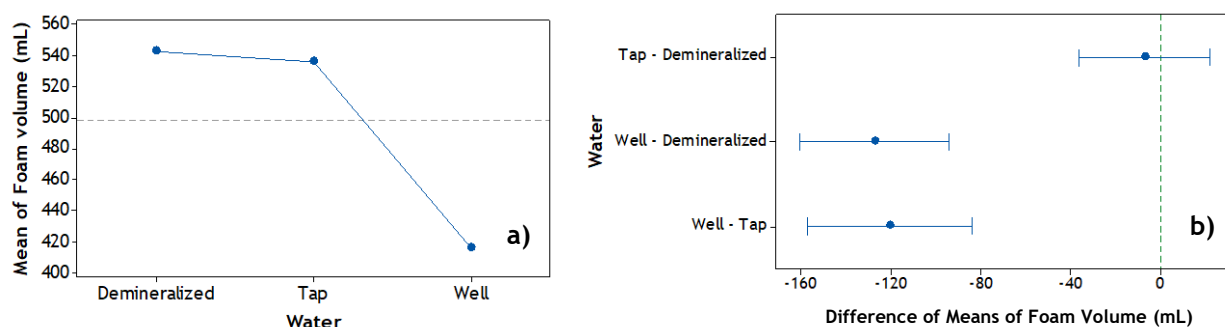


Figure 17 - Statistical analysis of type of water influence in dipping solution with VP Latex B: a) Mean foam volume vs water type; b) Tukey Simultaneous 95% Confidence intervals of the dip solution with VP Latex B and different types of water.

In Figure 18, there is the evolution of foam volume over time, in dipping solutions formulated with different types of water, demineralized, Tap and well, and for VP Latex C. In Table B.1.4, Appendix B, the values of foam volume are presented.

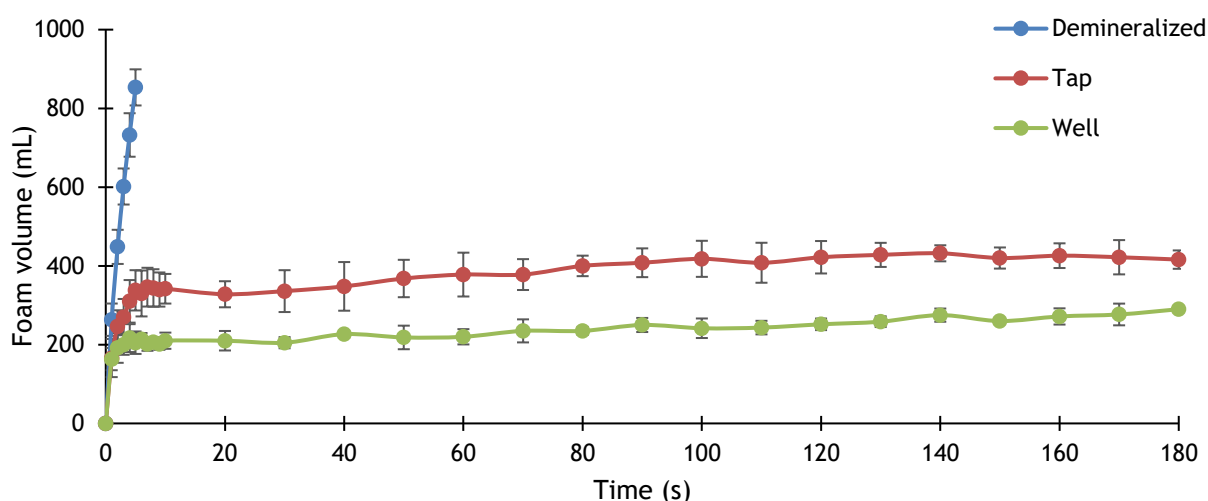


Figure 18 - Evolution of foam volume over time, in dipping solution formulated with VP latex C different types of water.

However, there is a large difference between dipping solution of VP latex C formulated with demineralized water and formulated with the other two types of water (tap and well) (Figure 18). There was no foam overflow observed for dipping solution prepared with tap water or well water even after 180 s. But foam overflow of dipping solution prepared with demineralized water was already observed at time 6 s.

Chemically, hard water and soft water are very different in their composition of dissolved salts. Dissolved salts in hard water, most notably Mg^{2+} and Ca^{2+} ions, interact with some surfactants and prevent foaming. Furthermore, soft water bubbles degrade at a slower rate than hard water bubbles. As a result, one can admit that hard water has an effect on the quality and stability

of a foam. (Williams, 2023). According to this, the dipping solutions prepared with tap water and well water (conductivity of 109.50 and 273.00 $\mu\text{S}/\text{cm}$, respectively) originated less foam volume than demineralized water (conductivity of 13.45 $\mu\text{S}/\text{cm}$), a softer water.

An ANOVA test was performed to investigate the effect of water type and duration time on foam formation. In this analysis, it was only considered the time duration between 1 and 5 s. The results are summarized in Table B.3 (in Appendix C). It can be concluded that the main effects of water type ($P\text{-value} < 10^{-16}$) and time duration ($P\text{-value} < 10^{-16}$) affect foam formation. Furthermore, there is an indication of interaction between these factors ($P\text{-value} < 10^{-16}$). Figure 19 a) supports the interaction effect since, on average, the foam volume changes depending on the water type for each time duration.

Tukey's multiple comparison method was used to compare individual means of foam volume of each water type. From Figure 17 b), it can be observed that the CI of mean volume foam differences between demineralized and well water, well and tap water and demineralized and tap water exclude zero therefore, it can be concluded that all the pairs of mean of foam volume are different.

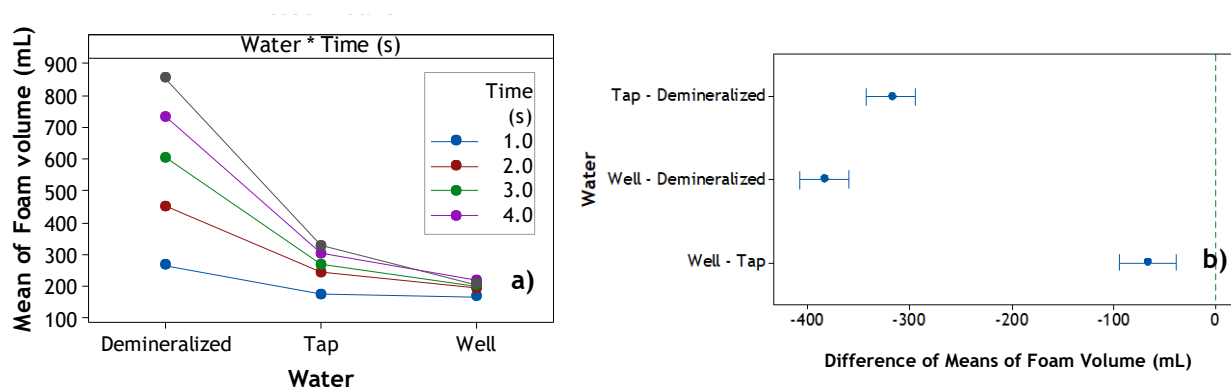


Figure 19 - Statistical analysis of type of water influence in dipping solution with VP Latex C: a) Mean foam volume vs water type for each time; b) Tukey Simultaneous 95% Confidence intervals of the dip solution with VP Latex C and different types of water.

4.1.4 Storage temperature influence

During the dipping process in the SECII equipment, a higher incidence of foam formation was observed at certain times of the year, which may have been related to temperature variation of the components.

To evaluate how temperature might influence foaming, the temperature of the dipping solution was manipulated. As solubility increases with decreasing temperature and follows Arrhenius-behavior. As the gas solubility in the aqueous solution increases, so does the amount of gas required to produce a certain volume of foam. As a result, the gas dissolves in the solution during foaming, reducing foaming efficiency (Farajzadeh & et al., 2014; Stevens & et al., 2017).

In evolution of foam volume over time in dipping solutions formulated at the different temperatures, 14 °C, 19 °C and 21 °C are presented in Figure 20 and the values of foam volume are presented In Appendix B (Table B.1.5). These temperatures correspond to the value before the foaming test with the respective dipping solution was started.

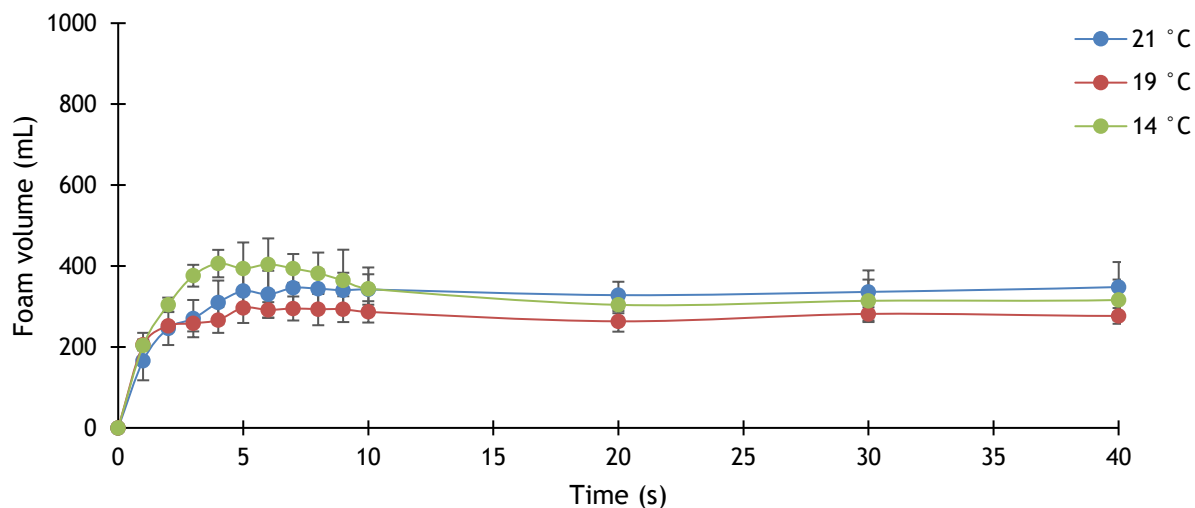


Figure 20 - Evolution of foam volume over time, in different dipping solution storage temperatures.

For all dipping solution storage temperatures, there is no foam overflow for dipping solution even after 180 s. There is also no apparent relation between dipping solution formulation temperature and foam volume. For the test realized at lower component temperature, 14 °C, was noted a peak at the beginning (foam volume maximum at 5 seconds) and, after that time, the foam volume decreased to similar values of other tests realized at higher temperature components (19 and 21 °C), which leads to the possible conclusion that this peak might be what happens in production process. However, to make a better evaluation of this parameter, more tests would be needed, changing the temperatures of the components more or even the temperature of the dipping solution storage. Since in a productive environment in winter the temperature drops a lot, it would be necessary to study temperatures of the order of 5 °C. In addition, it would be interesting to measure the temperature after each trial, to see what happens to the dipping solution temperature, after it has been blown with air.

An ANOVA test was performed to investigate the effect of water type and duration time on foam formation. In this analysis, it was only considered the time duration between 1 and 10 s. The results are summarized in Table B.4 (in Appendix C). It can be concluded that the main effects of water type (P -value $< 10^{-16}$) and time duration (P -value $< 10^{-16}$) affect foam formation. Furthermore, there is no indication of interaction between these factors (P -value = 0.269). The primary effect plot's interesting factors, in this case the storage temperature factor, is shown

in Figure 21 a). The storage temperature factor is significant for a dipping solution with VP Latex B, meaning that the mean of foam volume varies throughout the levels of type of water.

Tukey's multiple comparison method was used to compare individual means of foam volume of each storage temperature. From Figure 21 b), it can be observed that the CI of mean volume foam differences between 14 °C and 19 °C and 14 °C and 21 °C exclude zero therefore, are different. Furthermore, there are no significant differences between 19 °C and 21 °C since CIs of mean volume foam differences include zero.

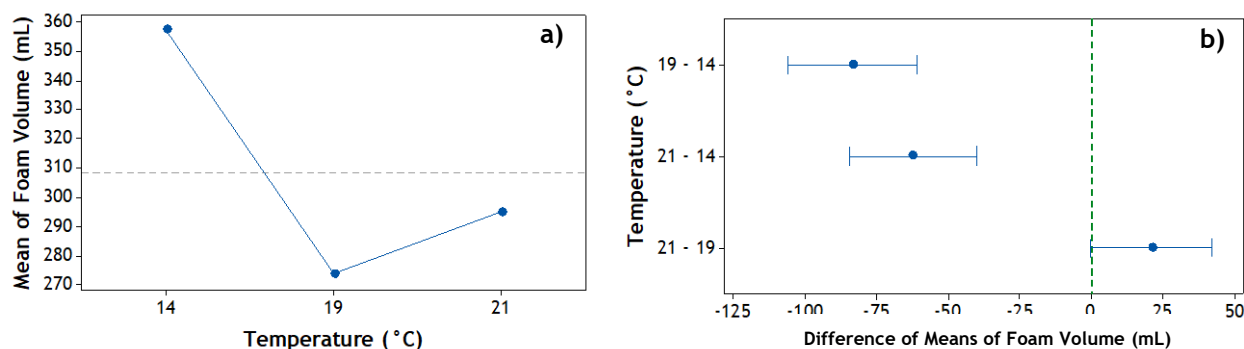


Figure 21 - Statistical analysis of storage temperature influence in dipping solution with VP Latex C: a) Mean foam volume vs storage temperature; b) Tukey Simultaneous 95% Confidence intervals of the dip solution with VP Latex C at different storage temperatures.

4.2 Antifoam concentration influence in foaming

In order to understand if it was possible to use an anti-foaming agent for the elimination or reduction of foaming that occurs with certain formulations of the dipping solutions and at certain times of the year in the production process, the next phase was the incorporation of an anti-foaming agent in the dipping solutions. Several dipping solutions of VP latex B and C were prepared with different concentrations of the anti-foaming agent (AF) and compared with a control test (0.00% of AF). So that is possible to optimize the amount of antifoam agent to be used and evaluate the amount of foam created for each concentration of AF. In Figure 22 and Figure 23, the evolution of foam volume over time, in the two-dipping solution formulated with VP latex B and VP Latex C with each concentration of AF is presented. The values of foam

volume over time for each concentration of AF and each VP Latex , are presented in Appendix B (Tables B.2.1 and B.2.2).

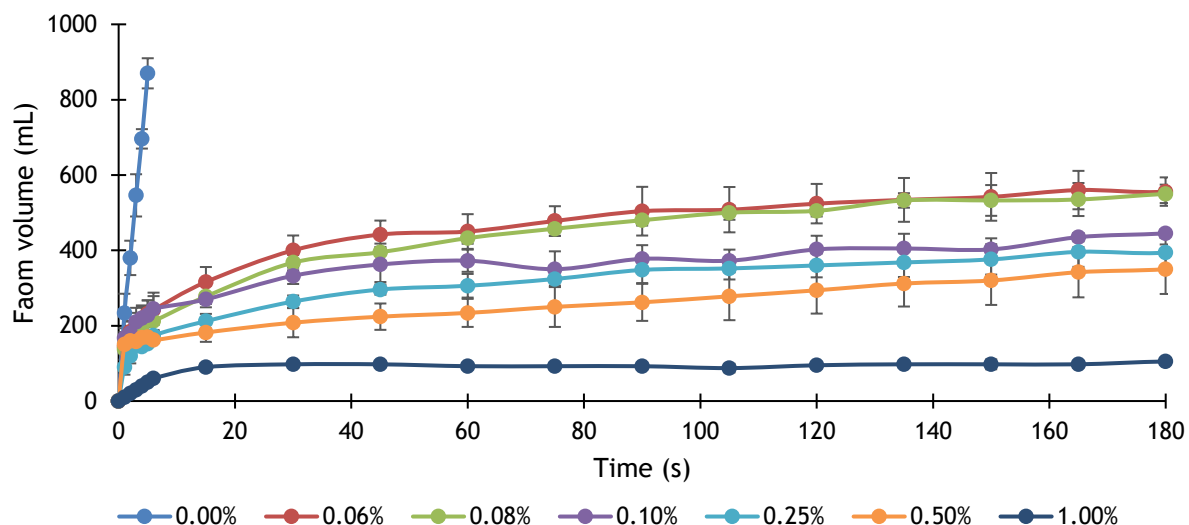


Figure 22 - Evolution of foam volume over time, in dipping solution formulated with VP latex B at each concentration of AF.

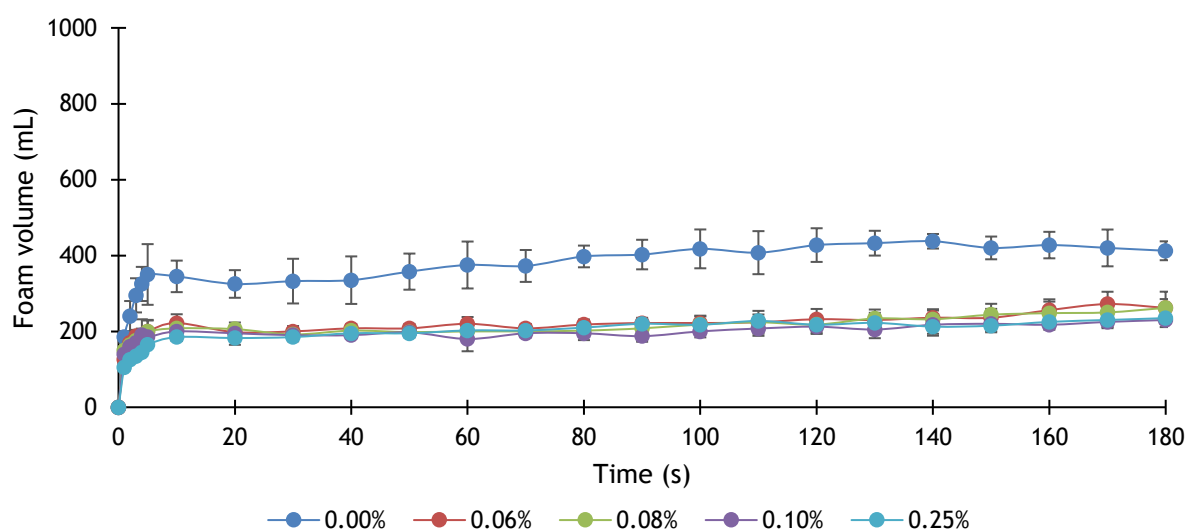


Figure 23 - Evolution of foam volume over time, in dipping solution formulated with VP latex C at each concentration of AF.

For dipping solution of both VP latex B and VP latex C, adding more anti-foaming reduces foam volume, as expected. For dipping solution with VP Latex B, the control test (0.00 % of AF) showed foam overflow for $t=5$ s, as previously observed (Figure 13). But the addition of 0.06 % of AF reduces the foam volume in, approximately, 30 %. For dipping solution with VP Latex C, it can be seen that there is no foam overflow even after 180 s, also as previously observed (Figure 13) and the addition of 0.06 % of AF reduces the foam volume in, approximately, 35 %. Although for the dipping solution with this VP Latex C, adding more amount of anti-foaming

agent does not reduce the foam volume much further (Figure 23). For VP Latex C, probably, could be used a lower concentration of AF.

Comparing dipping solutions with the two VP Latex, for dipping solution with VP Latex B to form the same foam volume as one with VP Latex C, it would be necessary to add 0.25% of AF to the former.

An ANOVA test was performed to investigate the effect of VP Latex type, AF concentration and duration time on foam formation. In this analysis, it was only considered the time duration between 1 and 180 seconds. The results are summarized in Table 13. It can be concluded that the main effects of VP Latex type (P -value $< 10^{-16}$) AF concentration (P -value $< 10^{-16}$) and time duration (P -value $< 10^{-16}$) affect foam formation. Furthermore, there is an indication of interaction between AF concentration and VP Latex factors (P -value $< 10^{-16}$), but no interaction between AF concentration and Time (P -value = 0.925).

Table 13 - Analysis of Variance.

<i>Source</i>	<i>DF</i>	<i>Adj SS</i>	<i>Adj MS</i>	<i>F-value</i>	<i>P-value</i>
<i>AF (%)</i>	3	510929	170310	63.82	$< 10^{-16}$
<i>Time (s)</i>	29	3922263	135250	50.68	$< 10^{-16}$
<i>VP Latex</i>	1	1402672	1402672	525.62	$< 10^{-16}$
<i>AF (%) *Time (s)</i>	87	181348	2084	0.78	0.925
<i>AF (%) *VP Latex</i>	3	110884	36961	13.85	$< 10^{-16}$
<i>Total</i>	737	9807376			

Figure 24 supports the interaction between AF concentration and VP Latex effect since, on average, the foam volume change depends on the AF concentration for each VP Latex. From this plot, it is confirmed that increasing the concentration of AF in a dipping solution with VP Latex C, does not have much impact on decreasing of foam formation expressed as foam volume.

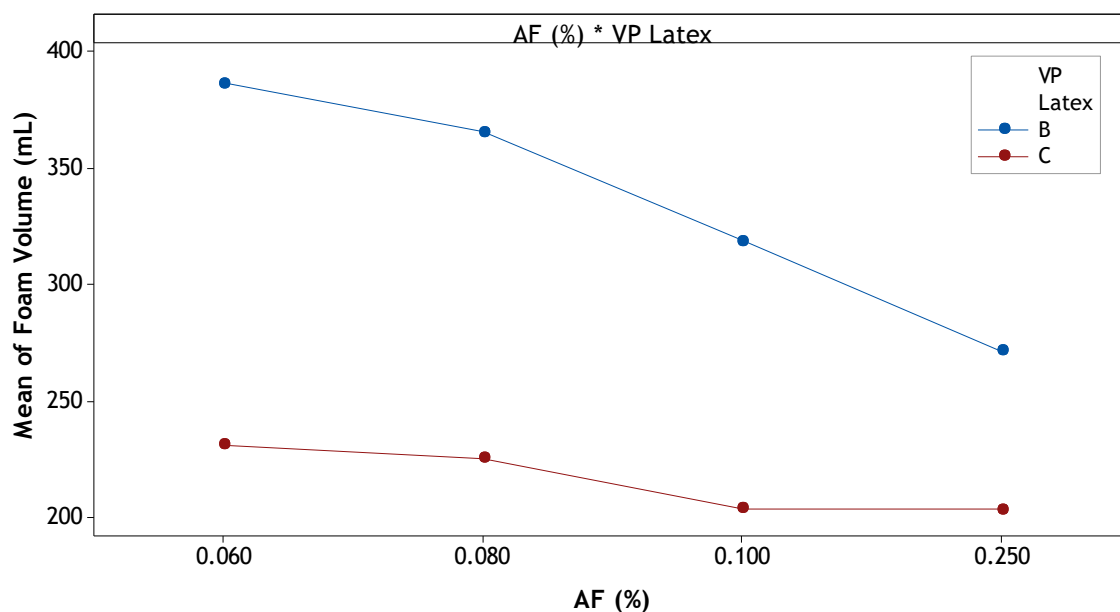


Figure 24 - Mean of foam volume vs AF concentration for each VP Latex.

Tukey's multiple comparison method was used to compare individual means of foam volume of each AF concentration. From Figure 25, it can be observed there are no significant differences between VP Latex B with 0.06% and 0.08% of AF, with VP Latex C with 0.06% and 0.08%, with 0.08% and 0.10%, with 0.08% and 0.25%, with 0.10% and 0.25% since their CI of mean volume foam differences include zero. Furthermore, the other CI of mean volume foam differences exclude zero.

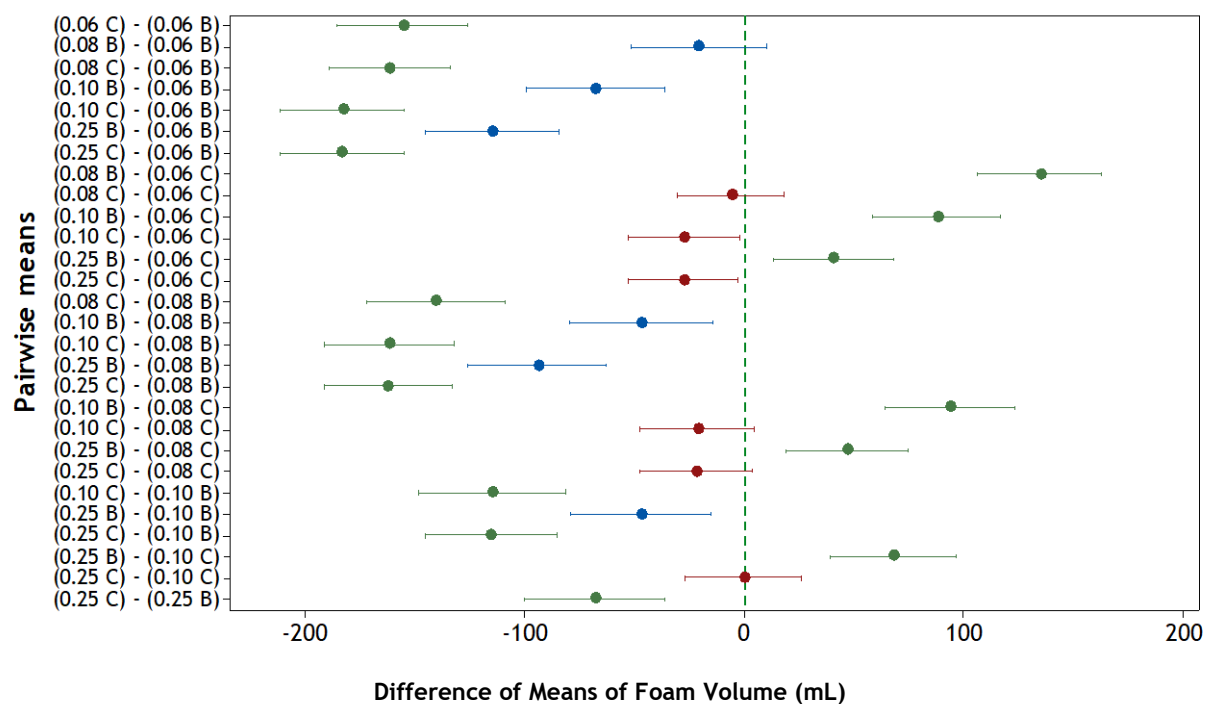


Figure 25 - Tukey Simultaneous 95% Confidence intervals of the dipping solution with each concentration of AF for both VP Latex.

As the primary objective of this part was to optimize the concentration of AF to use in a dipping solution, the statistical analysis helped achieving this. For both VP Latex B and VP Latex C, nothing indicates that the pair of means of foam volume of the dipping solution with 0.06% and 0.08% of AF are different. So, in order to minimize the possibility of the antifoam impacting the quality of the final product, it is ideal to add as little concentration of AF as possible, this being 0.06%.

4.3 Storage conditions influence

As stated in 2.4, previous projects were able to develop new dipping solution storage tanks, with different characteristics. In the second stage of this project, it was possible to replace the dipping solution conventional storage tanks, putting into operation the new dipping solution storage tanks. The new storage tanks have different agitator blades, compared to the conventional ones, have a different sizing, are closed, have an automatic cleaning system, among other differences. In order to validate these new storage tanks, was necessary to evaluate if they have an impact on reducing foaming in the production process.

Thus, four tests were performed, two in SEC II and two in SEC I and the storage time of the dipping solution was also different before performing the tests. However, as known at the Production level, and observed in section 4.1.2, the storage time of the dipping solution has no influence on the volume of foam formed.

Finally, for the tests done in Production, it was possible to observe the foam in the dipping bath and evaluate, qualitatively, the foam level of a dipping solution formulated with VP latex C and demineralized water. Table 14 shows the results of the tests carried out in a production environment. The foam level was classified as:

- No - No foam;
- Foam - Foam overflows from the dipping bath;

About 300L were spent for each test, and since four tests were scheduled, the dipping solution would not be enough for all, since only 1000 L of dipping solution were made. Therefore, on day 1 was only made one test so that dipping solution was enough to observe whether the tank protects the conditions of the dipping solution over time and study the aging of the dipping solution.

Test 28 in SEC II had good results, because there was no visible foam in the dipping bath. However, test 29 in SEC II, as described in the table, formed foam approximately 30 min after starting the equipment. It was necessary to slow down the operating speed to get the foam down. The differences between tests 28 and 29 are 2 aspects: storage time and weekly cleaning. Given the prior knowledge that dipping solution storage time should not influence in

foaming, then one could hypothesize that the fact that foam was formed had to do with the weekly cleaning factor of SEC II.

Table 14 - Results of foam level, adhesion and DPU, for tests in SEC II.

<i>Test</i>	<i>Equipment</i>	<i>t (min)</i>	<i>Foam level</i>	<i>Adhesion</i>	<i>DPU</i>
28	SEC II	150	No	Values within specifications	
29	SEC II	150	Foam between 30-60 min	No information	
30	SEC I	150	No	No information	
31	SEC I	150	No	Values within specifications	

However, for tests 30 and 31, SEC I was not subjected to weekly cleaning and there was no foaming, so it can be assumed that this is not the factor that justifies the result observed in test 29.

When analyzing the set of the 2 tests performed in SEC I (30 and 31) considering that there was no variation in the weekly cleaning factors; the difference between the storage time was the same as in the set of tests 28 and 29; and SEC II machine works at a higher speed than SEC I, then the reason for these results may have to do with the speed of the machine.

The higher running speed of the SECII will contribute to a greater amount of air intake during the passage of the cord into the dipping bath and therefore a greater amount of dissolved air in the dipping solution (see Figure 8) favoring the formation of a greater volume of foam.

Regarding the quality of the product, the results available so far from C-ITA Quality Control indicate that the cords coated in Tests 28 and 31 were within specification with respect to the DPU values and adhesion characteristics (Annex B, Figure B.1).

5 Conclusion

The first phase of this project was to study how certain components of the dipping solution can influence foaming during the production process. With that in mind, several trials, manipulating only one variable at a time, were carried out in a laboratory environment. These results allowed us to conclude that the dipping solution formulated with VP latex C, has the better performance in laboratory environment as it led to a lower foam volume. dipping solution storage time between 0 to 24 hours should not have any influence in foaming in the production process and there is also no apparent relation between dipping solution formulation temperature and foam volume. Finally, for VP Latex C, dipping solution with tap water and well water originates less foam than demineralized water.

Next, laboratory scale tests were carried out to study the application of an antifoam in the dipping solution, as well as the impact of this addition on the reduction of the amount of foam. In order to minimize the possibility of the antifoam impacting the quality of the final product, it is ideal to add as little concentration of AF as possible, this being 0.06 %.

In the second stage of this project, it was possible to replace the dipping solution conventional storage tanks, putting into operation the new dipping solution storage tanks. When analyzing the set of tests, the reason for the results may have to do with the speed of the machine.

Yet, to make a better evaluation of the dipping solution temperature parameter, more tests would be needed, varying the temperatures of the components more or even the temperature of the dipping solution storage. In addition, it would be interesting to measure the temperature after each trial, to check what happens to the dipping solution temperature, after it has been blown with air.

Also, it would be beneficial to test AF in a production environment to determine the true impact of the antifoam on foam reduction in SEC II. To have more variety of antifoams, some tests with another antifoam were done. In these the cord was dipped in 4 different ways: in Production, in Production causing foaming using the Lab Dipping Unit (LDU) and in LDU with AF. On a laboratory scale, the LDU can replicate a SE machine. The cord is subjected to one or two dipping baths in the LDU, followed by drying and heated stretching. Then, a sample from each test was sent to a new supplier to be able to formulate a suitable antifoam.

6 Assessment of the work done

6.1 Objectives Achieved

The goal of this project was to proceed with the study of the application of antifoams in dipping baths, as well as understanding the parameters impact in the equipment operation and foaming. With this study, it follows that some parameters have more influence in foam formation than others. And as expected, for VP latex adding more antifoam reduces foam.

6.2 Final Assessment

I am quite proud of this Master Thesis and all of the work I have completed, and I hope that all of this effort will contribute to C-ITA's productivity. It has been an honor to be able to work in this company and meet such wonderful people.

The deepening of the knowledge about manufacturing processes and their optimizations are extremely important factors for an industry, in view of the continuous improvement and search for the maximum quality of its products. With this project, it was found that working on such a broad area, with so many variables and a significant impact on final product attributes and industrial processes, to be astounding.

7 References

- Brewer, H. (2006). *The Pneumatic Tire*. National Highway Traffic Safety Administration.
- Bruker. (2023). *Ressonância Magnética*.
<https://www.bruker.com/pt/products-and-solutions/magnetic-resonance.html> (February 1, 2023).
- Butt H., & et al. (2013). *Physics and Chemistry of Interfaces*.
- CDRH Magnetic Resonance Working Group. (1997). *Medical Device Interactions with Magnetic Resonance Imaging Systems*.
https://users.fmrib.ox.ac.uk/~peterj/safety_docs/fda_primer.html (February 1, 2023).
- Chang, Q. (2016). Emulsion, Foam, and Gel. In *Colloid and Interface Chemistry for Water Quality Control*: 227-245.
<https://doi.org/10.1016/B978-0-12-809315-3.00011-6>
- Continental. (2013). *Tyre Basics - Passenger Car Tyres*.
- Continental. (2022a). *An inside look at the components that make up modern car tires*.
<https://www.continental-tires.com/car/tire-knowledge/tire-basics/tire-components>
 (October 18, 2022).
- Continental. (2022b). *Continental - Indústria Têxtil do Ave - Factos Históricos*.
- Costa, P. F. A. da. (2017). *Development and study of hybrid cords for tire reinforcement* [Master Thesis]. Escola de Engenharia da Universidade do Minho, Guimarães, Portugal.
- Crucible Chemical Company. (2023). *Antifoaming Agents vs Defoamers*.
<https://cruciblechemical.com/what-is-a-defoamer/> (February 6, 2023).
- Dalitz, F., & et al. (2012). "Process and reaction monitoring by low-field NMR spectroscopy." *Progress in Nuclear Magnetic Resonance Spectroscopy*, 60: 52-70.
<https://doi.org/10.1016/j.pnmrs.2011.11.003>
- Denkov, N. D., & et al. (2014). "Mechanistic understanding of the modes of action of foam control agents." *Advances in Colloid and Interface Science*, 206: 57-67.
<https://doi.org/10.1016/j.cis.2013.08.004>
- Drumond, N. (2013). *Adhesion optimization by new latex blends on rayon reinforcement for tyre application* [Master's Thesis]. Faculdade de Engenharia da Universidade do Porto, Porto, Portugal.
- Durairaj, R. (2005). *Resorcinol* (1st ed.).
<https://doi.org/10.1007/3-540-28090-1>

- Elhawary, I. A. (2010). Spin finishes for textiles. In *Advances in Yarn Spinning Technology*: 416-430
<https://doi.org/10.1533/9780857090218.2.416>
- Farajzadeh, R., & et al. (2014). Effect of Gas Permeability and Solubility on Foam. *Journal of Soft Matter*: 1-7.
<https://doi.org/10.1155/2014/145352>
- Fischer, K. (2011). Auxiliaries for Technical Textiles. In *Ullmann's Encyclopedia of Industrial Chemistry*: 161-182.
https://doi.org/10.1002/14356007.o26_o12
- Gochev, G., & et al. (2016). Foams. In *Ullmann's Encyclopedia of Industrial Chemistry*: 1-31.
https://doi.org/10.1002/14356007.a11_465.pub2
- Hornak, J. P. (1996). *The Basics of NMR*. Rochester Institute of Technology, Center for Imaging Science.
- Lewin, M. (2006). *Handbook of Fiber Chemistry* (M. Lewin, Ed.). CRC Press.
<https://doi.org/10.1201/9781420015270>
- Louis, A., & et al. (2016). Technologies for Polymeric Cord / Rubber Adhesion in Tire Applications. In *Proceedings of 186th Technical Meeting ACS Rubber Division*: 1-29.
- Mang, T., & et al. (2011). Lubricants, Components. In *Ullmann's Encyclopedia of Industrial Chemistry*: 413-451.
https://doi.org/10.1002/14356007.o15_o04
- Martins, A. (2013). *Zell, Single-End & LDU*. Continental
- Montgomery, D. C., & et al. (2003). *Applied Statistics and Probability for Engineers* (3rd ed.).
https://www.academia.edu/38614250/_Douglas_C_Montgomery_George_C_Runger_Applied_BookFi
- Nanjing Invelychem Co. (2020). *How to antifoam work?*
<https://www.ywlchemical.com/defoamer/> (January 13, 2023).
- Owen, M. J. (2001). Defoamers. In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc: 236 - 254.
<https://doi.org/10.1002/0471238961.0405061515230514.a01.pub2>
- Petkova, B., & et al. (2020). Foamability of aqueous solutions: Role of surfactant type and concentration. *Advances in Colloid and Interface Science*, 276.
<https://doi.org/10.1016/j.cis.2019.102084>

- Pugh, R. (2016). Antifoaming and defoaming. In *Bubble and Foam Chemistry*: 331-371.
<https://doi.org/10.1017/CBO9781316106938.011>
- Pugh, R. J. (2016). Bubble size measurements and foam test methods. In *Bubble and Foam Chemistry*: 372-404.
<https://doi.org/10.1017/CBO9781316106938.012>
- Rocha, I. (2019). *Study of Dip content in the tire textile reinforcements* [Master's Thesis]. Faculdade de Engenharia da Universidade do Porto, Porto, Portugal.
<https://hdl.handle.net/10216/119301>
- Santos, J. (2018). *Study of Dip content in the tire textile reinforcements* [Master's Thesis]. Faculdade de Engenharia da Universidade do Porto, Porto, Portugal.
- Silva, L. M. A., & et al. (2016). NMR investigation of commercial carbon black filled vulcanized natural rubber exposed to petrodiesel/biodiesel mixtures. *Fuel*, 186: 50-57.
<https://doi.org/10.1016/j.fuel.2016.08.060>
- Stevens, K. A., & et al. (2017). Influence of temperature on gas solubility in thermally rearranged (TR) polymers. *Journal of Membrane Science*, 533: 75-83.
<https://doi.org/10.1016/j.memsci.2017.03.005>
- Todt, H., & et al. (2001). Quality control with time-domain NMR. *European Journal of Lipid Science and Technology*, 103: 835-840.
[https://doi.org/10.1002/1438-9312\(200112\)103:12<835::AID-EJLT835>3.0.CO;2-P](https://doi.org/10.1002/1438-9312(200112)103:12<835::AID-EJLT835>3.0.CO;2-P)
- Vardar-Sukan, F. (1998). Foaming: Consequences, prevention and destruction. *Biotechnology Advances*, 16: 913-948.
[https://doi.org/10.1016/S0734-9750\(98\)00010-X](https://doi.org/10.1016/S0734-9750(98)00010-X)
- Wennekes, W. (2008). *Adhesion of RFL-treated cords to rubber : new insights into interfacial phenomena* [PhD Thesis]. University of Twente, Enschede, Netherlands.
- Williams, D. (2023). *Impact of Formulation and Water Hardness on Detergent Foamability*.
<https://www.rheologylab.com/laundry-detergents-how-foamability-is-affected-by-brand/#:~:text=Hard%20water%20contains%20dissolved%20salts,this%2C%20laundry%20detergents%20contain%20softeners>. (January 29, 2023).

Annex A - Adhesion Mechanism

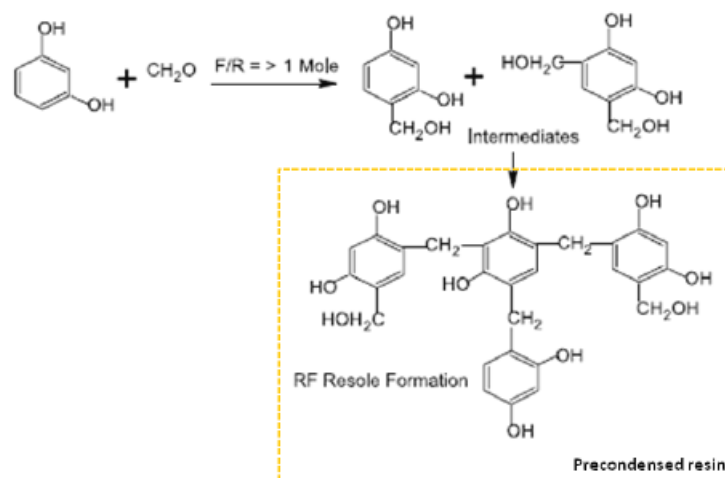


Figure A.1 - Schematic approach to trimethylol resorcinol (RF resole) formation/ presence on precondensed resin (Drumond, 2013).

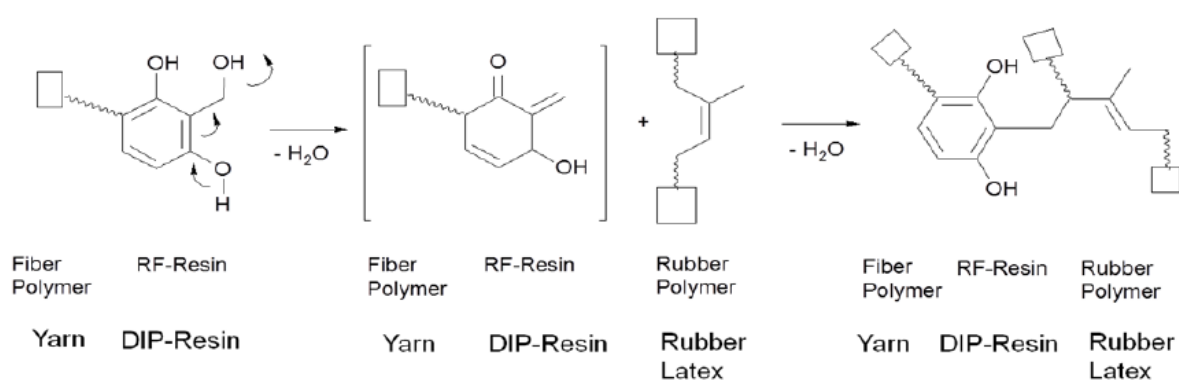


Figure A.2 - Greth and Hultzsch mechanism for adhesion chemistry on RFL - compound (Drumond, 2013).

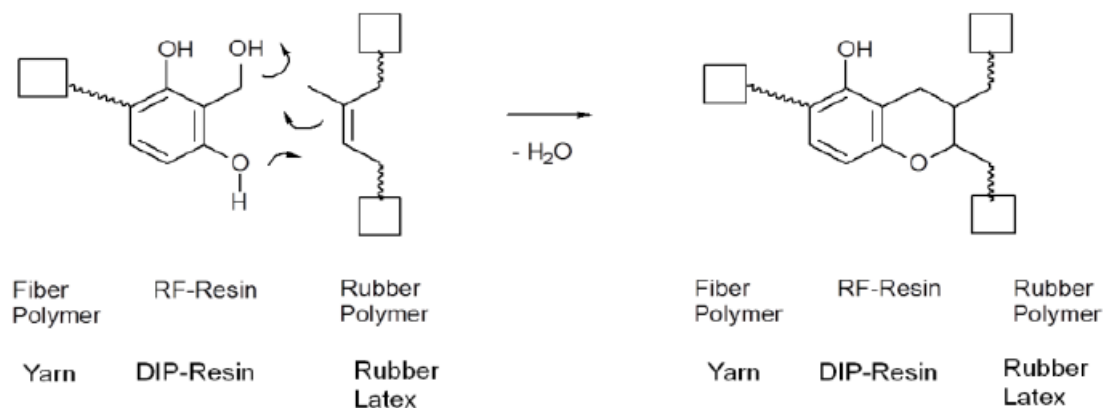


Figure A.3 - van der Meer mechanism for adhesion chemistry on RFL - compound (Drumond, 2013).

Annex B - Study of Dip content in the tire textile reinforcements

After the impregnation of the cords under the above conditions, the quality of the product was evaluated in the C-ITA Quality Control Laboratory to analyze cord-rubber adhesion and the amount of dipping solution in the impregnated cord.

One example is the "peel adhesion test" represented in Figure B.1, which involves splitting the complicated rubber plus cable into two sections and evaluating the adherence with a tensile tester. To consider the results satisfactory, the cords must be invisible to naked sight. (Rocha, 2019)



Figure B.1 - Example of a peel adhesion test results: showing a good result, on the left, and a bad one on the right (Rocha, 2019).

It is also important to determine the amount of dip in the cord after dipping so that the final product can be completely described. The DPU per greige cord is used to quantify the dip in the cord. The wet chemical approach, the weighing method, and the Time Domain-Nuclear Magnetic Resonance (TD-NMR) method are the three ways for calculating DPU. (Rocha, 2019; Santos, 2018)

B.1 Wet-Chemical Method

For this method, the DPU is determined by mass differences (gravimetric method), dissolving the fiber in an appropriate solvent, and having each material undergo a specified experimental protocol. (Santos, 2018)

The wet chemical procedure entails dissolving the fiber, filtering of the solution via a crucible, recovering the dip residue, drying the dip, and weighing the residue. The DPU is computed using Equation 4,

$$DPU = \frac{m_{dip}}{m_{dipped\ cord} - m_{dip}} \times 100 \quad (4)$$

where $m_{dipped\ cord}$ is the mass of dipped cord before dissolving and m_{dip} is the difference in crucible mass before and after filtration. (Santos, 2018)

B.2 Weighing Method

Because cords have a great affinity for water, they must be dried in the oven before being weighted. PET, unlike the other materials, has a very low hygroscopic tendency, hence dampness has no effect on the weight. In this scenario, the DPU can be calculated using a weighing method that does not involve fiber disintegration. The greige cord has been thermosetted and is being used as a reference value. The DPU is obtained by the Equation 5. (Santos, 2018)

$$\& DPU = \frac{m_{dipped\ cord} - m_{greiged\ cord}}{m_{greiged\ cord}} \times 100 \quad (5)$$

To dissolve the fiber, harmful chemicals to the environment are used. The wet chemical method is time-consuming and errors can occur during the procedure, making this method unsuitable for quality control. For example, obtaining DPU could take about five hours (for nylon and rayon) or three to five days (for aramid and hybrid cords) (Santos, 2018).

B.3 Time Domain-Nuclear Magnetic Resonance (TD-NMR)

The Nuclear Magnetic Resonance (NMR) approach, TD-NMR, creates a magnetic field with a low frequency around the sample to study and measure the energy re-emitted by the protons. This energy produces an electrical signal that is read in the temporal domain and is proportional to the number of protons present; the higher the dip concentration, the larger the signal received (Rocha, 2019).

TD-NMR, commonly known as low-field NMR, is a time-domain pulsed nondestructive approach. Despite these benefits, quantifiable data can only be obtained with further calculation or calibration of this device (Rocha, 2019).

The TD-NMR machine operates on the spin of protons (^1H) by creating a magnetic field in the area where the sample will be studied in order to excite the protons and change their energy level. The proton spins align with the induced magnetic field and are subjected to two types of magnetic pulses. The Hahn-echo sequence is used to apply this disturbance to the sample. Two rf (radio frequency) pulses comprise the pulse sequence. At 90° , the first pulse generates a

Free induction decay (FID) signal. The second pulse, emitted at 180° , is twice as long as the first, and the signal obtained is generated by the fiber's sample. Each angle has a particular effect on the spinning of the protons. The signal released by the sample's protons is at its strongest at the end of the pulse with 90° . When the pulse is discontinued, the spins return to their equilibrium position, expelling the energy that was required to shift them. As a result, the amount of dip can be calculated by subtracting the first and second signals, as shown in Figure B.3.1 (Bruker, 2023; CDRH Magnetic Resonance Working Group, 1997; Dalitz & et al., 2012; Todt & et al., 2001).

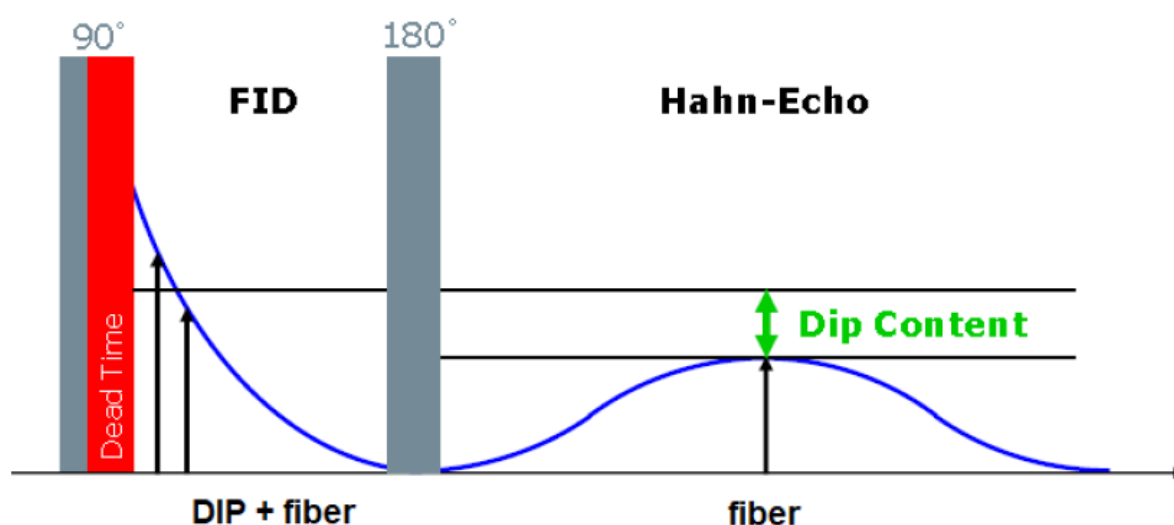


Figure B.3.1 - Hahn echo sequence representation (Adapted from Bruker, 2023).

The apparatus calculates the concentration of solid content by detecting the energy released by protons in a specific sample when activated by a low frequency magnetic field. This energy releases an electrical signal that is read by the device and is related to the number of protons and, as a result, the mass of the sample; thus, a higher sample mass leads to a higher signal emitted (Silva & et al., 2016).

The determination of DPU is based on the relaxation properties of the materials contained in the sample, specifically the cord and the dip, both of which are solid components, but the dip has a shorter relaxation time. Varied protons and dips have differing relaxation times because to their different constitutions (Hornak, 1996).

In the TD-NMR device, the dip pick-up evaluation follows a similar procedure, except that instead of comparing solid and oil-type materials, it compares different forms of solid matter (yarn and cured resin-type). Furthermore, because the yarn may contain some oil (spin-finish from the supplier), the software application employed removes both this signal and the one from the yarn, resulting in a dip measurement alone (Bruker, 2023).

Appendix A - Schemes

A.1 SEC II

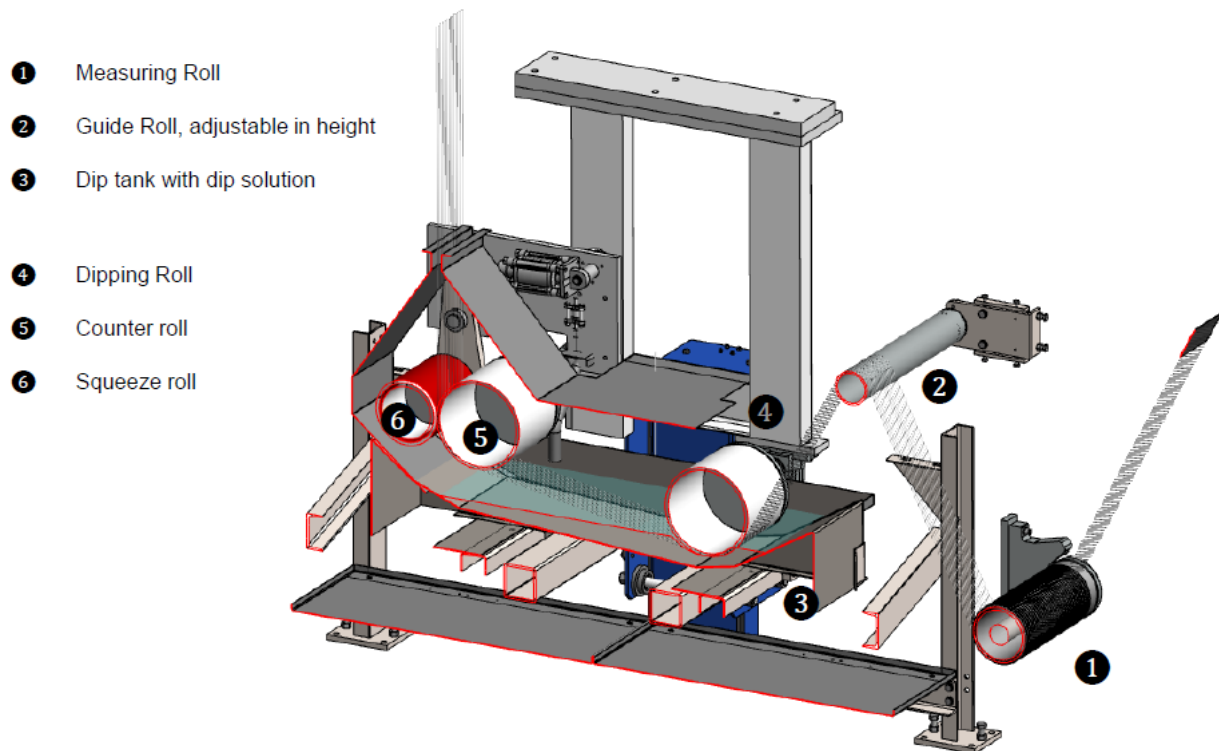


Figure A.1.1 - SEC II dipping bath scheme.

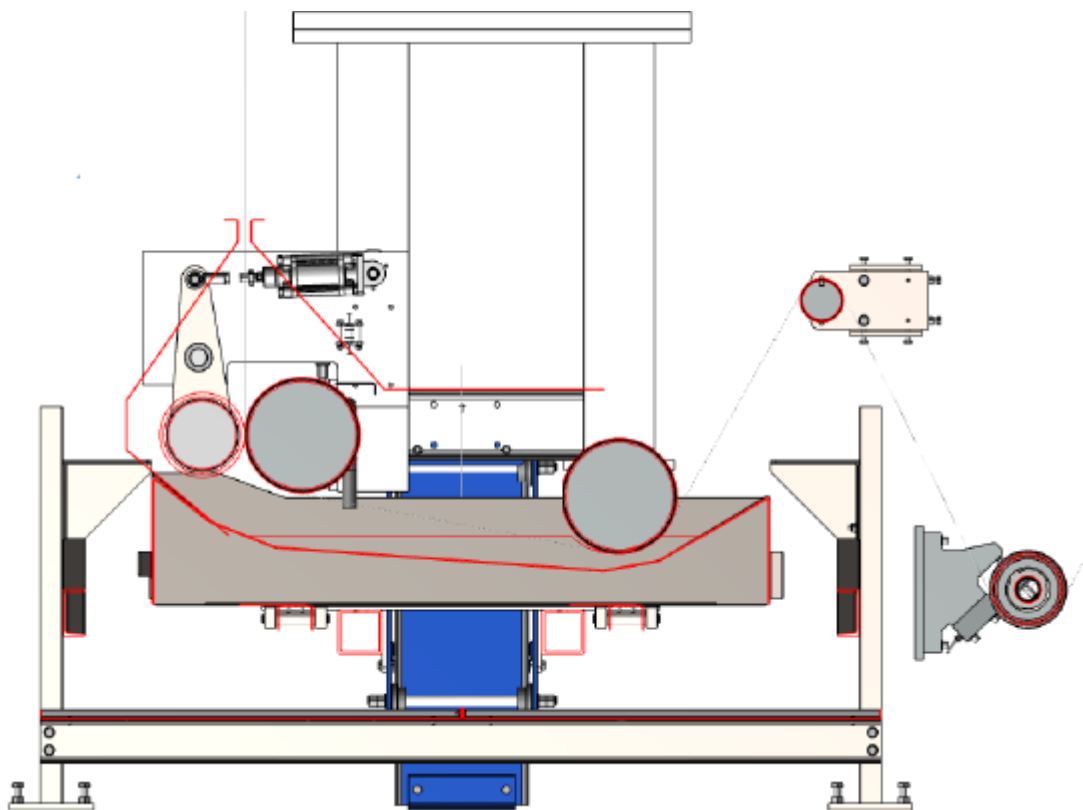


Figure A.1.2 - SEC II dipping bath scheme side cut.

A.2 New storage tanks

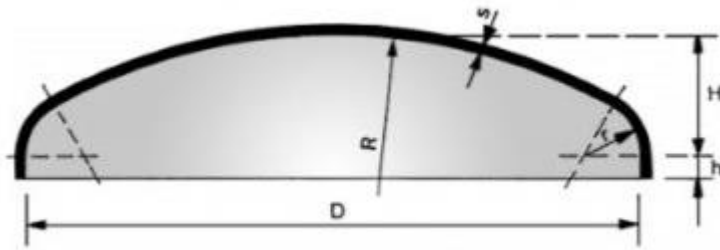


Figure A.2.1 - Kloppe top lid scheme.



Figure A.2.3 - This simulation is indicative at the viscosity level and may not coincide with the viscosity of the product in the quotation.

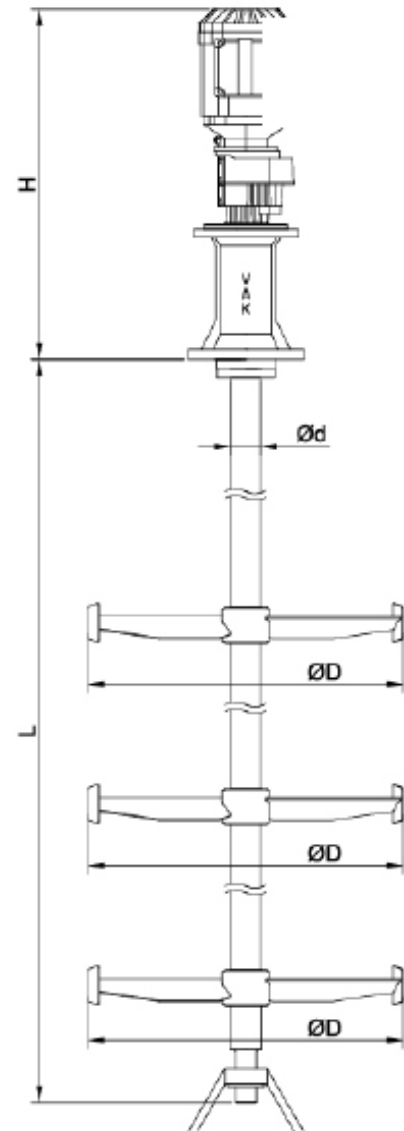


Figure A.2.2 - Upper atmospheric vertical agitator.



Figure A.2.4 - Alabnet axial propeller.

Appendix B - Laboratory Results

B.1 Dipping process parameters

Table B.1.1 - Foam volume for VP Latex from different suppliers.

<i>Time</i>	<i>VP Latex A</i>	<i>VP Latex B</i>	<i>VP Latex C</i>
<i>s</i>	<i>mL</i>		
0	0	0	0
1	274	275	178
2	400	400	220
3	530	523	242
4	662	647	257
5	770	787	258
6	857	840	272
7	Overflow	900	273
8		Overflow	275
9			278
10			283
20			297
30			322
40			323
50			320
60			322
90			343
120			343
180			377

Table B.1.2 - Foam volume for different dipping solution storage times.

<i>Time</i>	<i>0h</i>	<i>5h</i>	<i>24h</i>
<i>s</i>	<i>mL</i>		
0	0	0	0
1	293	273	283
2	396	410	413
3	550	547	553
4	660	717	683
5	790	760	787
6	870	790	870
7	Overflow	830	Overflow
8	Overflow		

Table B.1.3 - Foam volume for dipping solution formulated with VP latex B and different types of water.

<i>Time</i>	<i>Demineralized</i>	<i>Tap</i>	<i>Well</i>
<i>s</i>	<i>mL</i>		
0	0	0	0
1	273	234	195
2	409	380	318
3	559	546	435
4	676	696	518
5	798	816	615
6	Overflow	882	708
7	Overflow		793
8	Overflow		

Table B.1.4 - Foam volume for dipping solution formulated with VP latex C and different types of water.

<i>Time</i>	<i>Demineralized</i>	<i>Tap</i>	<i>Well</i>
<i>s</i>	<i>mL</i>		
0	0	0	0
1	263	166	163
2	448	246	192
3	602	270	200
4	733	310	217
5	853	338	205
6	Overflow	330	213
7		346	202
8		344	207
9		340	202
10		342	210
20		328	210
30		336	205
40		348	227
50		368	218
60		378	220
90		408	250
120		422	252
150		420	260
180		416	290

Table B.1.5 - Foam volume at different dipping solution temperature.

<i>Time</i>	<i>T = 14 °C</i>	<i>T = 19 °C</i>	<i>T = 21 °C</i>
<i>s</i>	<i>mL</i>		
0	0	0	0
1	204	205	166
2	304	252	246
3	376	258	270
4	406	267	310
5	394	297	338
6	404	292	330
7	394	295	346
8	382	293	344
9	364	293	340
10	344	287	342
20	304	263	328
30	314	282	336
40	316	277	348
50	338	282	368
60	340	293	378
90	364	340	412
120	396	375	407
150	432	387	407
180	446	412	408

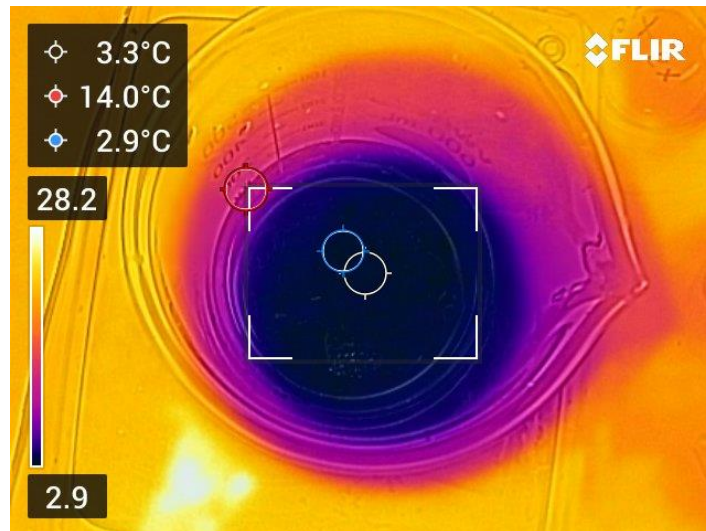


Figure B.1.1 - Water temperature for $T = 14.0$ °C trial.

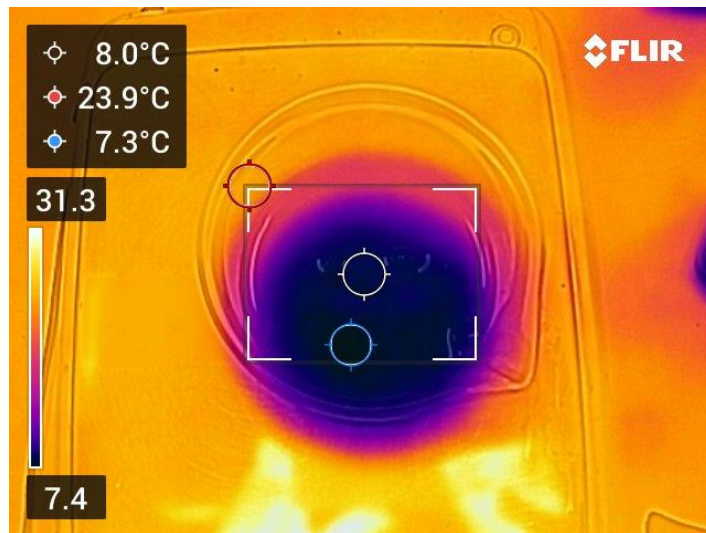


Figure B.1.2 - Latex temperature for $T = 14.0$ °C trial.

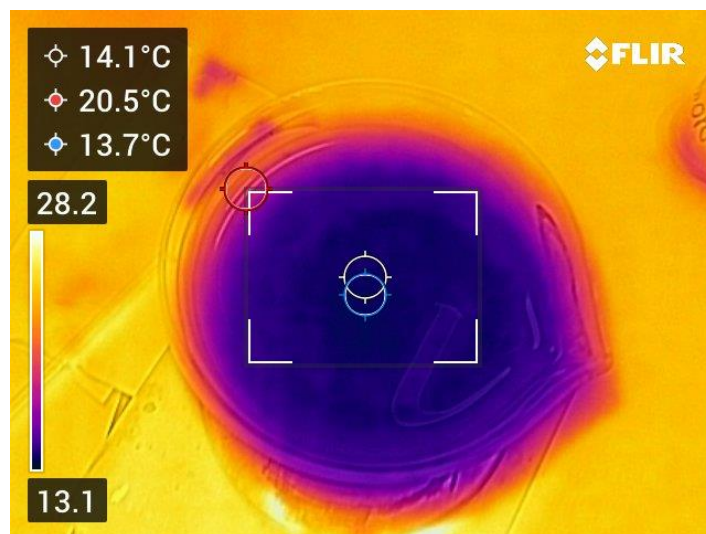


Figure B.1.3 - Dipping solution temperature for $T = 14.0$ °C trial.

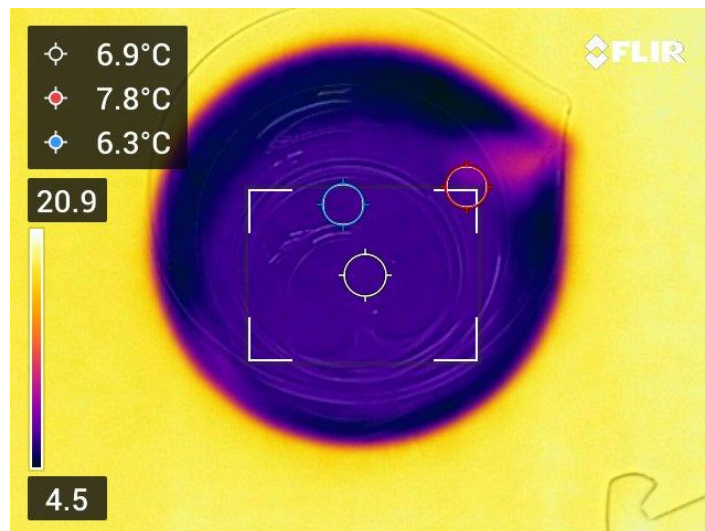


Figure B.1.4 - Water temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.

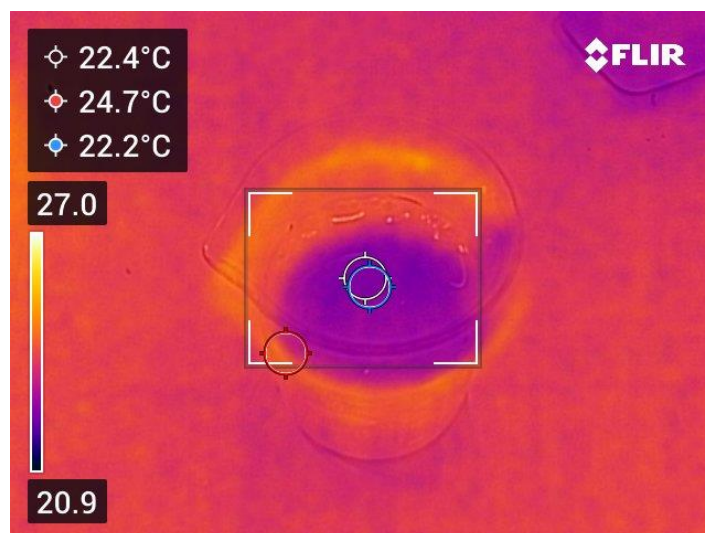


Figure B.1.5 - Latex temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.



Figure B.1.6 - Dipping solution temperature for $T = 19.0\text{ }^{\circ}\text{C}$ trial.

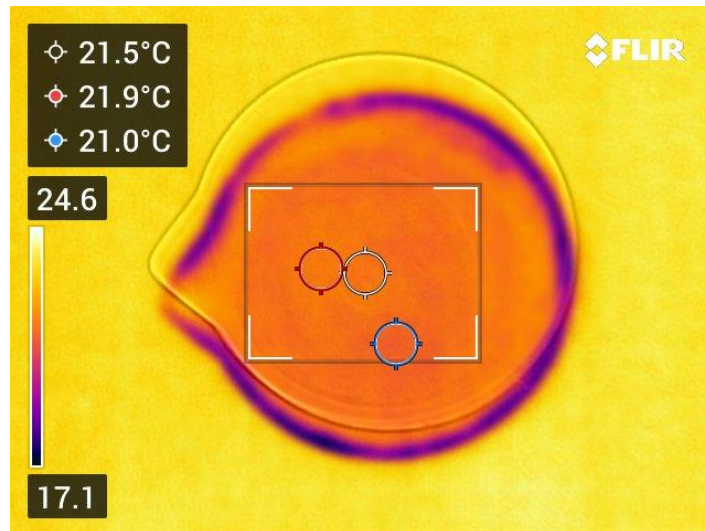


Figure B.1.7- Water temperature for $T = 21.0$ °C trial.

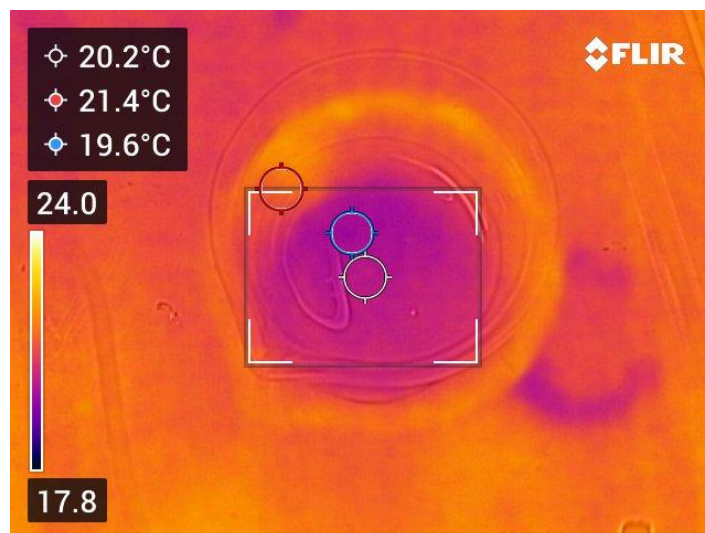


Figure B.1.8 - Latex temperature for $T = 21.0$ °C trial.

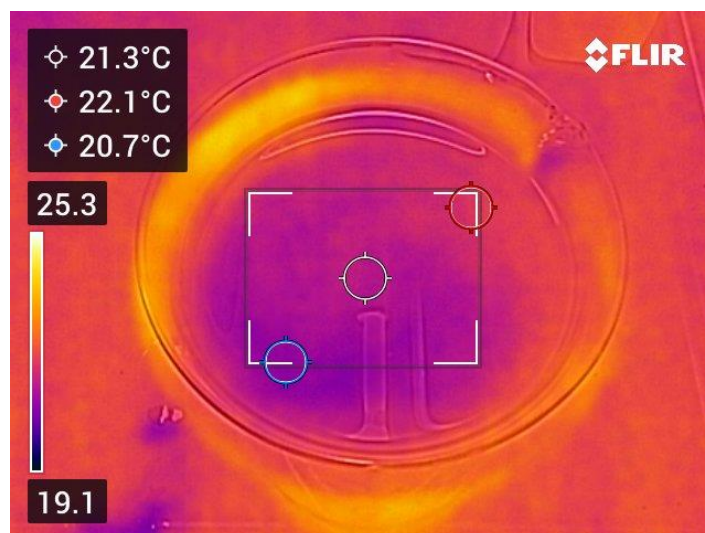


Figure B.1.9 - Dipping solution temperature for $T = 21.0$ °C trial.

B.2 Antifoam concentration

Table B.2.1 - Foam volume for each concentration of AF for dipping solution with VP latex B.

<i>t</i>	0.00 %	0.06 %	0.08 %	0.10 %	0.25 %	0.50 %	1.00 %
<i>s</i>	<i>mL</i>						
0	0	0	0	0	0	0	0
1	234	144	138	168	90	150	10
2	380	184	153	180	120	160	20
3	546	200	183	210	146	158	30
4	696	216	190	220	144	168	40
5	870	232	215	228	152	170	50
6	Overflow	242	213	245	174	162	60
15		316	278	270	212	182	90
30		400	368	333	264	208	96
45		442	395	363	296	224	96
60		450	433	373	306	234	92
75		478	458	350	324	250	94
90		504	480	378	348	262	92
105		508	500	373	352	278	86
120		524	505	403	360	294	96
135		534	533	405	368	312	96
150		542	533	403	376	320	98
165		560	535	435	396	342	98
180		556	550	445	394	350	104
195		592	560	460	428	372	104
210		600	565	498	438	388	96
240		602	588	505	470	420	92
270		646	620	565	494	430	90
300		666	640	593	538	460	108

Table B.2.2 - Foam volume for each concentration of AF for dipping solution with VP latex C.

<i>t</i>	0.00 %	0.06 %	0.08 %	0.10 %	0.25 %
<i>s</i>	mL				
0	0	0	0	0	0
1	185	126	150	140	105
2	240	170	164	160	125
3	295	188	176	170	135
4	325	186	186	190	145
5	350	200	200	185	165
15	345	222	208	200	185
30	325	198	206	195	183
45	333	200	192	190	185
60	335	208	202	190	195
75	358	208	198	198	195
90	375	220	200	180	103
105	373	208	200	195	103
120	398	218	202	195	110
135	403	222	208	188	125
150	418	222	218	200	218
165	408	224	224	208	228
180	428	232	218	213	218
195	433	230	234	205	223
210	438	236	232	218	213
225	420	236	244	220	215
240	428	256	248	218	225
270	420	272	250	225	230
300	413	262	262	230	235

Appendix C - Statistical Analysis

Table C.1 - Analysis of the variance for VP Latex influence.

Source	DF	Adj SS	Adj MS	F-value	P-value
Time (s)	5	1934821	386964	154.41	$< 10^{-16}$
VP Latex	2	2641863	1320932	527.10	$< 10^{-16}$
VP Latex*Time (s)	10	662135	66214	26.42	$< 10^{-16}$
Total	97	5036220			

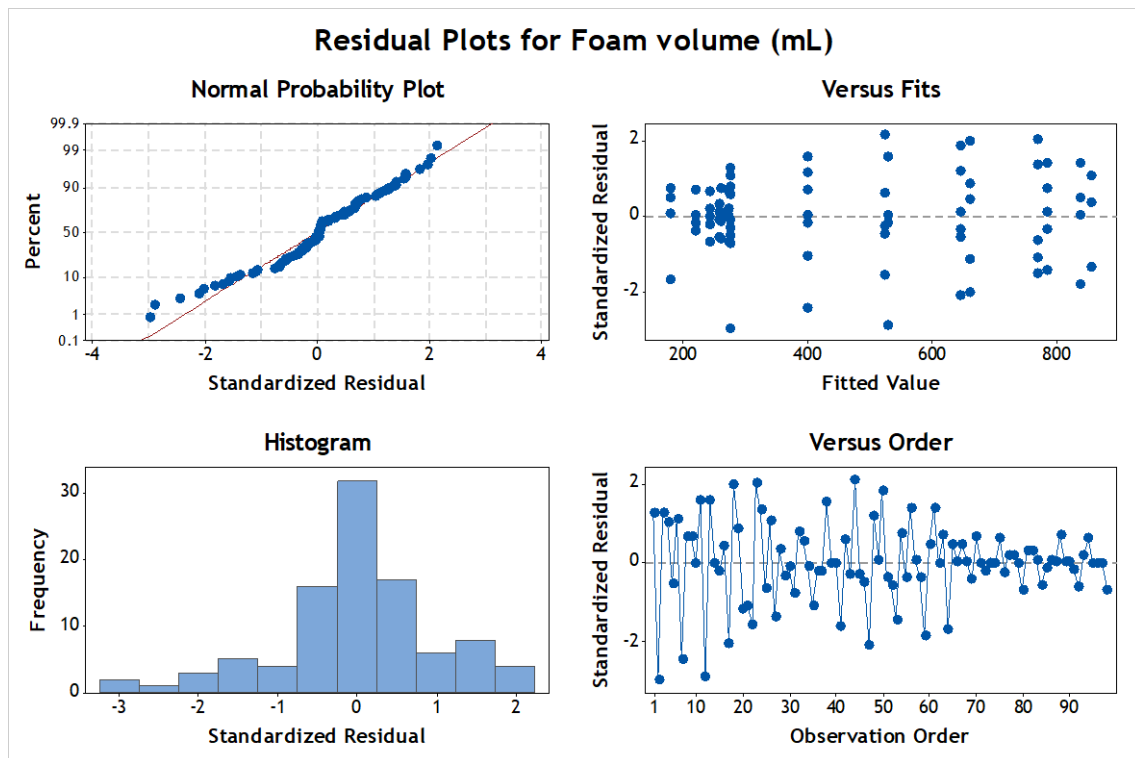


Figure C.1 - Statistical analysis of VP Latex influence: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.

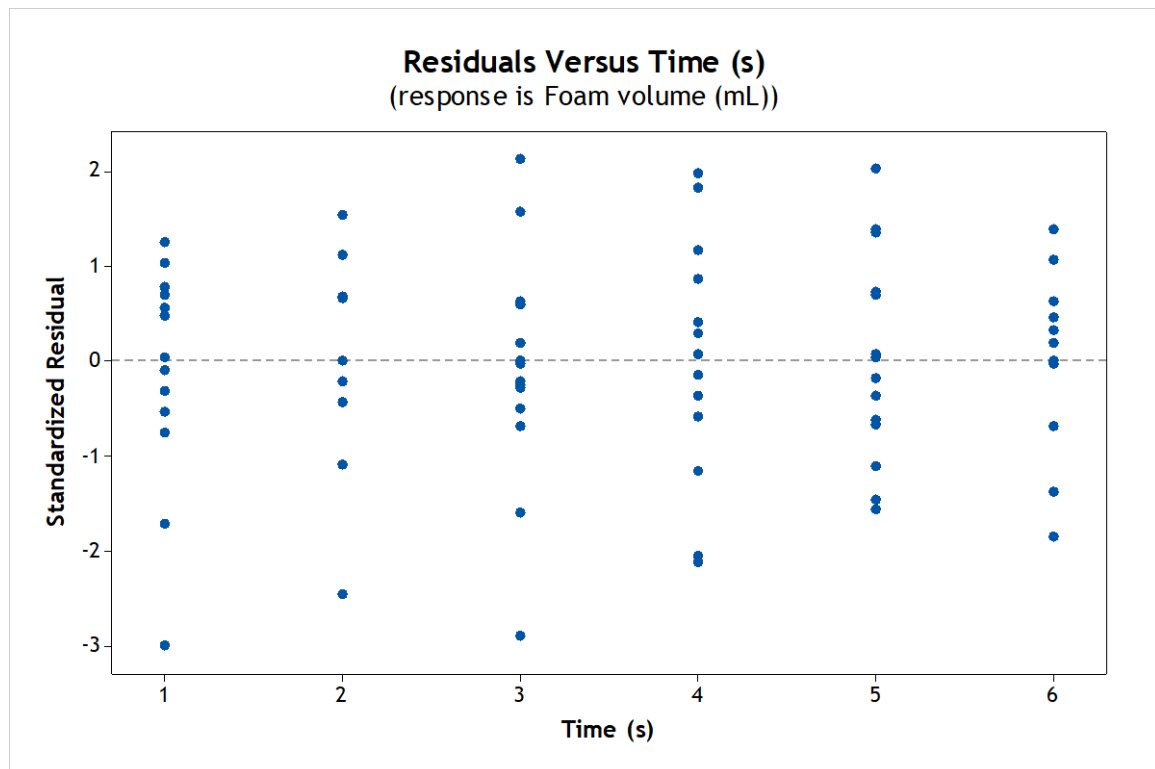


Figure C.2 - Statistical analysis of VP Latex influence: Standardized Residuals versus Time.

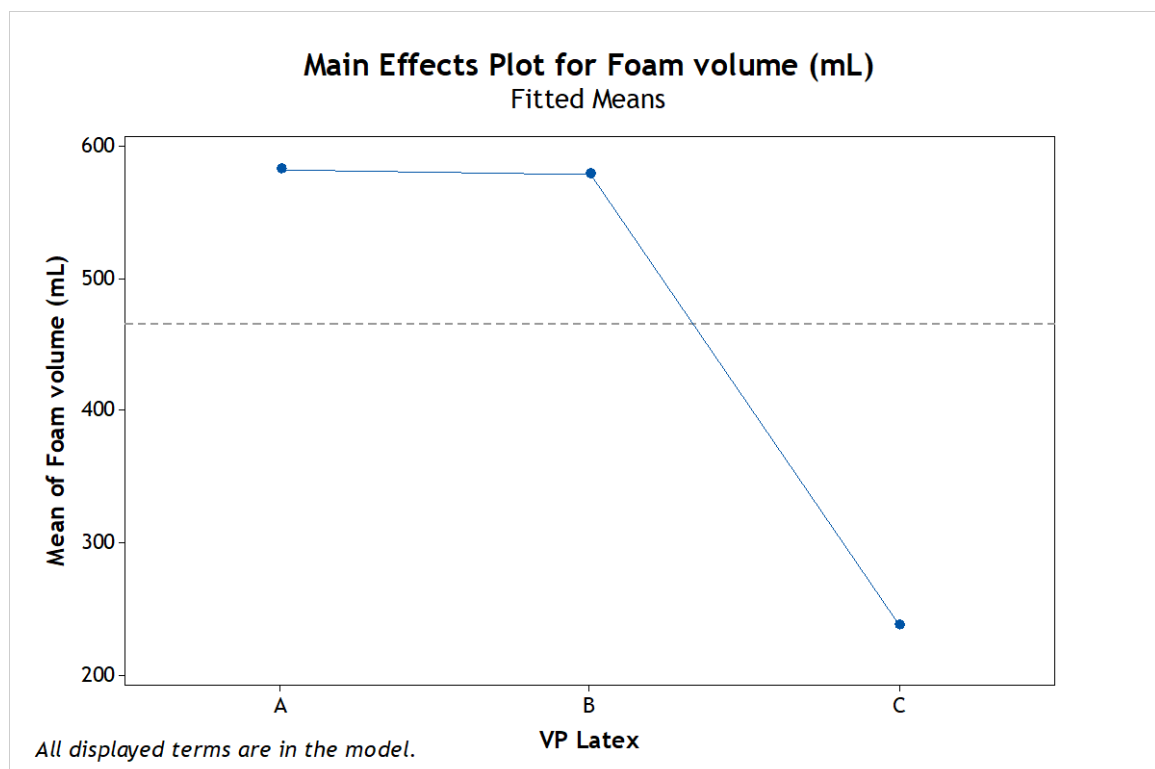


Figure C.3 - Main effect plot, mean of foam volume vs VP latex.

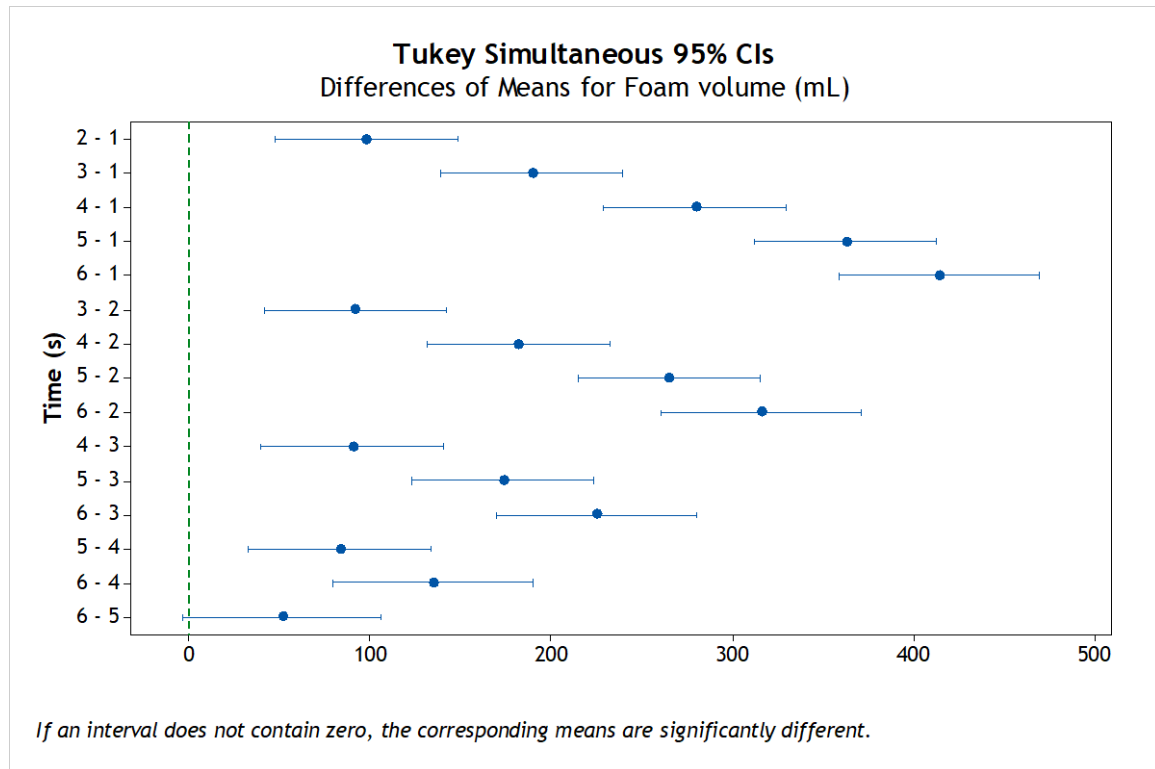


Figure C.4 - Tukey Simultaneous 95% Confidence intervals of the time of the dip solution with each Time for both VP Latex.

Table C.2 - Analysis of the variance for water type influence in dipping solution with VP Latex B.

Source	DF	Adj SS	Adj MS	F-value	P-value
Water	2	252674	126337	43.91	$< 10^{-16}$
Time (s)	4	2891997	722999	251.28	$< 10^{-16}$
Water*Time (s)	8	46032	5754	2.00	0.055
Total	104	4159225			

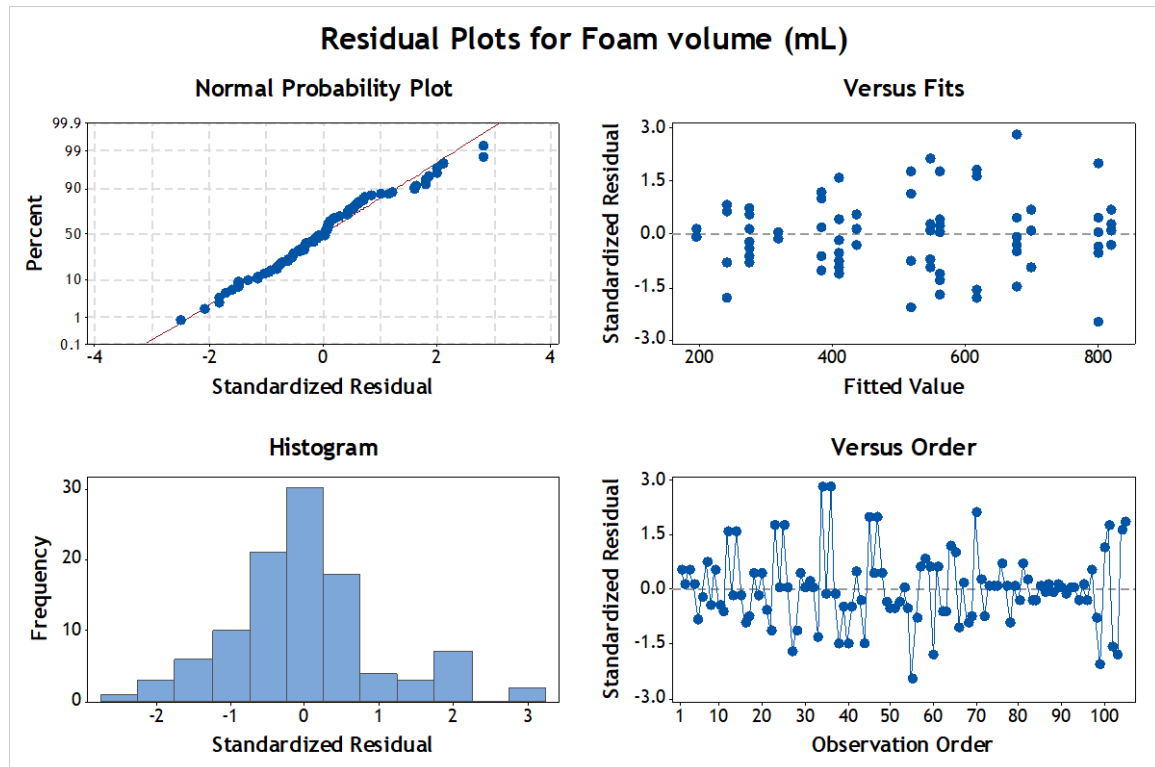


Figure C.5 - Statistical analysis of water type influence in dip solution with VP Latex B: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.

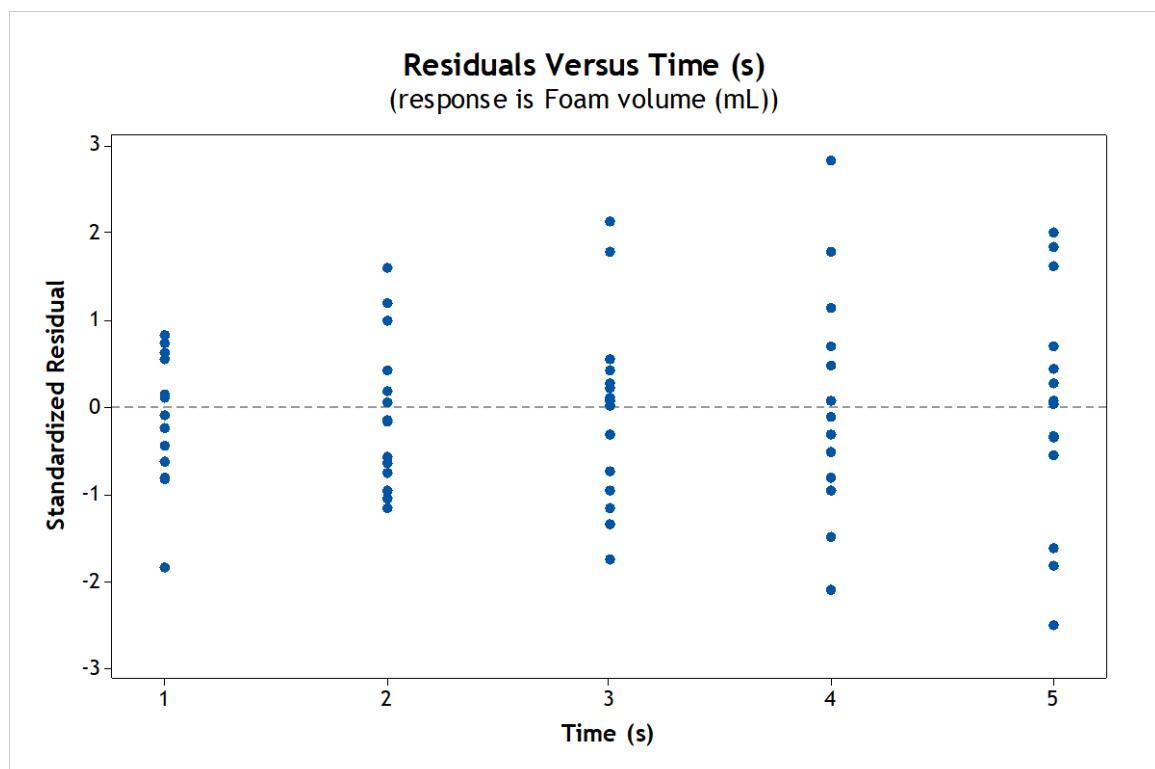


Figure C.6 - Statistical analysis of water type influence in dip solution with VP Latex B: Standardized Residuals versus Time.

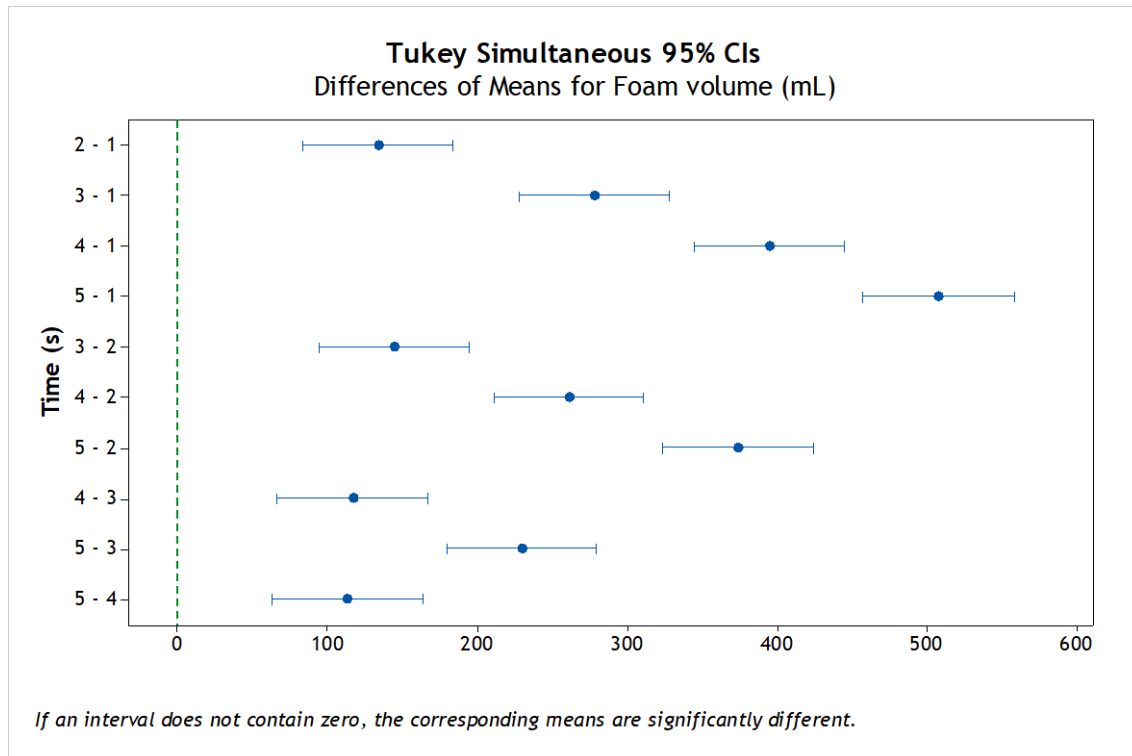


Figure C.7 - Tukey Simultaneous 95% Confidence intervals of the time of the dip solution with VP Latex B with each type of water.

Table C.3 - Analysis of the variance for water type influence in dipping solution with VP Latex C.

Source	DF	Adj SS	Adj MS	F-value	P-value
Water	2	3771907	1885954	885.92	$< 10^{-16}$
Time (s)	4	919701	229925	108.01	$< 10^{-16}$
Water*Time (s)	8	926230	115779	54.39	$< 10^{-16}$
Total	119	6682499			

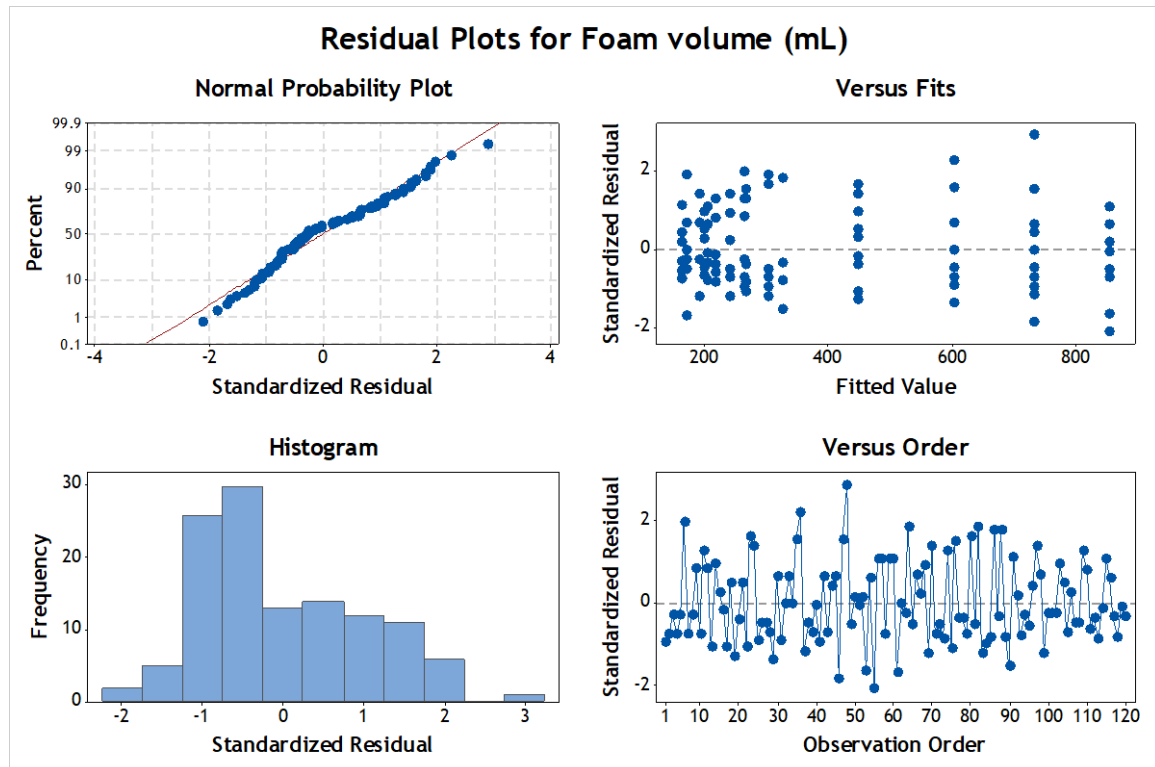


Figure C.8 - Statistical analysis of water type influence in dip solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.

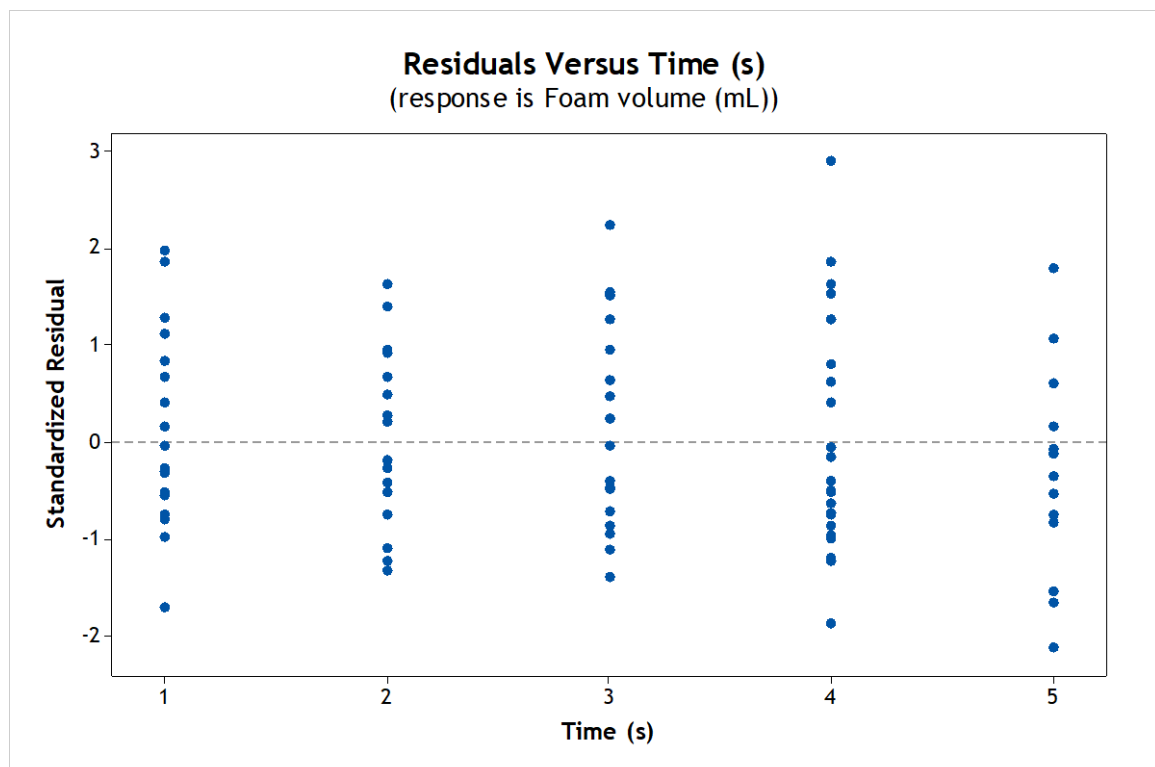


Figure C.9 - Statistical analysis of water type influence in dip solution with VP Latex C: Standardized Residuals versus Time.

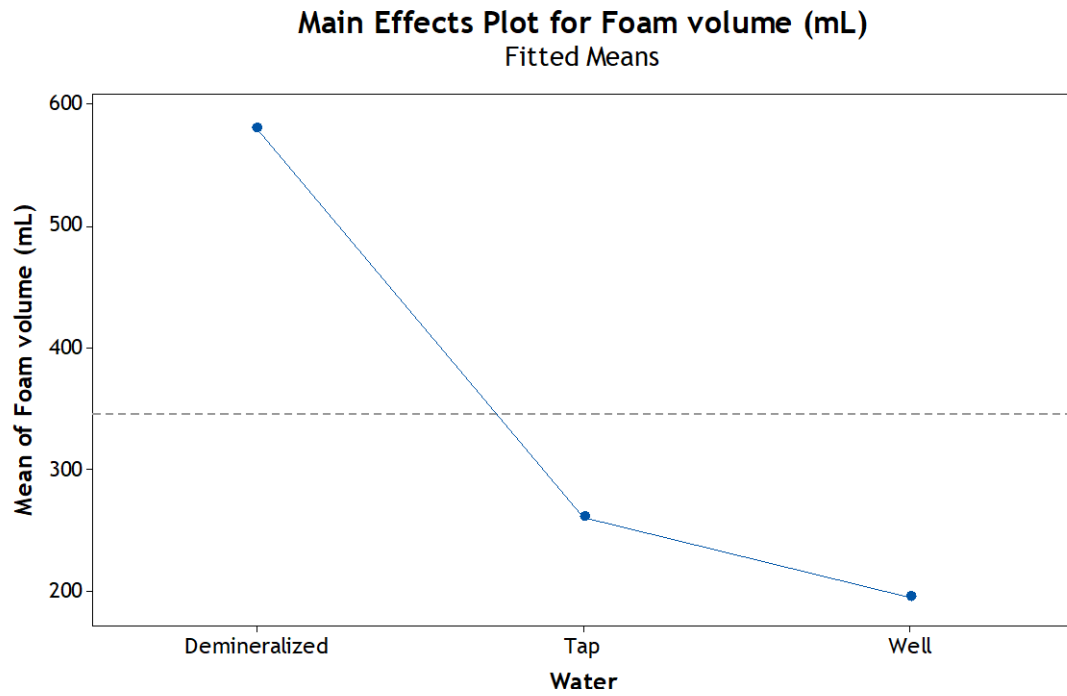


Figure C.10 - Main effect plot, mean of foam volume vs water type.

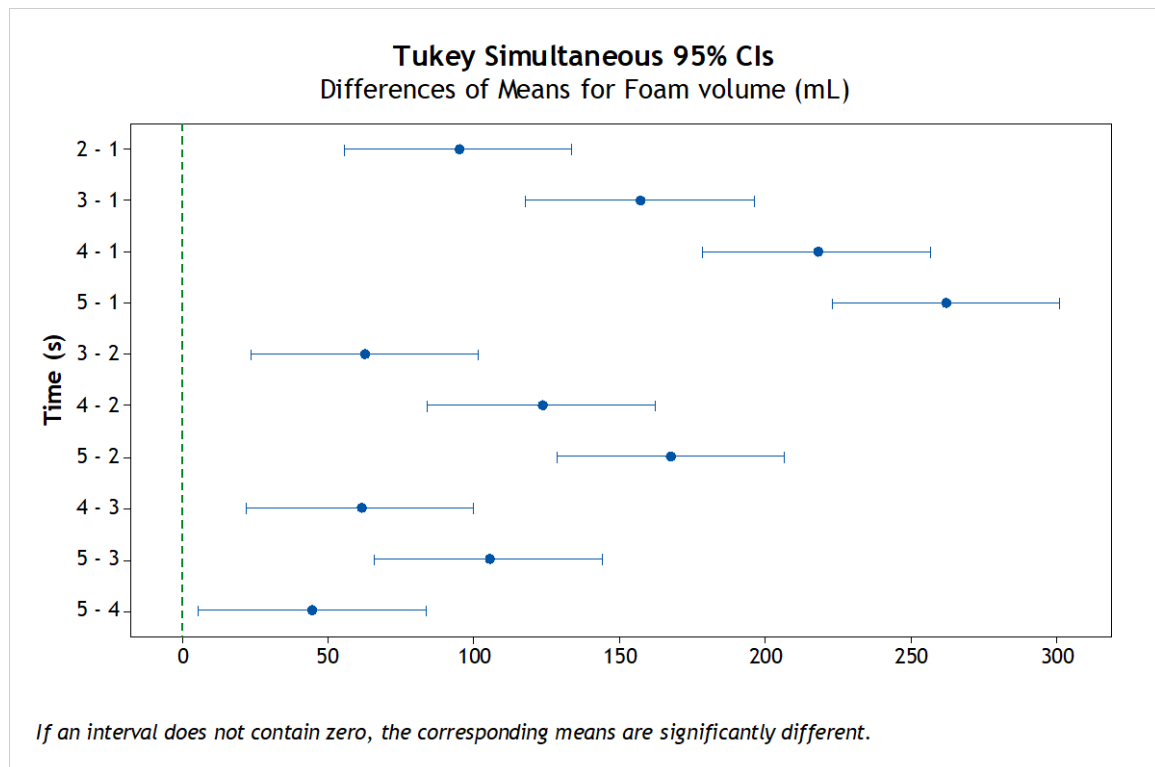


Figure C.11 - Tukey Simultaneous 95% Confidence intervals of the time of the dip solution with VP Latex C with each type of water.

Table C.4 - Analysis of the variance for storage temperature influence in dipping solution with VP Latex C.

Source	DF	Adj SS	Adj MS	F- value	P- value
Temperature (° C)	2	200626	100313	41.16	< 10 ⁻¹⁶
Time (s)	9	328434	36493	14.98	< 10 ⁻¹⁶
Temperature (° C) *Time (s)	18	52626	2924	1.20	0.269
Total	169	914751			

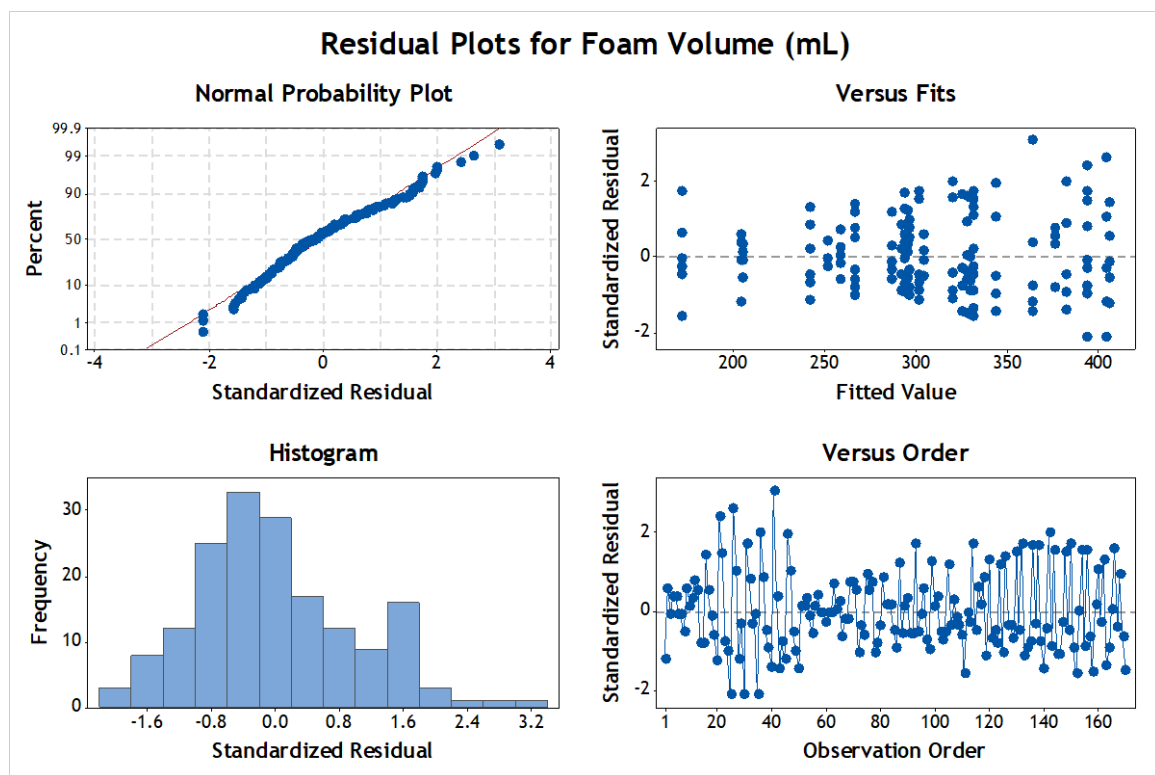


Figure C.12 - Statistical analysis of storage temperature influence in dip solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.

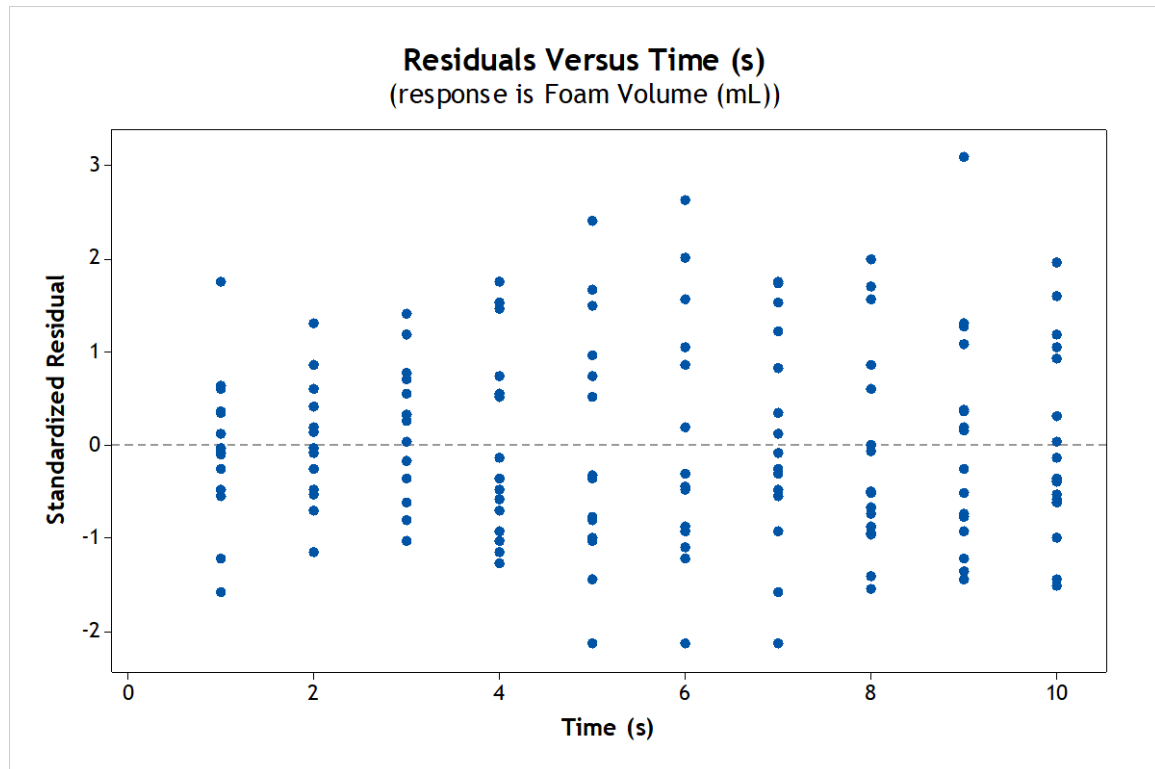


Figure C.13 - Statistical analysis of storage temperature influence in dip solution with VP Latex C: Standardized Residuals versus Time.

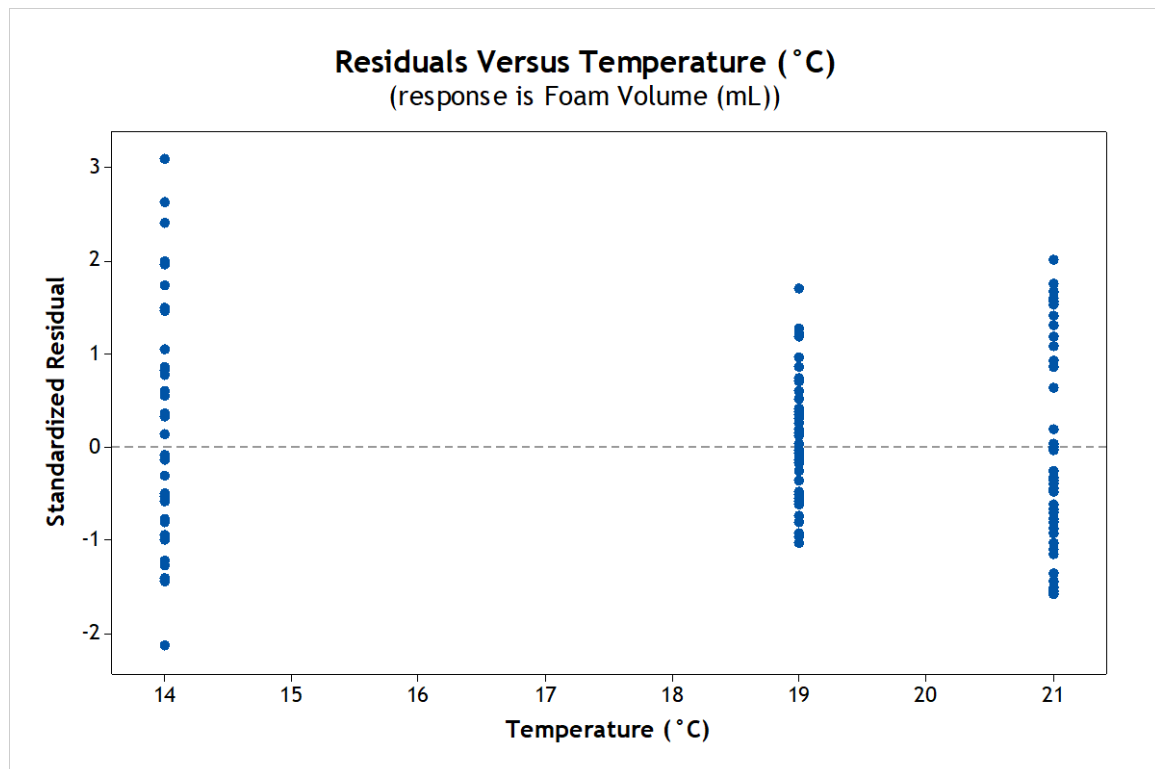


Figure C.14 - Statistical analysis of storage temperature influence in dip solution with VP Latex C: Standardized Residuals versus Temperature.

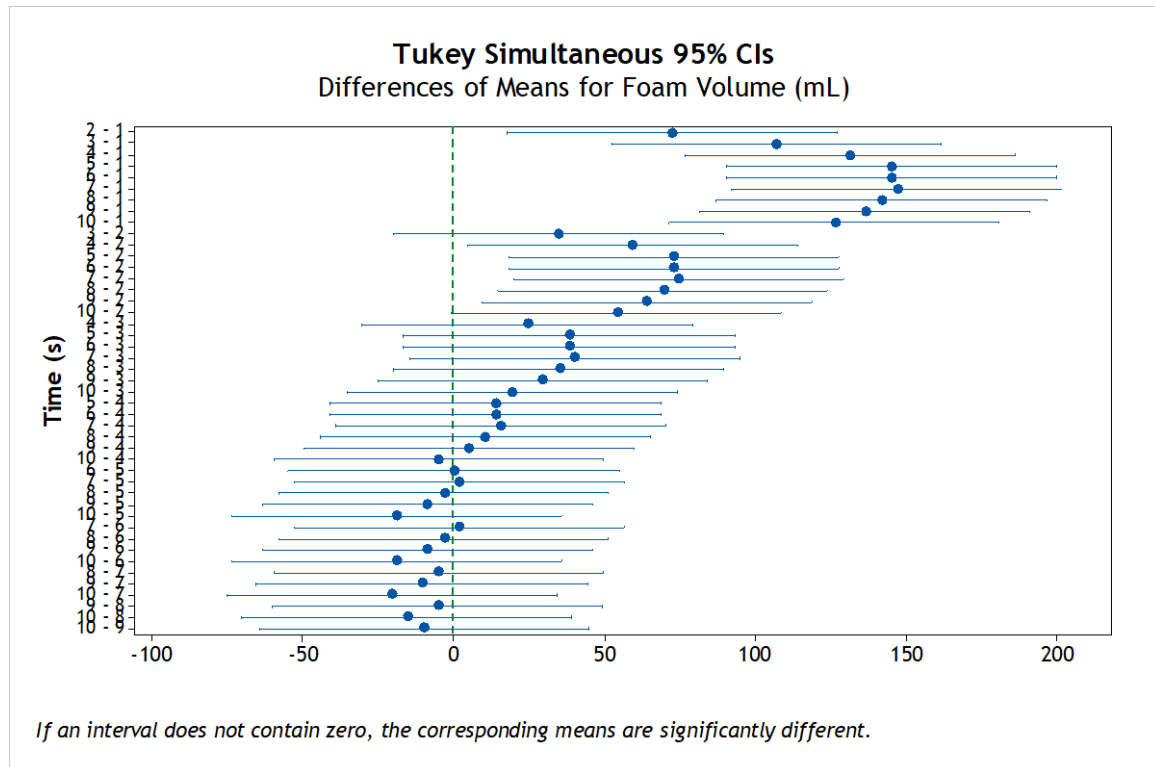


Figure C.15 - Tukey Simultaneous 95% Confidence intervals of time the dip solution with VP Latex C for each storage temperature.

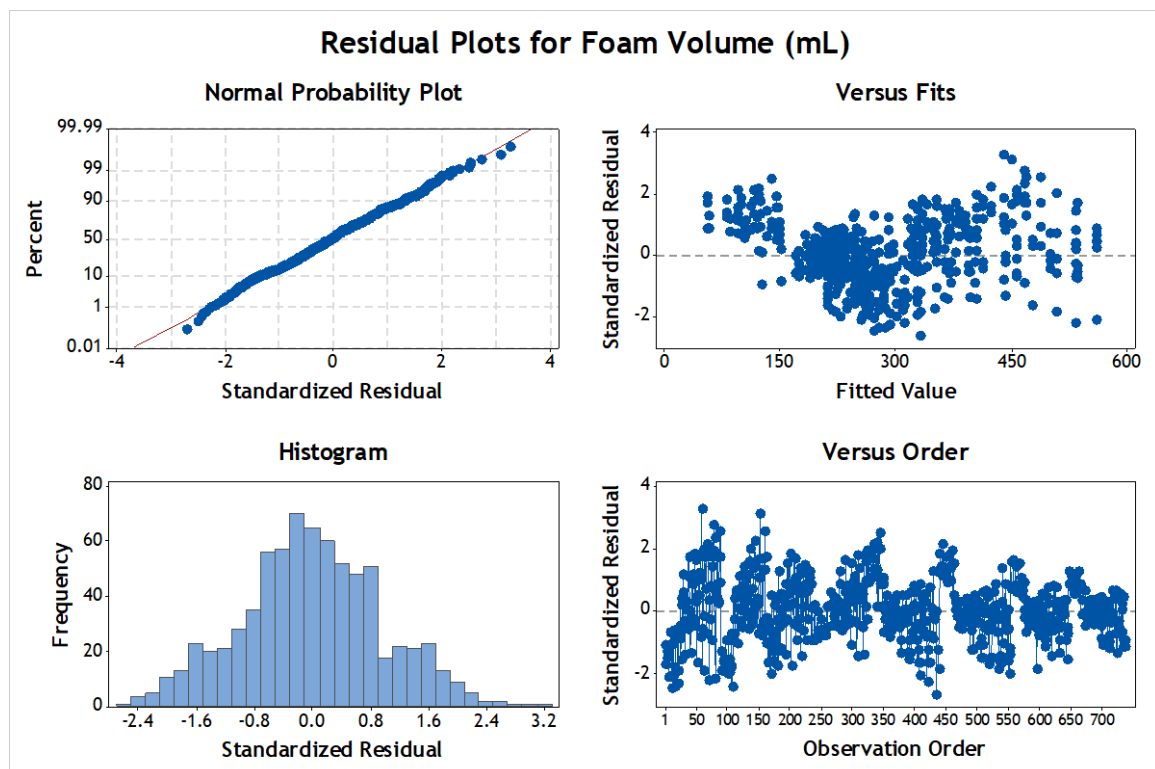


Figure C.16 - Statistical analysis of AF concentration influence in dip solution with VP Latex C: Normal probability plot of residuals; Standardized Residuals versus fitted values; Standardized Residuals versus order of data.

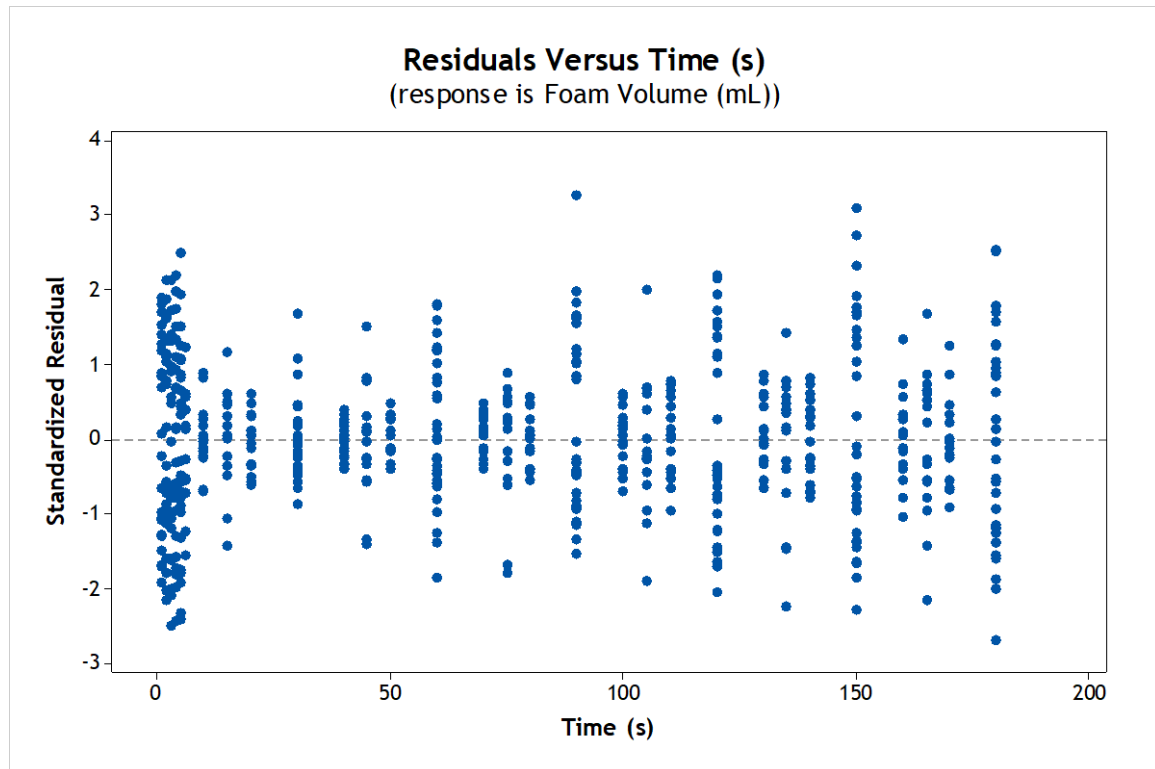


Figure C.17 - Statistical analysis of AF concentration influence in dip solution with VP
Latex C: Standardized Residuals versus Time.

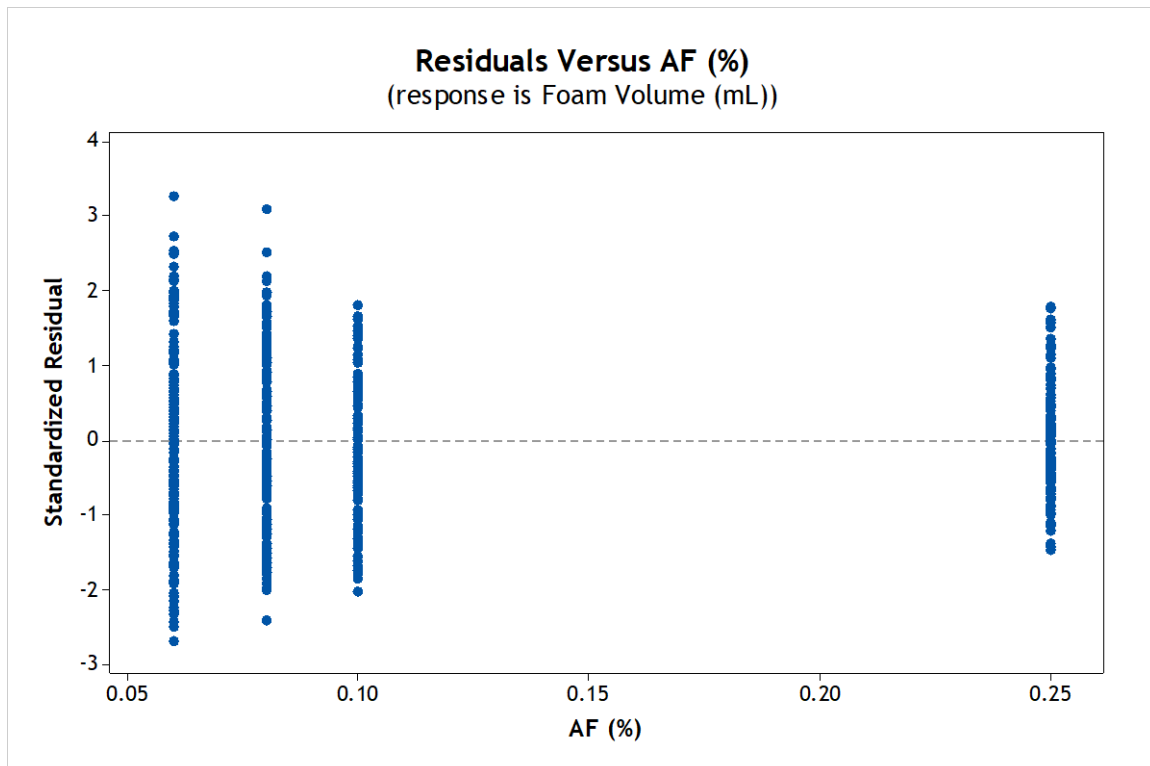


Figure C.18 - Statistical analysis of AF concentration influence in dip solution with VP
Latex C: Standardized Residuals versus AF concentration.

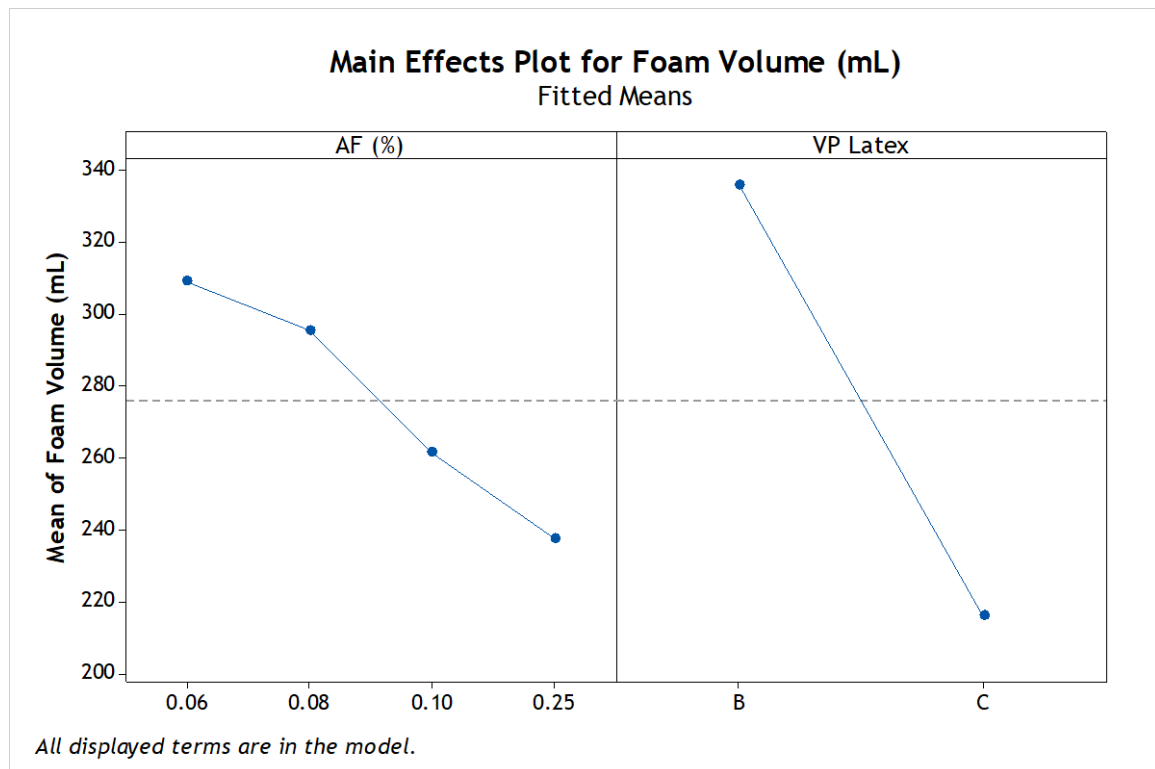


Figure C.19 - Main effect plot, mean of foam volume vs AF concentration and VP Latex.