Mestrado Integrado em Engenharia Química

Development of New Aerosol Valve Generations

Tese de Mestrado

desenvolvida no âmbito da disciplina de

Projecto de Desenvolvimento em Ambiente Empresarial

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Resumo

Este projecto baseia-se na investigação e desenvolvimento de novas gerações de válvulas de aerossóis para espuma de poliuretano, com maior vida útil, usando diferentes modelos e materiais.

A vida útil destes aerossóis é dependente do tempo que a válvula ainda funciona sem ficar obstruída. Este prazo de validade depende da impermeabilidade da válvula à água e da sua capacidade para isolar o gás dentro da lata de aerossol. A difusão de água através do anel de borracha que permite a activação da válvula ('grommet') ou a existência de água no interior destes sistemas (nas matérias primas que compõem a espuma de poliuretano) promovem a reacção das moléculas de água com os grupos funcionais "$R-N=C=O$" (Isocianato) do sistema, resultando na formação de um composto endurecido, poliureia. Esta reacção leva ao aparecimento de uma camada dura em torno da válvula ('sticked valve') e em regiões preferenciais do anel (regiões sob tensão de corte, 'stucked valve'), dificultando ou impedindo a abertura da válvula.

Com o objectivo de melhorar as válvulas padrão da Altachem, as perdas de gás, forças de activação, rendimento e resistência química das válvulas dos diversos fornecedores e competidores foram submetidas a um seguimento exaustivo. Em particular, é imperativo o estudo do número de semanas após as quais válvula continua a abrir, libertando espuma. Após efectuar o controlo de qualidade e a análise das diferentes válvulas ('benchmarking') observou-se quais dos materiais e modelos têm um melhor comportamento.

Palavras-chave: Válvula, aerossol, espuma de poliuretano, anel de borracha, 'benchmarking'.

Abstract

This internship's consist in the study and development of new aerosol valves generations for polyurethane (PU) foam, with longer shelf-life, using different designs and materials.

The shelf-life of the aerosol cans depends on the time that the valve still works without being blocked. This is dependent of the impermeability of the valve to the water and of its capacity to isolate the gas inside the can. Diffusion of water vapour through the rubber which allows the valve activation (grommet) or existence of water already in the interior of the can (water content in the raw materials or polyol) can cause serious problems in the valves behaviour. The water will react with free functional "$R-N=C=O$" groups (Isocyanate) of the "One Component polyurethane Foam (OCF)", resulting in the formation of a harder compound (polyurea) that will grow near the valve and in the interior of the grommet, increasing its hardness. This reaction can create a harder layer next to the valve, called the "crunch". The grommet can be hardened in preferred locations (regions under to shear stress). The crunch and/or the hardened locations in the grommet will difficult the opening of the valve, sticking and/or stucking the valve respectively.

To improve the Altachem standard aerosol valves, gas losses, activation forces, outputs and chemical resistance of Altachem suppliers and competitors where submitted to a rigorous analysis. In particular, it is important to study the number of weeks after which the valve continues opening and releasing foam. After performing the benchmarking and quality control of the different valves, it was concluded which materials and designs have a better behaviour.

Keywords: Valve, aerosol, polyurethane foam, grommet rubber, 'benchmarking'.

About Altachem NV

Altachem NV is located in Deinze, a municipality in the Belgian province of East Flanders. Established since 1992, Altachem is acting mainly in the market of 1, 1&½ and 2 components polyurethane foams in aerosol cans, being the one-component foam (OCF) most developed producer.

Over the years, this company has invested a lot of time in developing and producing aerosol can valves, foam applicators and Foam Controlling Additives (FCA) for the foam industry.

This company tends to innovate and the R&D department is therefore a crucial element in Altachem NV. All the studies done and the current projects give an exclusive and distinctive knowledge in OCF that can be applied to the valves and guns.

Nevertheless, new ideas to incorporate health and environmentally friendly aspects based in new technologies are being developed; this includes the ECOFAST project.

Since the one-component foam market keeps expanding, testing procedures and benchmarking methods are needed and gaining more relevance over the years.

Therefore, Altachem NV is looking for partnerships worldwide in the field of building chemicals and in particular on OCF[1].

[1] *More information about Altachem can be seen in www.altachem.com*

List of Contents

Notation and Glossary

GL	Gas Loss	g
$GL/_{year}$	Gas Loss per year	g
$GL_{8th\ week}$	Gas Loss for the 8th week	g
M_1	Crucible weight	g
M_2	Crucible + sample weight	g
M_3	Crucible + material not burned weight	g

List of Acronyms

C	Creep
CH	Can Horizontal
COH	Can On Head
CV	Can Vertical
DMDEE	2,2 – Dimorpholinodiethylether
DME	Dimethyl Ether
DOT	Department of Transportation
F22	Freon 22
FCA	Foam Controlling Additives
EO	Ethylene Oxides
GL	Gas Loss
LPG	Liquefied Petroleum Gases
MDI	Methylene Diphenyl Diisocyanate
NCO	Isocyanate Functional Group ($R-N=C=O$)
OCF	One Component Foam
OP	Output/valve flow
pbw	Parts by weight
PE	Polyethylene
PO	Propylene Oxide
PP	Polypropylene
PPO	Propylene Glycol
PU	Polyurethane
RH	Relative Humidity
SS	Sticking & Stucking
TCCP	Trichloropropylphosphate
TPE	Thermoplastic Elastomers

1 Introduction

1.1 Background and Project Presentation

The time that the aerosol valves work is dependent of the impermeability of the valve to the water and of its capacity to isolate the gas. Water diffusion through the grommet[1] and/or existence of water already in the interior of the can damage the valves. The water will react with the free "$R - N = C = O$" groups of the materials inside the can, resulting in the formation of a harder compound (polyurea) that will grow near the valve and in the grommet pores, increasing its hardness.

These free "NCO" groups or isocyanates refer to the functional group of atoms described in Figure 1. Any organic compound which contains an isocyanate group may also be referred to in brief as an isocyanate. An isocyanate may have more than one isocyanate group.

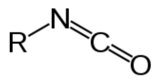

Figure 1 – Isocyanate functional group: free "NCO" group

The polyurea formation reaction can create a harder layer next to the valve, called the "crunch"; also the grommet can be hardened in preferred locations. The crunch and/or the hardened locations in the grommet will difficult the opening of the valve, sticking and/or stucking the valve respectively.

When my internship at Altachem started, there were some projects unfinished which I have continue developing. I had also the possibility to start new projects. The project chosen for this thesis consists in a benchmarking which compares different types of valves and foams. Altachem standard valves needed to be approved on all the formulations of a possible client. Since they do not have the capacity, Altachem provided the service of comparative testing between the currently used valves by the customer and the Altachem valves.

Because of being a project with different types of foams involved, the results allow to make comparisons between the different formulations, so Altachem can provide

[1] *A brief definition of this term is performed in Annex 1, p. 50.*

its new client a brief analysis of the valves behaviour depending on the kind of foam, in order to improve the investigation.

Of each type of valve and foam, 12 cans were received from the client. Standard 'Sticking and Stucking (SS)' and 'Gas Loss and Creep (GL/C)' tests[1] were performed. The main objectives of these tests are to study the gas losses, valve deformations, opening forces and outputs (valve flows) of the valves received.

The thesis has two main objectives:

1) To perform the benchmarking study of some of the valves available in the market, in order to demonstrate a possible new customer that Altachem valves are a competitive solution for their necessities.
2) To achieve competences in the aerosol valves for polyurethane foams development area.

The thesis starts describing the acquired knowledge about OCF's, polyurethanes[2] chemistry and aerosol valves. After this, the tests performed for the main project are reported, as well as a result's discussion. The document ends with some general conclusions, the conclusions for the project chosen and the evaluation of the work. Annexes contain the definitions for some of the terms used, a description of the coding of Altachem valves, an explanation about other tests performed, remarks about the main project accomplished and the discussion for two more projects.

1.2 Contributions for Innovation

The innovative aspect and enhancement of this thesis resides in the analysis not only of different aerosol valves, but also of different foam's behaviours for the valves analysed. The results allow comparing Altachem and competitor's valves, as well as the standard formulations used by the customer, in order to improve the investigation.

After the analysis of the tests results, the quality and competitiveness of Altachem valves were proved, and the company was able to obtain a new client. Altachem valves were approved on all the customer formulations.

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[1] *These two tests are described with detail in chapter 3, 'Test Performed'.*
[2] *A brief definition of this term is performed in Annex 1, p. 50.*

1.3 Organization of Thesis

This thesis starts with a description of the polyurethane foams technology, based in three parts:

- One Component Polyurethane foams – History and remarkable points about the performance and applications of this type of foam.
- Polyurethane Chemistry – Isocyanate functional group reactivity and foam formulations description.
- Aerosol Valves – Types of valves analysis.

Chapter 3 describes the main tests performed for the chosen project. Chapter 4 shows and discusses the results for the tests accomplished in the benchmarking project: Gas losses, creep, opening forces of the valves, outputs and special cases.

Conclusions chapter is divided in two parts: general conclusions about the work performed and conclusions for the project selected. An evaluation of the work can be found in Chapter 6, alongside with the objectives accomplished, a brief description of other projects performed, limitations and future work explanations and a final assessment.

As it was said before, annexes contain the definitions for some of the terms used, a description of the coding of Altachem valves, an explanation about other tests performed, remarks about the main project accomplished and the discussion for two more projects.

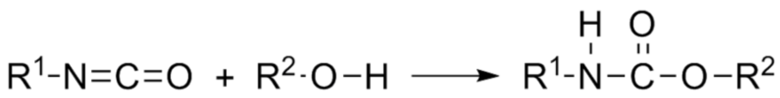
2 State of the Art

2.1 Introduction to Polyurethane Foams

Although the present study is mainly about research and development of aerosol valves and rubber material behaviour, polyurethane foams are always present in all projects.

2.1.1 One Component Polyurethane Foam (OCF)

Developed by Otto Bayer and his group of scientists in 1937, polyurethane (PU) foam was synthesized by the polymerization[1] reaction between isocyanate and diol.



Scheme 1 - Reaction between isocyanate and diol to form urethane (Dhaenens, H., 2007)

Over the years, polyurethane (PU) foam turned out to be a successful story as a business of many billion dollars. PU is a generic term, which refers to the repeating unit "$NH - CO - O -$", resulting from the reaction of isocyanate functionality with hydroxyl groups (Aster De Schrijver, 2001).

One-component polyurethane foam (OCF) was invented in UK within Imperial Chemical Industries in 1969 and, since that time, it is used in several different applications. It contains a pre-reacted mixture of polyol, isocyanate, blowing agents and additives.

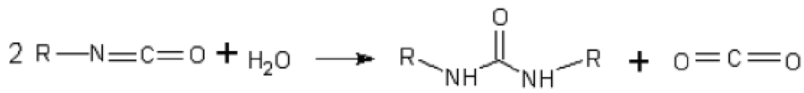
Polyol is a macromolecule of polyhydric alcohols with molecular weights ranging from '200 – 8000' and functionalities ranging from 2 to 8. The "-OH" group of the polyol, in the presence of suitable catalysts, reacts with the "$-NCO$" radical of the isocyanate forming a urethane linkage (-NC). The catalysts accelerate the reaction to the required level and the blowing agent blows the cells, increasing its volume, and forming the light weight PU foam. The surfactants promote and stabilize the polyurethane cells and help to retain its shape into which it has been blown (Aster De Schrijver, 2001).

[1] *A brief definition of this term is performed in Annex 1, p. 50.*

Because OCF foams are supplied in pressurized vessels (like cans or cylinders), they are also called aerosol foams. Due to the gas pressure inside the container, the material inside is self-dispensed. While dispensing the mixture from its pressurized vessel, it expands to form a sticky froth that will adhere to the majority of surfaces. This froth reacts with atmospheric moisture expanding to the final form cured foam.

The OCF foaming process has two stages. At the first stage, an aerosol can is filled in with a mixture of a polyol blend, isocyanate, different additives and physical blowing agents like Liquefied Petroleum Gases (LPG)* and Dimethyl ether (DME)*. The prepolymerization reaction occurs inside the can: the polyol reacts with isocyanate which is present in excess (Aster De Schrijver, 2001; Tim Thomson, 2005).

At the second stage, while dispensing, the liquid pre-polymer leaves the can and starts to expand to low density froth by vaporization of the physical blowing agent. Polymerization and blowing reactions take place simultaneously during foam formation, and the heat given out from the polymerization reaction under adiabatic cure conditions (due to the insulating nature of the foam bun) enhances the blow reaction.



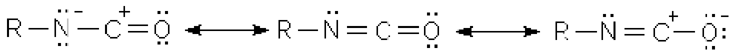
Scheme 2 – "Blowing Reaction" between isocyanate and water forming urea and CO_2

In general, to guarantee minimum acceptable foam properties in building applications, it is important that the foam presents good adhesion and elasticity, a certain resistance when compressed (measured by the compression strength at 10% deformation), dimensional stability and a certain yield per can. The minimum required physical properties should be independent from the ambient temperature, can temperature and from the age of the can.

Most PU is useful because of their physical properties, and the breadth of applications is remarkable. They can be stiff enough to be used as structural members and soft enough for cosmetic applicator sponges. They can serve as the wheels of inline skates or cushions for furniture. In these applications and hundreds of others, the chemistry can be summed up as a combination of hard segments and soft segments with varying degrees of cross-linking. It can be soft and flexible with entirely open cells, used as sealant for doors and windows frames, gap filling around pipes (pipe insulation), coatings and adhesives. With other structures, PU foam can be used as thermoplastic elastomers (TPE)* and fibbers.

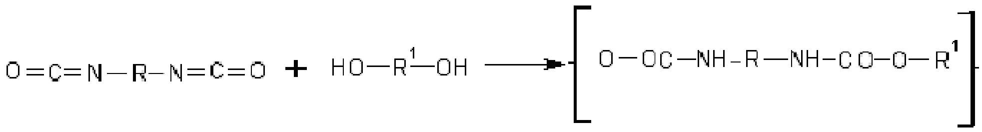
2.1.2 Polyurethanes Chemistry

The reactivity of the “-NCO” radical is determined by its resonances (Scheme 3). Isocyanates react with polyol to form polyurethanes (Scheme 4) and with water to form polyurea, releasing CO_2 (Scheme 2, Blowing Reaction). Besides these reactions, isocyanate groups can also react with urethane and urea* (Aster De Schrijver, 2001).



Scheme 3 - Illustration of the three resonance structures of the isocyanate group

Commercial polyurethanes are typically made by the reaction of a diisocyanate with a molecule containing two or more active hydrogen’s. The reaction is self-sustaining and relatively easily controlled, without secondary product formation (Aster De Schrijver, 2001).



Scheme 4 - Reaction of polyaddition between polyol and isocyanate to form polyurethane*

Even though the polyurea forming reaction occurs to a much less extent than the primary reactions, its importance should not be underestimated (Aster De Schrijver, 2001).

For the two component PU foam, isocyanate is added to the mixture while dispensing[2]. The foaming will be carried out, for example with a physical blowing agent; the reaction between isocyanate and polyol produces polyurethane linkages with the release of heat of reaction. The blowing agent vaporizes, and the gas is trapped in the closed cells of the foam (Aster De Schrijver, 2001).

Polyurea can form hard segments of foam domains, with strong secondary bonds (hydrogen bonds). The blow reaction (Scheme 2) not only helps in foam expansion, but also leads to the generation of polyurea hard segments (Mayr A.E. et al, 2000).

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* *A brief definition of this term is performed in Annex 1, p. 50.*

[2] *The explanation for the One Component PU Foam (OCF) is located in Chapter 2.1.1.*

In addition, at higher water contents (and thus at higher hard segment contents), the urea micro domains are known to aggregate and form larger urea rich structures commonly termed as "urea balls" or "urea aggregates". The isocyanate-water reaction proceeds faster compared to the reaction between the isocyanate and the polyol. This leads to the formation of oligomeric polyurea species which are termed as urea hard segments (Mayr A.E. et al, 2000; Armistead J.P., 1985).

The glycol[*] most commonly used is the polypropylene glycol (PPG)[*], which is obtained through anionic polymerization of propylene oxide (PO)[*], propylene[*] and ethylene oxides (EO)[*] copolymerization[*]. Changes in a limited number of component parts allow a wide variety of products to be made. The foams used in Altachem are two standard foams, designated by 4230 and 3733, with different products and quantities (Table 1). The detailed formulations used by Altachem to produce one can are described on Tables 2 and 3.

Table 1 - Raw materials[*] used to produce OCF foams

Raw Materials		Formulation	
		4230	**3733**
Polyol		GP1000[1]	GP1000 and VD1000[2]
Extender		FCA100[3]	FCA100
MDI		Methylene Diphenyl Diisocyanate	Methylene Diphenyl Diisocyanate
Additives	**Surfactant**	-	Saxol 8002 or Struksilon 8002
		Tegostab B8871	
	Frame Retarders	Cereclor S45[4]	Cereclor S45
		TCPP[5]	TCPP
	Catalyst	DMDEE[6]	Niax A1[7]
			DMDEE
Blowing Agents	**LPG**	75%	45%
	DME	25%	55%

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[*] *A brief definition of this term is performed in Annex 1, p. 50.*
[1] *GP1000: Polypropylene Triol - Voranol CP 1055*
[2] *VD1000: Polypropylene Diol - Voranol P 1010*
[3] *FCA100: "1,2 - Propylene Glycol or Propane-1,2-diol"*
[4] *Cereclor S45: Chlorinated Paraffin*
[5] *TCCP: Trichloropropylphosphate*
[6] *DMDEE: "2,2 - Dimorpholinodiethylether"*
[7] *Niax A1: 70% bis-(2-dimethylaminoethyl-)ether and 30% dipropylene*

Table 2 – Standard 4230 Formulation for a can of $375\ mL$[1]

Formulation 4230 (375 mL)		
GP1000	73,00 g	100,00 pbw
FCA 100	2,29 g	3,14 pbw
TCPP	36,50 g	50,00 pbw
cereclorS45	29,20 g	40,00 pbw
tegostabB8871	5,84 g	8,00 pbw
DMDEE	0,95 g	1,30 pbw
Total polyol	**147,77 g**	**202,44 pbw**

Polyol per can	147,8 g	
Suprasec 5025	165,2 g	
Propane	19,5 g	39,0 mL
butane	14,1 g	24,4 mL
Isobutane	8,4 g	16,8 mL
DME	18,0 g	26,9 mL
Tot gas	59,9 g	107,1 mL
Total LPG (P/B/IB)	42,0 g	80,3 mL
Total weight chemicals	**373,0 g**	**375,00 mL**

Table 3 - Standard 3733 Formulation for a can of $375\ mL$

Formulation 3733 (375 mL)		
GP1000	56,2 g	70,0 pbw
VD 1000	24,1 g	30,0 pbw
FCA 100	1,9 g	2,3 pbw
CereclorS45	68,2 g	85,0 pbw
Saxol 8002	6,4 g	8,0 pbw
DMDEE	1,0 g	1,2 pbw
Niax A1	0,2 g	0,2 pbw
Total polyol	**157,9 g**	**196,7 pbw**

Polyol per can	157,9 g	
MDI	147,1 g	
Propane	12,4 g	24,4 mL
butane	8,9 g	15,3 mL
Isobutane	5,3 g	9,5 mL
Total LPG (P/B/IB)	26,6 g	49,1 mL
DME	40,0 g	59,6 mL
Tot gas	66,6 g	108,7 mL
Total weight chemicals	**371,6 g**	**375,0 ml**

2.2 Aerosol Valves

The valve is also crucial, as well as the foam and gun or adaptor, to obtain good results when using OCF. The various valve components used in tilting and vertical valves must meet a large number of criteria set by each OCF manufacturer like

[1] *pbw: Parts by weight (total polyol equals to* $100\ pbw$*).*

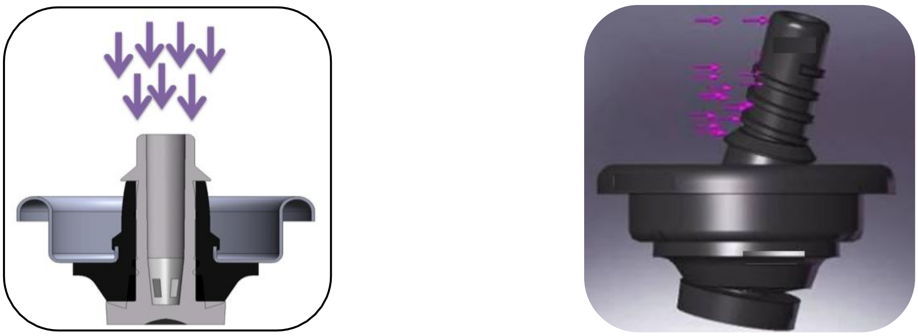
chemical resistance to different blowing agents and polyurethane chemicals; and a shelf-life guaranty of 15 months, when stored vertically at different temperatures.

The valve is an essential element in every aerosol dispenser. The valve can be a gun valve (Figure 2, A) or a tilting one (Figure 2, B). Gun valves are activated by a gun for aerosol cans and the tilting valves are activated by an adapter. When actuated, the valve releases the product from confinement. They can deliver a very fine mist, a coarse spray, a very long beat, foam, or even a viscous gel or paste (Jhonsen M.A., 1982).

Figure 2 - Examples of gun (A) and tilting (B) valves.

Gun valves belong to the vertical activation valves, which are also known as gun type. This valve is used adapting it to a Non Blocking System (NBS) foam gun, where a vertical force applied into the stem will activate the valve (Figure 3, a). When the gun is depressed it pushes the valve stem through the grommet and the orifices are uncovered, allowing the foam to pass through the valve and into the gun.

Tilting valves name is a result of the lateral opening force applied in the stem to activate the valve, as shown in 'Figure 3, b'. Once the valve is built, the adapter or actuator can be fitted. When the actuator is depressed it pushes the valve stem through the grommet, and half of the orifices are uncovered, allowing liquid to pass through the valve and into the adapter (Dhaenens, H., 2007).



(a) (b)

Figure 3 – a) Gun valve opening force; b) Tilting valve opening force.

A typical aerosol valve is made up from 4 components (Figure 4):

A. Valve stem, which has orifices inside to allow the dispensing of the foam.

B. Inlayed gasket, which is the seal between the valve cup and the aerosol can, usually made of Buna rubber (copolymers).

C. Grommet, usually made from vulcanized rubber, like Neoprene®[1] (red circle).

D. Cup, generally made of tin plated material.

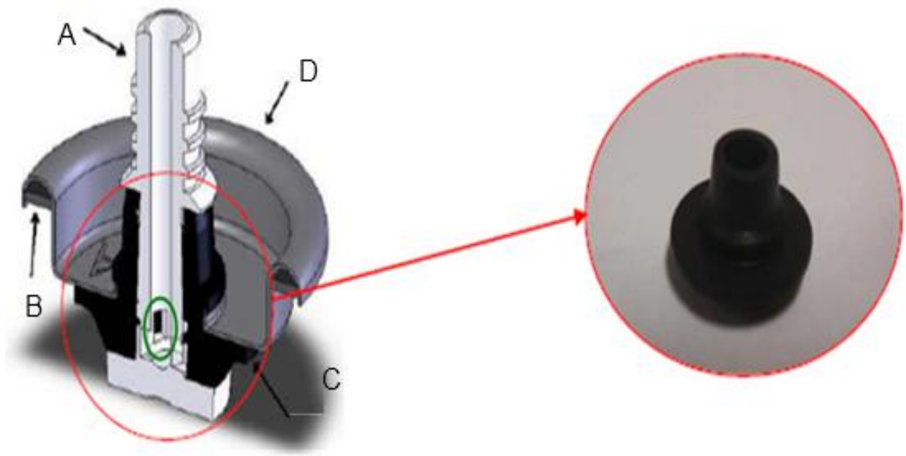


Figure 4 - Aerosol valve (left) and grommet (right)

Some stems contain 3 or even four orifices (Figure 4, green circle), depending on the nature of the product to be dispensed (density and output required). In the closed position the orifices are covered by the grommet, so the valve is closed, entrapping the foam and gas inside the can. When the actuator is depressed, it pushes the valve stem through the soft grommet and the orifices are uncovered, allowing the foam to pass through the valve and into the applicator. When the pressure is released by the operator, the stem is pushed upwards due to the force applied by the grommet, covering the orifices (Jhonsen M.A., 1982).

The applicators are a very important tool to open tilting and gun valves. It can be a simple adapter with straw screwed on the tilting valves or, for gun valves, a "Non-Blocking System" (NBS) foam gun. These systems reduce the valve opening forces and control the output (OP). Examples can be observed below (Figure 5).

[1] *A brief definition of this term is performed in Annex 1, p. 50.*

Figure 5 - Applicator systems.

2.3 Altachem Valve Generations

Altachem has four valve generations:

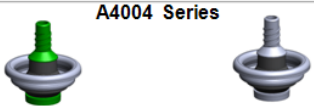
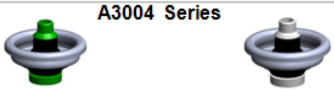
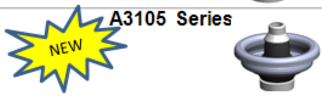
- Generation 1 – Valves A2000 or A3000, with the lowest shelf-life. The stem is made of plastic material;
- Generation 2 – Valves A3004 or A4004. The stem is made of reinforced plastic, with a better shelf-life;
- Generation 3 – Valves A3105 or A4105. The stem is made of a superior plastic material, with the best shelf-life;
- Generation 4 – Non sticking valve – A5000 valve[1]

The series A2000, A4004 and A4105 are tilting valves and the series A3000, A3004, A3105 and A5000 are gun valves.

The 3rd generation allows the longer shelf-life of all valves, high efficiency and less sticking of the valve. The cost of this generation is much higher comparatively with the generations 1 and 2. Table 4 represents the first three generations of valves referred. In order to improve the behaviour of the stems, the Altachem R&D Department is looking to reinforce the plastic materials of the stems with glass fibbers or mixtures of glass fibbers and other kind of fibbers.

[1] *Due to Altachem confidentiality norms, it is not possible to describe this type of valve with detail.*

Table 4 - Altachem valve generations

	Generation I	Generation II	Generation III
ADAPTER	**A2000-A4000 Series** 	**A4004 Series** 	**A4105 Series** 
GUN	**A3000 Series** 	**A3004 Series** 	**A3105 Series** 
CHARACTERISTICS	Standard Tilting Valve (A2000, A4000) & Gun Valves (A3000) Daily proven technology by Altachem Valve: High Modulus Polyolefine &Vulcanized Rubber Shore M70 Mounting Cup: tinplated 0,4 mm	Less Sticking Robust Tilting (A4004) & Gun Valve (A3004) Up to 5 x less sticking Valve: Special Copolymer & Rubber Material Mounting Cup: tinplated 0,4 mm Increasing shelf life of the valves	Less Sticking Robust Tilting (A4105) & Gun Valves (A3105) Designed for use in warm & humid climates Valve: Unique Rubber and Stem materials for maximum security and efficiency Mounting Cup: tinplated 0,4 mm

A description of the coding of valves in development and production can be found in Annex 2.

3 Tests Performed with Polyurethane Foam

Many tests are performed in the laboratory to assess the efficiency of the valves. All of them are realized based on Altachem norms and compared with the previous ones. This chapter describes the tests performed to obtain the results for the main project explained in the thesis[1].

3.1 Gas Loss and Creep Test (GL/C)

Gas loss and creep (valve deformation) measurements are performed in most of the test. The gas loss is extremely important for the final product performance: if a can runs out of gas, there won't be enough pressure inside the can to have an acceptable output when sprayed, and also the foam will not have a good quality (Gas loss implies an increment in the product density, while the average foam cell size decreases). The gas loss is measured with a common balance, with $0.1\,mg$ error, comparing the weight of the can with the initial value.

Figure 6 shows 3 preferential regions that can let the gas diffuse in a valve. The region in yellow colour is the most critical region where the diffusion of the gas can occur; the region in blue is important to control too but the probability of diffusion in this region is lower than in the yellow region. The red region is a "secure" region considering that is almost impossible for the gas to escape from there.

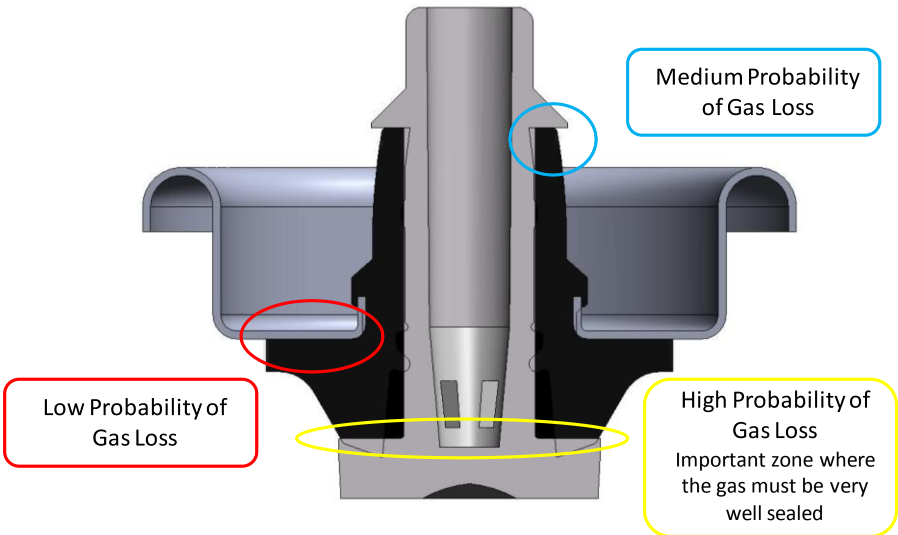


Figure 6 - Possible gas loss regions in the A3004 valve.

[1] *All the other tests performed and learned during the internship can be found in Annex 3 (p. 57): Chemical and Mechanical Tests.*

Plastics exhibit a time-dependent strain response to a constant applied stress, this behaviour is called creep. In a similar approach, if the stress on a plastic is removed it exhibits a time dependent recovery of strain back towards its original dimensions (Crawford, R.J., 1998). The creep is also very important characteristic of an aerosol valve, for example, if creep increases too much, the valve may have difficulties to seal properly, and gas looses will occur. The creep checks the integrity of the valve during the tests due to the can's internal pressure (around $5\,bar$) and chemical interaction with the raw materials and blowing agents. The creep of a valve is tested measuring the distance between the top of the can and the top of the stem, as the 'Figure 7, b' shows.

(a) (b)

Figure 7 – a) Creep measurement apparatus; b) distance between the top of the cup and the top of the stem.

The specific GL/C Test method covers the determination of the sealing performance and the gas diffusion of aerosol valves used for OCF's. An oven, a freezer, a scale and equipment to measure the creep are needed to perform this test.

The aerosol cans are filled with different polyurethane foams, and assembled valves are clinched on the cans. Then, the cans are stored vertical for 24 hours in a climate-controlled chamber at $23\,°C, 50\%\,RH$ (Relative Humidity)[1], and weight and creep are measured for first time.

Next step is to store the cans at three different environments ($-20\,°C$, "$23\,°C, 50\%$ RH" & "$45\,°C,\ 80\%\,RH$") to ensure that the behaviour of the valve is analyzed in all critical environments. Then, gas loss and creep are measured weekly

[1] *A brief definition of this term is performed in Annex 1, p. 50.*

until the 8th week. To ensure an average, the test is realized with 3 cans at each temperature.

- At $23\ ℃,\ 50\%\ RH$ and $45\ ℃,\ 80\%\ RH$, the cans are stored vertically (CV).
- At $-20\ ℃$, the cans are stored on head during the first week using a cap so the pressure decline over the valve due to the gas contraction created by the low temperature is countered with the pressure exercised by the polyol and the MDI over the bottom part of the valve. The cans are removed from the freezer in the 1st week, and stored vertically at $23\ ℃,\ 50\%$ RH until the 8th week.

The gas loss values previously studied with the standard valves are around $8-10\ g/year$; and the absolute creep values previous studied with the standard valves are around $0.03\ mm$ in 8 weeks at $23\ ℃,\ 50\%\ RH$[1]. Thus, the aim is to find a valve with lower absolute creep and gas loss to improve the cans performance[2].

3.2 Sticking & Stucking Test (SS)

This test is made with aerosol cans previously filled with polyurethane foam – polyol, MDI and blowing agents (DME and LPG gases) – to study the behaviour of the valves during their shelf-life on the sticking and stucking field, storing the aerosol cans under real or aging conditions.

Cans are recommended to be vertically stored, so the isocyanate free functional groups are not in contact with the bottom part of the valve to avoid the sticking/stucking behaviour[3]. In these tests, cans are stored horizontally (half of the bottom part of the valve in contact with the referred substances) or can on head (full contact) to recreate the worst possible conditions.

The test can be carried out in different types of environments (Dhaenens, H., 2007):

1) Sticking & stucking at $23\ ℃, 50\%\ RH$ – cans stored horizontally (CH);

[1] *This is the creep value for the standard Altachem valves studied in this thesis; other standard valves series use a flat grommet which performs a lower creep (Anti Blocking System (ABS) valves).*

[2] *Results examples for these tests alongside with their discussion can be found in Chapter 4.*

[3] *Even there is no polyurea formation in this case; the grommet can increase its hardening due to the rubber characteristics. A low possibility of stucking behavior of the grommet also exist when cans are stored vertically because of a liger contact between the MDI and the bottom of the valve when cans are filled and shacked to mix the reagents. The MDI is a viscous fluid so a little quantity of it remains glued to the bottom part of the valve.*

2) Sticking & stucking at $45\,°C, 80\%\,RH$ - cans stored horizontally (CH);

3) Sticking & stucking at $45\,°C, 100\%\,RH$ – cans stored on head (COH) with water in the cap so the valve is in contact with the water (Dhaenens, H., 2007).

In the first case, the "common" environment of the can is created during 50 weeks, simulating the polyurethane can dispenser shelf-life. To promote faster results from the new developed valves, the second and third options accelerate the aging process. The temperature and RH increments promote worst conditions, subjecting the valve to higher quantity of water vapour and, therefore, to higher water diffusion through the grommet. One day at $45\,°C,\ 80\%\,RH$ correspond more or less to one week at $23\,°C,\ 50\%\,RH$ (Dhaenens, H., 2007).

Normally options 1 and 2 are performed. For each tested valve type, 20 cans have to be filled with foam formulations and labelled with the date of filling. Once this is done, cans are placed vertically for 24 hours at $23\,°C,\ 50\%\,RH$. After this 24 hour period, the weight and the creep are registered for first time (Dhaenens, H., 2007).

Table 5 - Sticking & Stucking general test plan for Altachem standard valves

Sticking & stucking Test		
Valves	Cans at	
	23°C CH	45°C CH
A2000	10	10
A2005-02	10	10
A3000	10	10
A3004	10	10
A3105	10	10
A4004	10	10
A4105	10	10

For the $23\,°C,\ 50\%\,RH$ test, cans are removed every 5 weeks. The $45\,°C,\ 80\%\,RH$ cans are removed each 2 weeks, after the 4th week. After removed, cans are stored for 24 hours at a $23\,℃,\ 50\%\,RH$ room temperature before the measures are performed[1].

The weight and the creep are registered each time the cans are tested (Dhaenens, H., 2007). The sticking test is performed on an INSTRON[2] machine (Figure 8, a), using associated MERLIN software. Depending on the valve type (gun or tilting) the extensions and rates used differ. The sticking test method covers the determination of the force needed to mechanically open the valves, defining the snappiness of the valve. The snappiness of the valve is a designation for the easy opening of the valve simultaneously with the return of the valve to its initial position. It is important to guarantee that the valve is easily opened by the adaptor or gun system, but at the same time the valve needs to close as fast as the load applied is released, to avoid releasing more foam (Armistead, J.P., 1985). The results are presented by a graph of Load (N) vs. Extension (mm).

Afterwards, the flow/output (OP) test is performed, dispensing foam inside a box during $10\,s$. The box is weighted before and after the OP test and this should be at least $40\,g$, otherwise the valve is seen as blocked (Dhaenens, H., 2007).

(a)

(b)

Figure 8 – a) View of the INSTRON machine; b) Stuck test performed to obtain the load applied to open a gun valve.

The gun valve is vertically opened (using a gun adaptor shaped tool) over a distance of $2\,mm$ with an opening speed of $10\,mm \cdot min^{-1}$. Then, the corresponding opening force is measured. 'Figure 10, a' is an example of the test performed in a gun valve, where is shown the load applied by the INSTRON per extension $(2\,mm)$. The

[1] *This way, the blowing agents are located at the top of the cans, so no foam will release during testing the valve opening, and the equipment will not get dirty.*

[2] *A brief definition of this term is performed in Annex 1, p. 50.*

maximum in the ‘Figure 10, a’ (circle in red) is the necessary load applied to open the valve, showing that the valve was sticked (Dhaenens, H., 2007).

After this opening force test, the cans are provided with a foam ring and screwed onto a gun holding an adaptor. The OP is checked (if there is any) at $23\ ^{\circ}C$ during $10\ s$ (Figure 9) (Dhaenens, H., 2007).

(a) (b) (c)

Figure 9 – a) Gun used to perform the OP test for the gun valves; b) OP test; c) foam detail.

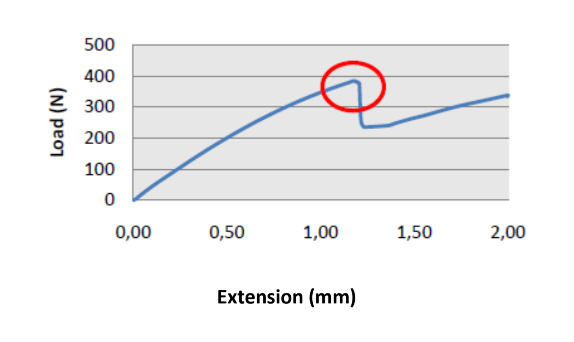
After unscrewing the gun, the valve is examined for gas/foam leakages and the box with foam is weighted[1].

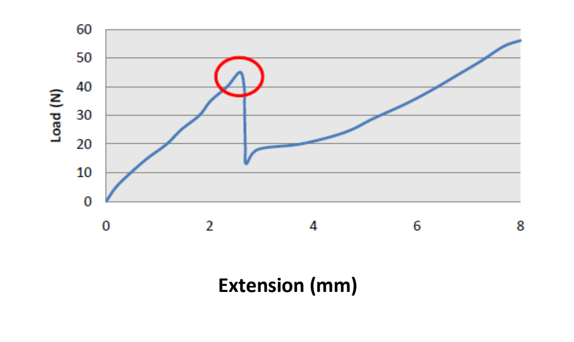
The tilting valve is activated (using an adaptor shaped tool) over an extension of $8\ mm$ with an opening speed of $50\ mm \cdot min^{-1}$; then, the corresponding opening force is measured. The maximum in ‘Figure 10, b’ (circle in red) is the necessary load applied to open the valve, showing that the valve was sticked. The tilting valve can be sticked (stem “glued” to the grommet, formation of polyurea near the valve) and/or stucked (hardened grommet in a specific diffusion area) (Dhaenens, H., 2007). After this, the OP value is measured by tilting the valve during a maximum of $10\ s$ at $23\ ^{\circ}C$. This is done with a standard Altachem angle adapter for tilting valves. Finally, the total weight of the foam that has been dispensed out of the can is measured.

Sticking and stucking behaviours usually increase with similar rates. Sticking behaviour is important for both gun and tilting valves, while stucking problems are

[1] *Cans showing incidents are opened and the valve is examined with more detail to check possible causes.*

more important for the tilt valves than for the gun valves, due to the lateral force required for the valve's activation.





(a) (b)

Figure 10 – Load vs. Extension results: a) Sticked gun valve; b) Sticked tilting valve.

As it was commented before, the sticking behaviour can be noticed in the Load vs. Extension graph by a maximum or "peak" point. These points represent the moment the polyurea union between stem and grommet "breaks" (a "crack" is audible at this moment). The better way to recognize the stucking behaviour is to open the can, separate the valve pieces and cut the grommet in two, to check if the rubber is hardened in the regions under shear stress; also, if the tilting stems are broken when the valve is activated, it usually means that the grommet was not flexible anymore (stucked) so the force applied broke the stem. 'Figure 11, a' shows the polyurea formation near and between the stem and the grommet (sticked valve); while 'Figure11, b' shows that the grommet presents hardened regions due to the polyurea formation inside the rubber pores (stucked valve)[1].

(a) (b)

Figure 11 – a) Representation of "crunch" in the aerosol can after aging. Can before aging (left) and can after aging (right); b) Area hardened from the grommet due to aging (red circles).

A discussion of a complete SS Test can be found in Chapter 4 (p. 26).

[1] *Visually, is it possible to notice a liger brightness in the hardened regions, but the better way to prove that the rubber is hardened is to perform manually a force on the grommet. Altachem laboratory is provided with a hardness measuring machine that is sometimes used during the swelling tests to investigate further.*

4 Discussion of Results - Benchmarking Project

The objective of this project is to obtain a new customer for Altachem. Different standard valves need to be approved on all their formulations. Altachem provides the service of comparative testing between the currently used valves (the ones from competitors) and the Altachem valves. Comparisons between the different foams are also performed in order to improve the investigation.

Of each type of valve and type of foam, 12 cans were received from the client. Standard SS and GL/C tests were performed.

Table 6 resumes the models involved in the project and which foams and valves where used for each test. Competitors and foams specific names are omitted due to Altachem Confidentiality Norms. Foams are numbered from 1 to 8 (F1, F2, etc...), and the same foam colour coding is used for all the result tables, in order to facilitate the understanding of the data.

Foam 4 was excluded for testing because it arrived in bad condition. Gun valves from “Competitor C”, Foam 1, where also excluded because of arriving in bad state. Foam 8 was only used for the GL/C Test also because there were not enough cans in good condition to perform the SS Test.

Table 6 – Benchmarking Project Overview

Type	Valve Name	F1	F2	F3	F5	F6	F7	F8
Gun	C.A (Competitor A)	GL/C SS	X	X	GL/C SS	GL/C SS	GL/C SS	GL/C
	C.B PU 55 (Competitor B)	GL/C SS	X	X	GL/C SS	GL/C SS	GL/C SS	GL/C
	C.C 961 (Competitor C)	X	X	X	GL/C SS	GL/C SS	GL/C SS	GL/C
	A3105 (Altachem)	GL/C SS	X	X	GL/C SS	GL/C SS	GL/C SS	GL/C
Tilt	C.B PU 784 (Competitor B)	X	GL/C SS	GL/C SS	X	X	X	X
	C.C 971 (Competitor C)	X	GL/C SS	GL/C SS	X	X	X	X
	A4105 (Altachem)	X	GL/C SS	GL/C SS	X	X	X	X

4.1 Gas Loss & Creep Test at $23\ ^\circ\mathrm{C}, 50\%\ RH$, Cans Stored Vertically

For this test, two cans of each valve and foam where stored vertically at $23\ ^\circ\mathrm{C}$, $50\%\ RH$ during 8 weeks. Weight and creep were measured each week[1], and results were used to make graphs that show the evolution of the variables.

4.1.1 Gas Loss

The graphs with the results for this test can be found in Table 7 (p. 24). The graphs show the gas loss per year[2], which is calculated by the following equation:

$$GL/_{year}\ (\mathrm{g}) = \mathrm{GL}_{8\mathrm{th\ week}}\ (\mathrm{g}) \cdot \frac{1}{8\ \mathrm{weeks}} \cdot \frac{52\ \mathrm{weeks}}{1\ \mathrm{year}} \qquad (4.1)$$

From the graphs, it is possible to conclude that:

- Cans with the foams 2, 3, 5, 6 and 8 have larger gas looses ($6 - 12\ g/year$), except for the C.A valve that almost does not lose gas, which means that Altachem client uses a larger quantity of blowing agents on those formulations, increasing the cans internal pressure.
- Cans with the foams 1 and 7 suffer a minor gas loss (less than $6\ g/year$), corresponding with a lower gas amount and therefore a lower can internal pressure.

Observing the results for the gun valves, C.A valve is clearly superior to the rest of valves. This valve is also more expensive due to its design and materials, which has notable differences contrasting with the rest (Figure 12). Altachem client will need to make a balance taking into account the expenses and the quality of the valves, but it will be desirable to considerate the output results better than the gas loss ones, because of this characteristic being the most important for a valve. The results for the other two competitors and Altachem valves are similar, suffering little variations (less than $2\ g/year$) depending on the different foams. This is a result of the similar designs and materials used in the C.B PU 55, C.C 961 and A3105 valves.

Results for the tilt valves are not conclusive for comparing Altachem and competitors, because of being almost the opposite for the two foams tested. Nevertheless, it is possible to conclude that Altachem and competitors tilting valves

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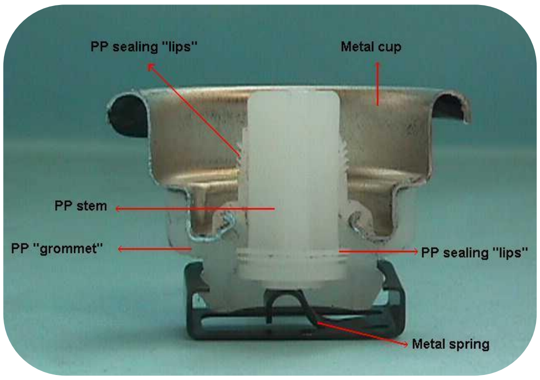
[1] *There are no measurements points for some of the weeks and valves due to mistakes during the test or because these points escape clearly from the general trend, so they were omitted when making the graphs.*

[2] *Table 7 only takes into account the 8th week GL measurement. The evolution of the gas losses with time is showed in Annex 4, Table 20 (p. 63). All the valves tested illustrate a GL increasing linear evolution with time, with no specialties.*

suffer similar gas losses ($7 - 11\ g/year$), as a result of using similar designs and materials.



Competitor A valve

Altachem A3105 valve

Figure 12 - Comparison of C.A valve with the A3105 valve.

4.1.2 Creep

The graphs with the results for this test can be found in Table 8 (p. 25). Comparing Tables 8 and 20 (GL vs. Time, Annex 4, p. 63), it is observed a proportional relationship between the creep and the gas loss for all the valves and formulations: a larger absolute value for the creep have repercussions in the valves sealing, increasing the possibility of gas losses by the areas described at Chapter 3 (p.13).

Normally the creep suffers an increasing or decreasing tendency during the entire test, but the trend can also vary with time for some of the valves[1]: An oscillation between the increasing/decreasing of the dimensions seems to exist. This oscillation is due to the natural variability of the experimental method[2].

Looking at the <u>gun valves</u>, the C.A valve suffers similar creep to the rest of valves while having minor gas looses, this is an exception because of being a different model with other type of design (see Figure 12 showed above). C.A valve sealing is due to a metal spring that forces the stem to return to its initial position once the valve is activated. The grommet is made of polypropylene (PP) material instead of rubber, because it does not need to be flexible. This PP material is much less porous than the rubber one so the gases cannot escape trough the grommet. The stem and the grommet are reinforced with PP sealing lips. All this technology increases the product final price (the detailed pieces need a finest production, and their assembling requires the utilization of more expensive machines). Due to all these reasons, a better behaviour for this valve will be proven in almost all the test

[1] *An example of this can be checked at the graph for the A3105 valve, F1, showed in Table 8 (p. 25).*
[2] *A $0.01\ mm$ absolute error is involved in the creep measurement.*

performed. As it was said before, the economic study comparing price-quality of the valves analysed is led to the client.

The general tendency for the gun valves creep is to decrease as maximum $0.03\ mm$ or resting stable (creep never increases more than $0.01\ mm$). Special mention for the creep of the C.B PU 55 valve with the foam 8, which decreases more than $0.05\ mm$, breaking the general tendency. The only possible reason for this is that any of the blowing agents used in the foam 8 has important repercussions in the stem and/or grommet materials of the C.B PU 55 valve[1].

The reason for both increasing/decreasing of creep's behaviour is that the materials involved suffer dilatation/shrinkage in contact with the raw materials inside the can[2], while the cans high internal pressure has an impact in the valve increasing its creep.

Observing the results for the tilt valves, C.B PU 784 valve creep is almost inexistent for the two foams tested[3], due to an almost inexistent interaction of the foams 2 and 3 with the valve materials[4]. Altachem A4105 valve's creep also stays stable, not passing a decline of $0.02\ mm$ for the foam 2; this can be also explained by a low interaction between the blowing agents and materials involved. Results for the C.C 970 valve differ with the foam used: for the foam 2, creep increases till a value of $0.03\ mm$, while for the foam 3 it decreases till $0.04\ mm$. It is clearly observed for this example how the different blowing agents affect the bottom part of the valve, increasing or decreasing the creep.

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[1] *A further Swelling Test for the stems and grommets using the blowing agents of the foam 8 would provide some interesting information about this matter (See Annex 3, p. 57).*

[2] *Altachem Swelling tests are performed to study this type of behavior (See Annex 3, p. 57).*

[3] *C.B PU 784 creep line for the foam 3 is exactly the same as the A4105 valve, so it is difficult to differentiate these two lines in the graph.*

[4] *For the two competitors and Altachem, the materials used in the gun and tilt valves analysed are the same. "Competitor C" gun valve suffered a normal creep for the gun valves results, so the reason of an inexistent creep for the "Competitor C" tilt valve comparing with the gun one cannot be a matter of differences between these two valves material.*

Table 7 - Gas Loss Results for the Benchmarking Project

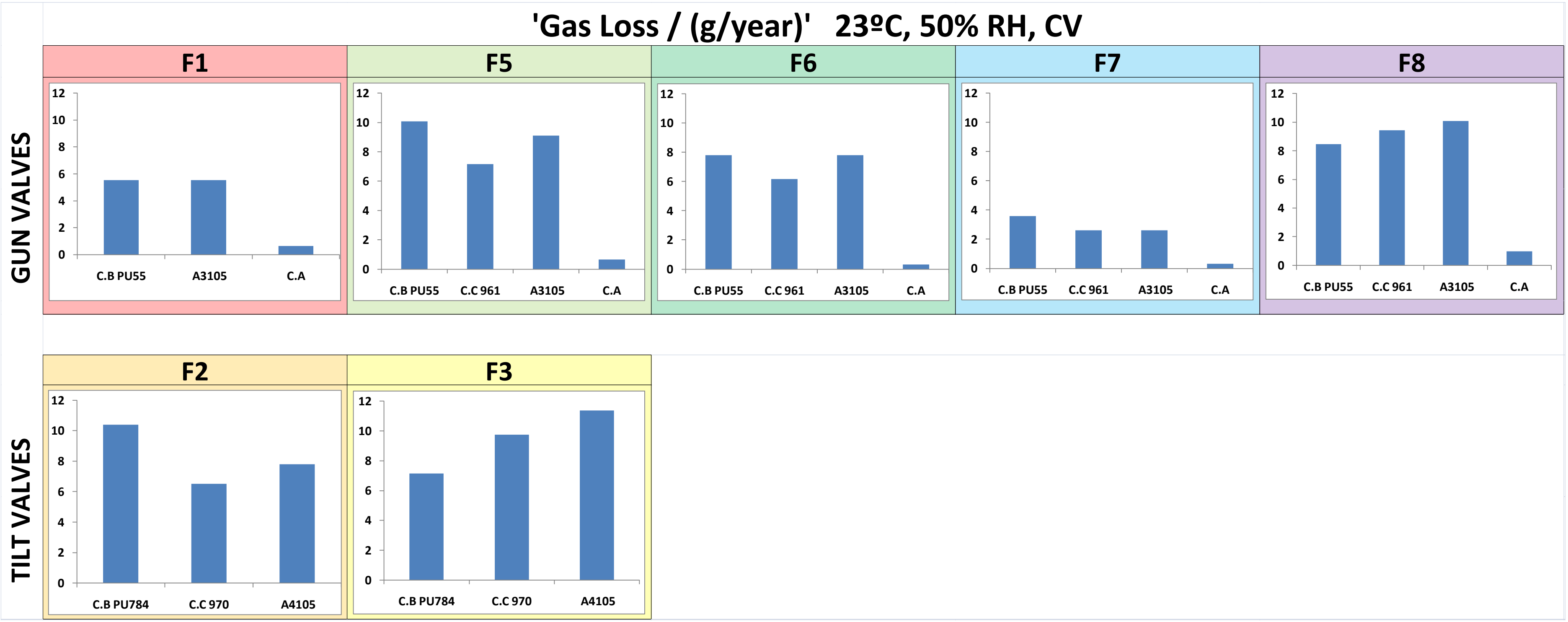
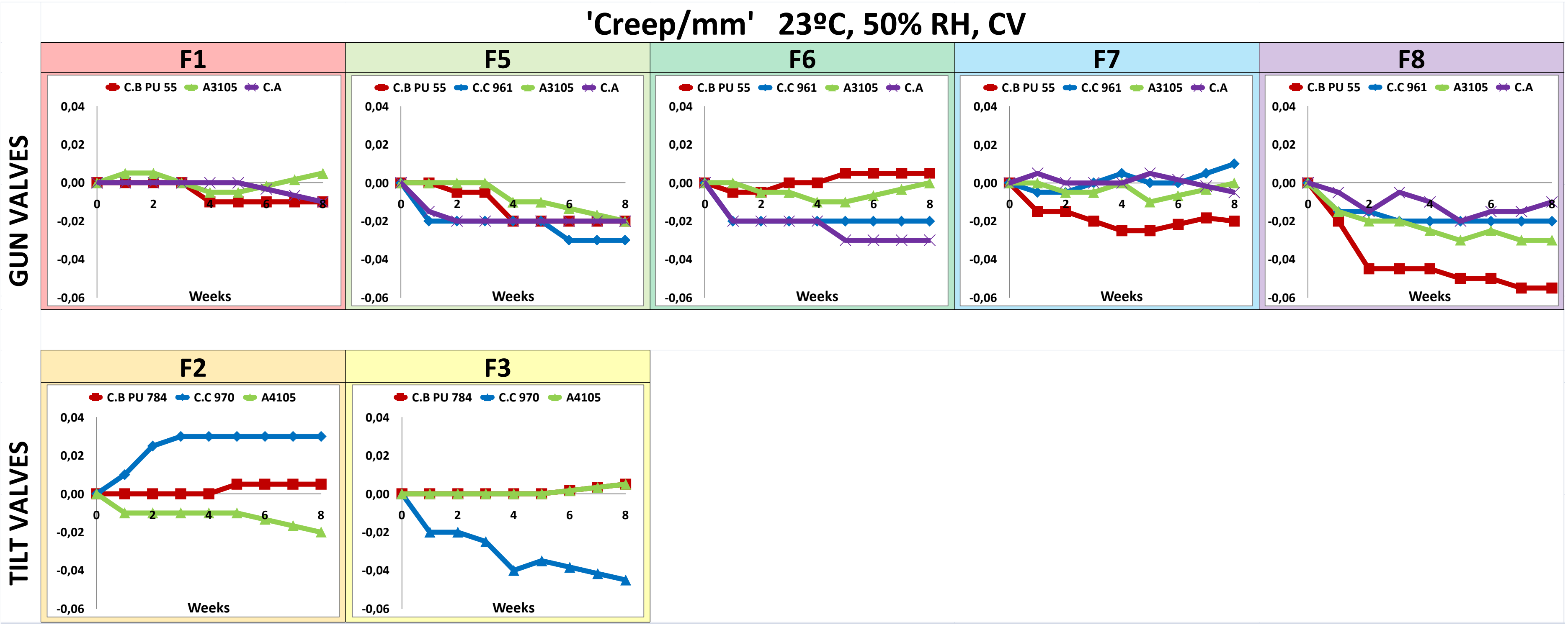


Table 8 - Creep Results for the Benchmarking Project



4.2 Sticking & Stucking Test at $45\,°C, 80\%\,RH$, Cans Stored Horizontally

For this test, 10 cans of each valve and foam were stored horizontally in an oven at $45\,°C,\ 80\%\,RH$. One can of each valve and foam was retired each two weeks, starting the 4th week[1]. Weight, creep, opening forces and output in ten seconds where measured for each can. This test was not performed for the foam 8 because these cans arrived to Altachem in a bad state. GL and C values at $45\,°C,\ 80\%\,RH$, CH (aging conditions) are higher than at $23\,°C,\ 50\%\,RH$, CV (normal storing conditions) as it was expected[2,3].

4.2.1 Gas Loss

The graphs with the results for this test can be found in Table 9 (p. 28). They show that cans with the foam 7 suffer a minor gas loss comparing with the rest of valves (less than $0.4\,g$ in 22 weeks). Foam 1 also suffers low gas losses (less than $0.6\,g$ in 22 weeks as maximum). These results correspond with a low can internal pressure due to an inferior amount of the formulation blowing agents, as is it also showed in the GL/C Test at $23\,°C,\ 50\%\,RH$ commented before (Chapter 4.1.1, p. 21).

Observing the results for the gun valves, C.A valve is superior to the rest ($GL < 0.4\,g$), due to its superiors design and materials (Figure 12, p. 22). The results for the other two competitors and Altachem valves are similar (the differences do not exceed $0.3\,g$ of gas loss), excepting a slightly higher gas loss observed for the C.B PU 55 valve in foams 1, 5 and 6; this means that the C.B PU 55 valve is more affected by the high temperature and humidity than the rest of the valves, while the materials of the Altachem A3105 and C.C 961 valves have a similar response for these hard environment conditions. Gas losses with foam 7 are clearly minor comparing with the rest of foams tested with gun valves, due to the low internal pressure of the cans with this foam. All the valves tested for the foam 7 have the same gas loss value at week 24, but a better behaviour can be observed for the C.A valve followed by the Altachem gun valve: GL takes more time to arrive to the maximum value.

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[1] *It is possible to check in the graphs that some of the cans were not tested exactly each two weeks. When any problem exist, usually the test is perform in advance to check as fast as possible the problem, or sometimes it is not possible to perform the test in the exactly day which has been programmed.*

[2] *This fact can be proved comparing Tables '20 (p. 63) vs. 9 (p. 28)' and '8 (p. 25) vs. 10 (p. 31)'.*

[3] *For the SS tests purpose, it is supposed that one day at $45\,°C, 80\%\,RH$ equals a week at $23\,°C, 50\%\,RH$, so 16 weeks at $45\,°C, 80\%\,RH$ equals to two years at $23\,°C, 50\%\,RH$. This fact is proved for the foams behavior, but not properly proved for the valves behavior, so the discussions will not take this fact into account.*

Results for the tilt valves show that C.B PU 784 valves loose more gas than the rest; so it is possible to conclude that the materials used by the "Competitor B" behave worst facing high temperatures and humidity than the rest of the valves. Altachem and "Competitor C" valves have a similar behaviour (around $0.6\ g$ of gas loss in 18 weeks), due to their similar design and materials.

Once the GL is tested at $23\ ℃,\ 50\%\ RH$, CV and $45\ ℃,\ 80\%\ RH$, CH, is possible to conclude that[1]:

- Making an average for all the foams involved, "Competitor A" valve is the one with lower gas looses; followed by Altachem and "Competitor C" valves, which perform a similar behaviour.
- "Competitor B" valves perform slightly higher gas losses comparing with the rest of valves.

For the two different environments tested, a higher gas loss can be observed for the tilt valves[2], but these valves are tested with their own foams, so both or one of the following reasons for this higher gas loss are possible:

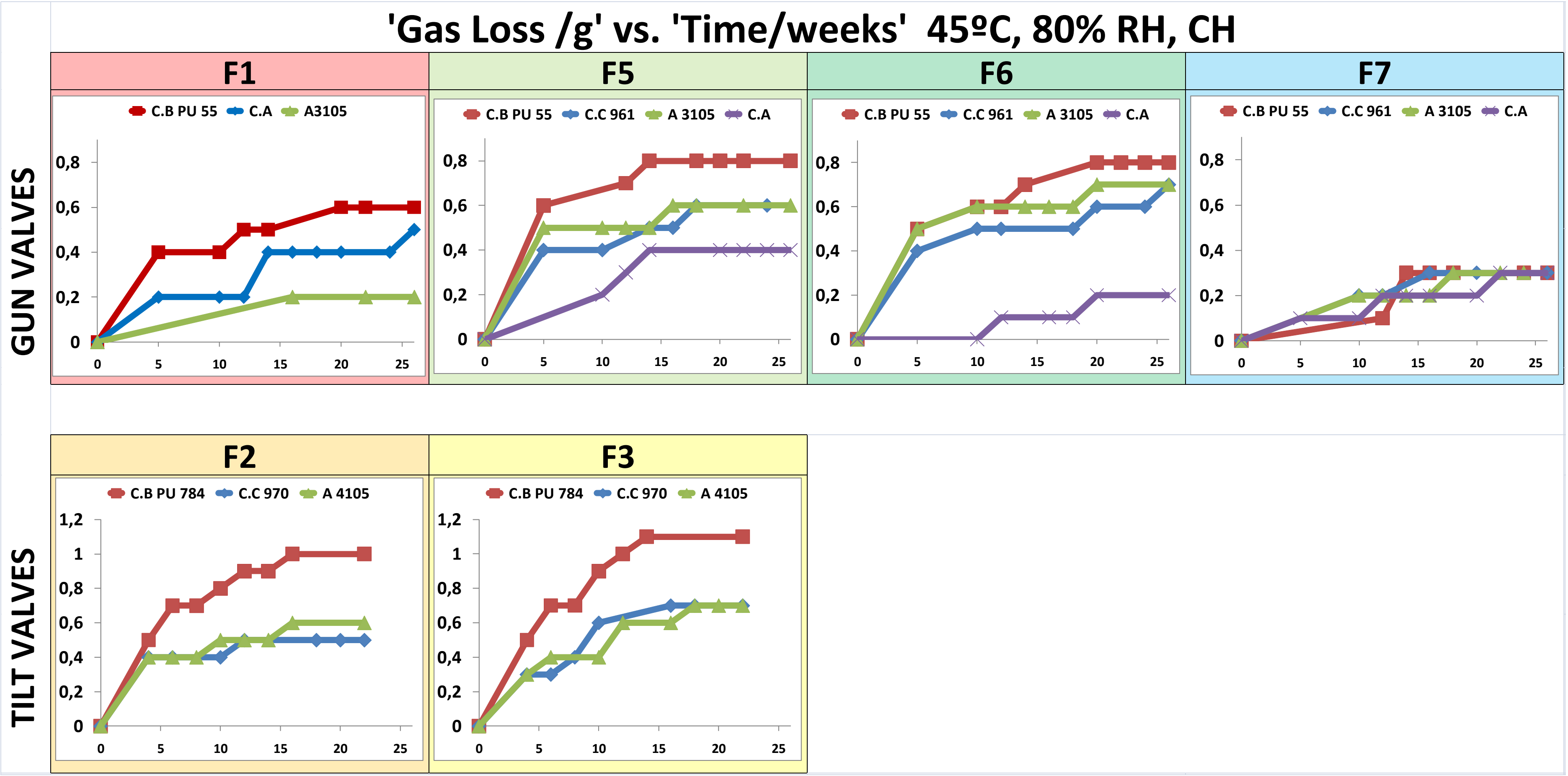
1. The differences between gun and tilt valves designs cause higher gas losses in the tilting valves, or
2. The involved foams for the tilting valves studied in this project have a large amount of blowing agents, increasing the cans internal pressure and therefore causing high gas losses.

Other projects performed comparing gun and tilt valves with the same materials and foam demonstrate that there are no big differences between the gas losses of the tilting and gun valves; so just the option 2 is the correct one.

[1] *This conclusion can be assumed for both gun and tilting valves, without taking into account "Competitor A" for the tilt valves ("Competitor A" only produces gun valves).*

[2] *For example, in 24 weeks at $45\ ℃,\ 80\%\ RH$, CH, the maximum gas loss for the tilt valves is $1.2\ g$ while for the gun valves is $0.8\ g$.*

Table 9 - Gas Loss Results for the SS Test of the Benchmarking Project



4.2.2 Creep

The graphs with the results for this test can be found in Table 10 (p. 31). It is observed a general proportional relationship between the creep and the gas loss for all the valves and formulations as in the previous test (Chapter 4.1.2, p. 22)[1].

Looking at the gun valves is it possible to perform the following comments:

- C.A valve, which has superior design and materials, performs a minor absolute creep comparing with the rest of valves for all the foams involved ($< 0.1\,mm$ after the 24th week). This lower creep for the C.A valve is not seen at the $23\,°\mathrm{C},\ 50\%\,\mathrm{RH}$ test commented before (Chapter 4.1.2, p. 22) because at aging conditions the valves different qualities are more evident.
- For the foams 5, 6 and 7, the general creep tendency is to decrease $0.5 - 0.8\ \mathrm{mm}$ in 12 weeks approximately[2].
- The graph for the foam 1 shows the better quality of the “Competitor A” gun valve, followed by the Altachem and “Competitor C” gun valves. “Competitor B” valve suffers a higher creep than the Altachem valve for this foam, so it is possible to conclude that these valve materials are more affected by the blowing agents of the foam 1 comparing with the other foams tested.

Observing the results for the tilt valves, all of them reach around $-0.3\,mm$ creep in the 4th week, excepting C.B PU 784 valve for the foam 3, which creep remains stable showing a low interaction of this valve materials with the blowing agents inside the can.

Creep results at the two different environments tested ($23\,°\mathrm{C},\ 50\%\,\mathrm{RH}$ and $45\,°\mathrm{C},\ 80\%\,\mathrm{RH}$) correspond with each other, taking into account that the creep variations are more evident at aging conditions. The only exception is for the C.C 970 tilt valve with the foam 1: It is possible to conclude that the storing position of the cans affects to this stem. When cans are stored vertical (CV), the C.C 970 valves creep increases, but when cans are stored horizontal (CH) the behavior is just the opposite. As explained before, valves creep behavior depends on the stress forces suffered by the stems and/or the chemicals in contact with the stem and grommet. For cans

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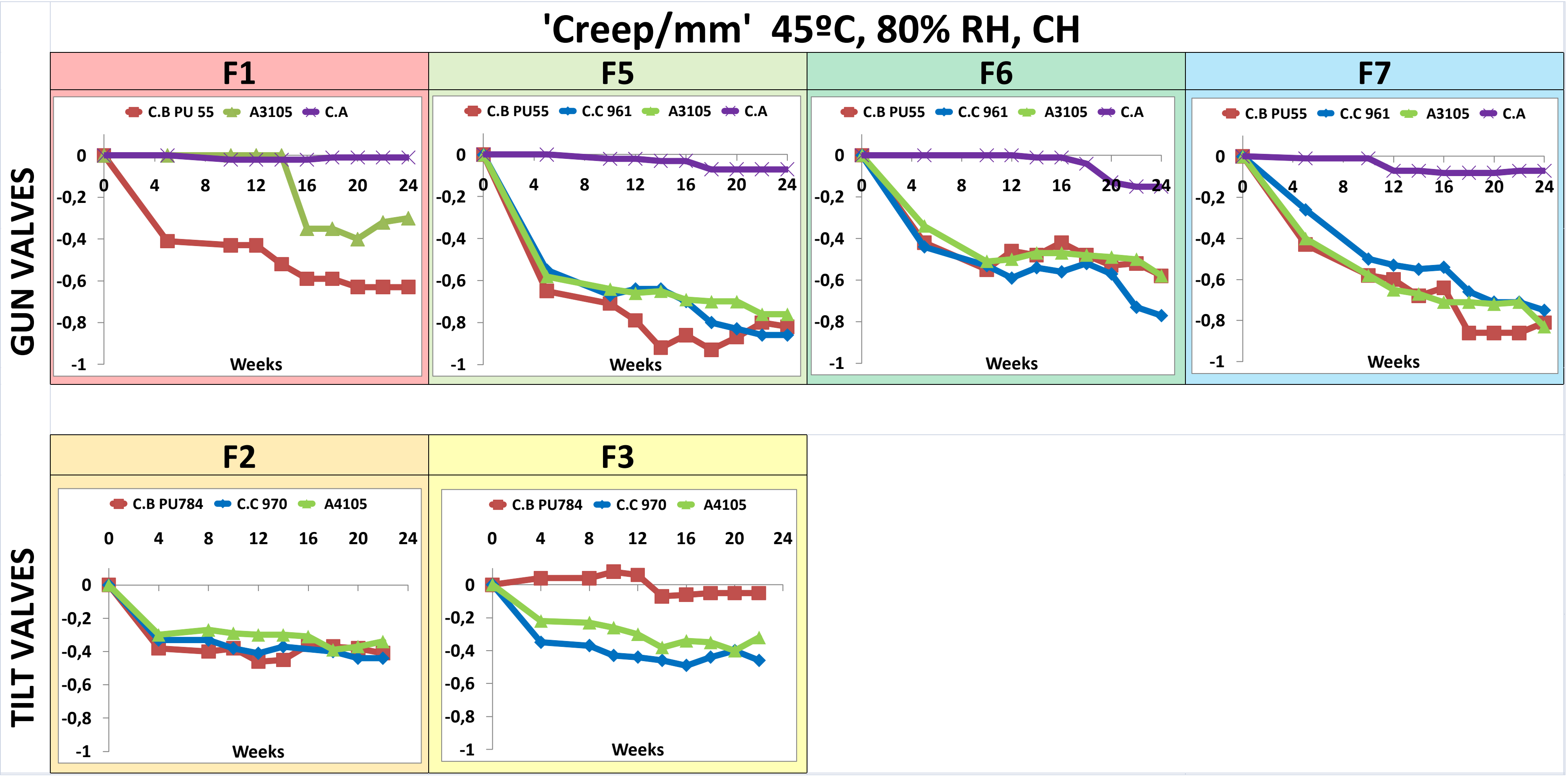
[1] *As explained before, a larger absolute value for the creep has repercussions in the valves sealing, increasing the possibility of gas losses by the areas described in Chapter 3 (p. 13).*

[2] *As it was said before, the reason for both increasing/decreasing of creep’s behaviour is that the materials involved suffer dilatation/shrinkage in contact with the raw materials inside the can. Cans internal pressure also has an increasing impact in the creep behaviour.*

stored vertical (CV), the chemicals in contact with the bottom part of the valve are the blowing agents; for cans stored horizontal (CH), the bottom part of the stem and grommet is in contact not only with gases, but also with the polyol and the MDI (Methylene Diphenyl Diisocyanate). The most common reason to explain why creep increases when cans are stored vertical but decreases when stored horizontal is that the DME from the blowing agents is usually absorbed by some of the stems material, increasing the size of the bottom part of the stem. If the grommet is not hardened due to polyurea formation, it allows the stem to go up because of the cans internal pressure. But, when the grommet is hardened (as happens when cans are stored horizontally), the stem goes down because the hardened grommet does not allow it to rise, decreasing the valves creep[1].

[1] *For further investigation, it would be desirable to perform a DOT Test to study the pressure impact over the valve; as well as a Swelling Test to learn how the chemicals interact with the stems material of the C.C 970 valve (See Annex 3, pgs. 57-58 for the explanation of the tests referred).*

Table 10 - Creep Results for the SS Test of the Benchmarking Project



4.2.3 Load vs. Extension

The graphs with the results for this test can be found in Tables 11 (p. 34) and 12 (p. 35). As a general tendency, it is possible to observe an increment of the opening forces with time. When cans are stored horizontally at aging conditions, part of the valve's bottom is in contact with the raw materials inside the can; the high temperature accelerates the polyurea formation and the high humidity provides the necessary H_2O molecules for this reaction; so the "crunch" is easily formed and there is an increment of the sticking/stucking behaviour with time that causes an increment in the valve opening forces.

Tilt valves opening forces ($\approx\ 50\,N$) are much lower than gun ones ($\approx\ 200\,N$) because tilt valves have to "break" only part of the polyurea union between the stem and grommet to be activated, while gun valves need to "break" this union in all the stem-grommet contact surface.

For some of the graphs, Instron test shows a negative load just after the polyurea unions rupture[1], which means that the grommet did not oppose any resistance at this moment of the test, and the Instron machine recognizes the weight of the adaptor as a negative load. This phenomenon may also occur in the first moment of the test, due to a bad adjustment between the valve adaptor and the Instron support, or at the last moment of the test (when the adaptor is coming back from the maximum extension) due to a low snappiness of the grommet (once the grommet is compressed it does not return to its initial form so the adaptor and the support are not in contact)[2].

Looking at the gun valves results, it is possible to conclude that:

- All the valves (excepting the C.A one, with superior design and materials) show sticking/stucking behaviour since the 4th week, because of being tested under aging conditions[3].
- C.B PU 55 valve requires a larger force to be opened than the rest of the valves, with maximums that reach $400 - 500\,N$ for the foam 5. As showed before, this valve suffers a higher creep comparing with the rest of valves tested; so the probability of polyurea formation in the interstices between stem and grommet, that has an increasing impact in the opening forces, is larger.

---

[1] *See for example the graphs of the valves "C.B PU 55, foam 5, week 14", "C.B PU 784, foam 2, week 16" and "C.C 970, foam 2, week 16" (Tables 11 (p. 34) and 12 (p. 35)).*

[2] *This grommet wrong behavior is due to the polyurea formation inside its pores (stucked grommet).*

[3] *As explained in Chapter 3 (p. 19), sticking behavior is detected when a "peak" point or maximum is visible in the Load vs. Extension graph. Stucking behavior increases at a similar rate as the sticking behavior; and the method to prove this is to open the valve and cut the grommet in two, to check if the hardened regions exist or not. For tilting valves, if the stem is broken during the test it usually means that the grommet is stucked.*

- A3105 and C.C 961 valves show a very similar behaviour, corresponding with the GL/C results at both different environments tested (23 ℃, 50% RH and 45 ℃, 80% RH). Most of the results for the tests performed demonstrate similar characteristics between these two valves.
- Foams 1 and 6 behave better than foams 5 and 7. There is a lower polyurea formation so valves are less sticked and require lower opening forces. This phenomenon can be explained by a lower MDI quantity in their formulations.
- C.A valve shows a completely different behaviour than the rest, and seems to never get sticked. Its opening forces do not vary with the different types of foams. As it was said, this valve has a better performance due to its design and materials.

Observing the tilt valves, the following comments can be done:

- The tilt valves sticking behaviour is less visible than in the gun valves graphs[1], but it also exists[2]. This phenomenon occurs because the polyurea union between stem and grommet rupture is different for the gun and tilt valves. For gun valves, a vertical force is performed and the union rupture normally occurs at one time; for tilting valves, a lateral force is performed so several “little” ruptures occur.
- Opening forces for the “Competitor B” are higher than for Altachem and “Competitor C” valves, showing a similar behaviour with the gun valves. The reason for this phenomenon is the same as commented for the gun valves[3]: this valve suffers a higher creep, so the probability of polyurea formation in the interstices between stem and grommet, that has an increasing impact in the opening forces required, is larger.

[1] *Instead of a clear maximum load point in the graph, as occurs with the gun valves, several maximums can be seen (‘C.B 784 - F2 - W8 (2)’ graph, Table 12 (p. 35)).*

[2] *For example, it is possible to see how the C.B PU 784 valve, for the foam 3, week 10, is so stuck that did not even open (this can be confirmed with the posterior output test).*

[3] *The materials used for gun and tilt models are the same in each producer for all the cases (Altachem and competitors), so this conclusion can be made.*

Table 11 - Instron Results for the Benchmarking Project, Gun Valves

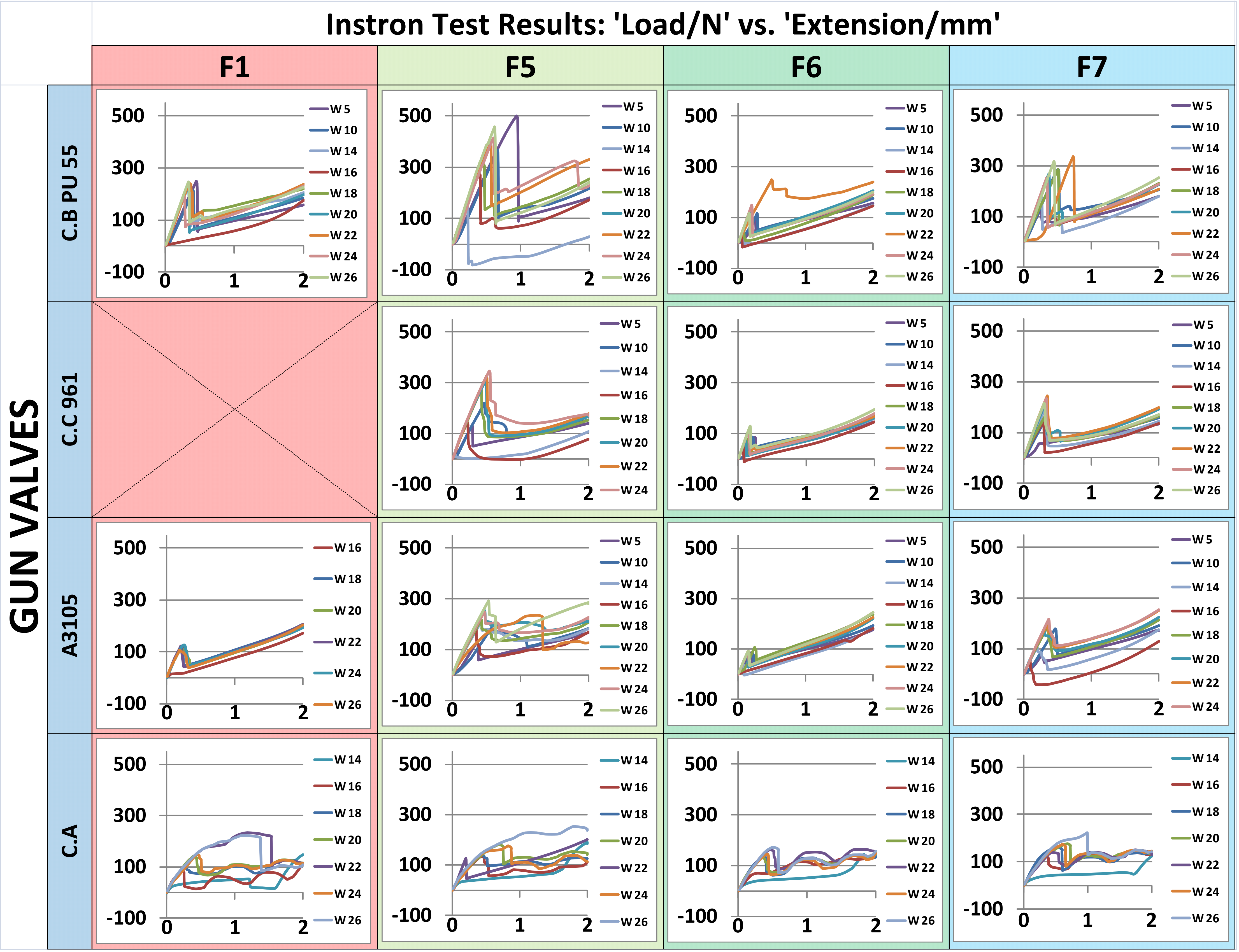
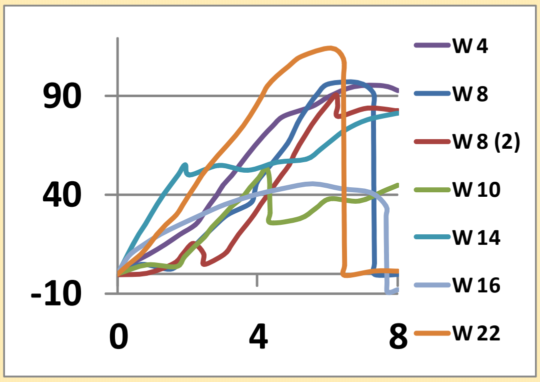
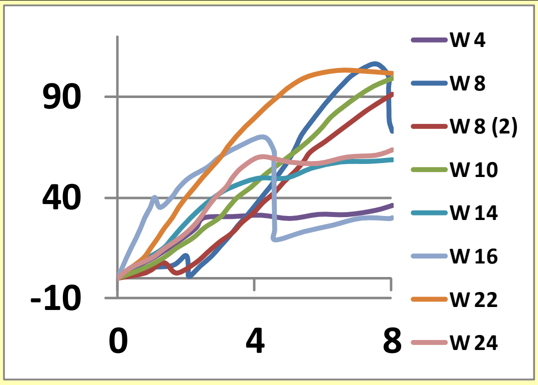
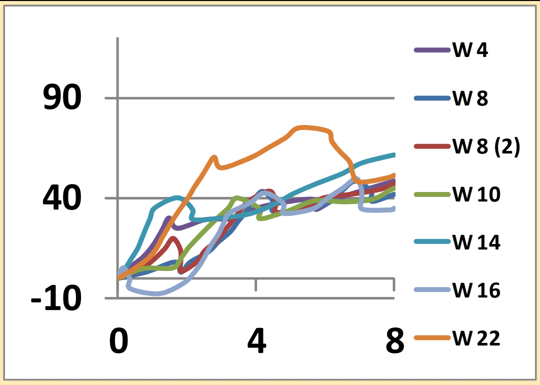
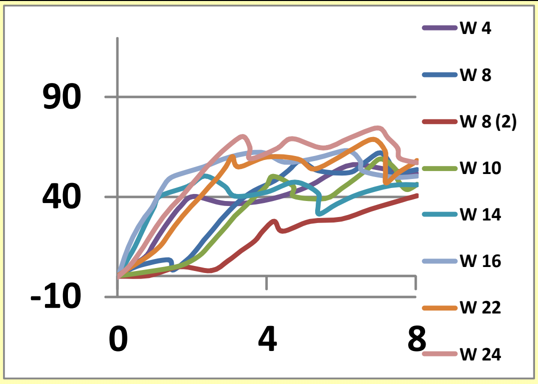
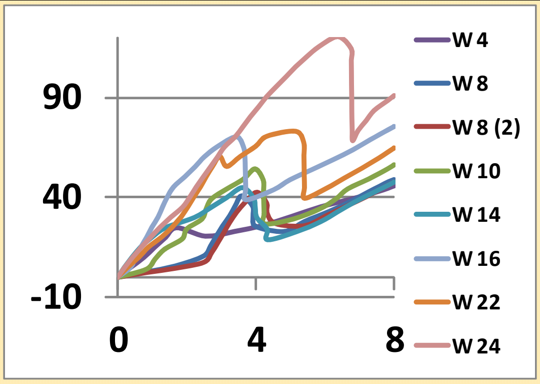
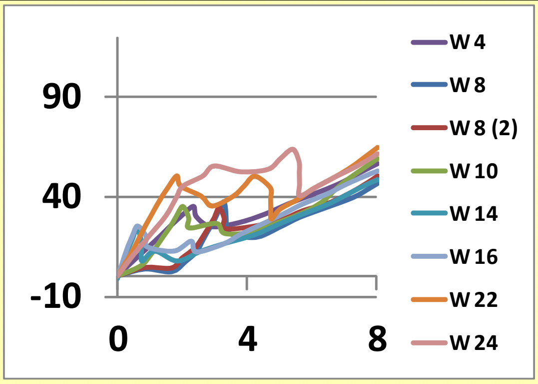


Table 12 - Instron Results for the Benchmarking Project, Tilt valves

<table>
<tr><td></td><td></td><td colspan="2">Instron Test Results: 'Load/N' vs. 'Extension/mm'</td></tr>
<tr><td></td><td></td><td>F2</td><td>F3</td></tr>
<tr><td rowspan="3">TILT VALVES</td><td>C.B PU 784</td><td></td><td></td></tr>
<tr><td>C.C 970</td><td></td><td></td></tr>
<tr><td>A4105</td><td></td><td></td></tr>
</table>

4.2.4 Valve Flow/Output

Output Conclusions:

The graphs with the results for this test can be found in Table 13 (p. 37). In all the graphs, a general decreasing tendency of the output with time is observed: Sticking/stucking behaviour increases with time, making difficult for the valve to open and therefore decreasing the flow. Also gas loss increase with time, so the can internal pressure decreases and cans perform lower outputs.

Foams 5 and 7 perform lower outputs than the rest of foams, almost not passing the acceptable minimum after week 14^{th}. This can be a result of one or both the following reasons:

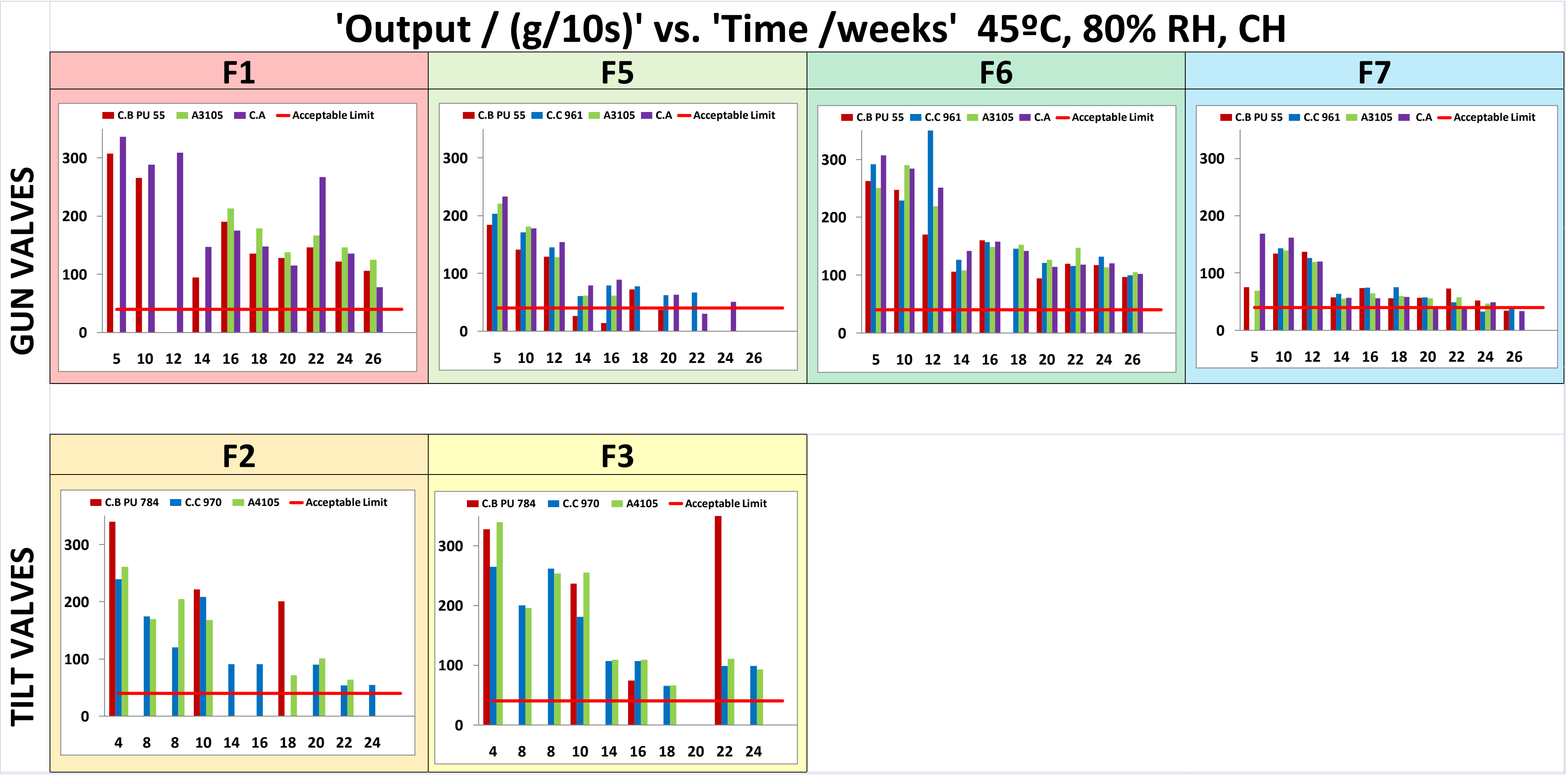
1) A high density of the pre-polymers involved, that can be explained by
    a. Too much catalyst (Catalysts increases the branches between the main reagents: polyol and MDI, leading to a higher density foam).
    b. Low amount of MDI.
    c. Low amount of TCCP (Flame retardant).
2) A low pressure inside the cans, due to a minor quantity of gas in its formulations.

Option 2 corresponds with the GL results commented before for the foam 7, but not for the foam 5; so the bad outputs results for the foam 5 must be explained just by the first option. It is not possible to know which one of the “a”, “b” or “c” secondary reasons is the correct one, because the client does not provide Altachem with information about their formulations.

Looking the results for the gun valves, is possible to conclude that all the valves tested have a similar behaviour, so Altachem valves can clearly compete with the rest in the output matter (the most important characteristic for a valve). Special cases are studied further in this report, alongside with picture examples (Annex 5, p. 64).

Tilt valves perform less regular flows comparing with the gun ones; some of these valves can be blocked or perform large outputs without a visible reason at any moment during the weeks in which the test is performed. All the valves that presented estrange behaviours without an evident cause were opened and divided in parts to check what their problem was. All pictures for the output special cases can be found in Annex 5 (p. 64), where is also detailed the valve model and the week when the problems occurred. Conclusive comments for the tilt valves are not possible to perform due to the irregular results, just remark that Altachem A4004 valve can also compete with the rest of valves tested, having good outputs results till the 22^{nd} week, as it happens for the Altachem A3105 gun valve.

Table 13 - Benchmarking Project Output Results



5 Conclusions

5.1 General Conclusions about Valves Study

In order to improve the quality of the final polyurethane can product, it is necessary to achieve efficient outputs, lower gas losses, lower absolute creeps and lower opening forces for the new valve generations, increasing the cans shelf-life.

The gas loss test covers the determination of the sealing performance and the gas diffusion of aerosol valves. The blowing agents of an aerosol cylinder can escape by some preferential regions of the grommet rubber; this fact implies an increment in the foam density and a decline of the cans internal pressure, causing lower output values. Standard valves loss around $8 - 10\ g/year$ of gas.

The creep checks the integrity of the valve due to the can's internal pressure and chemical interaction with the raw materials and blowing agents. The standard absolute creep values are around $0.03\ mm$ in 8 weeks at normal storing conditions.

Gas loss and creep variations at aging conditions are higher/more evident than at normal storing conditions. Gas loss is directly proportional to the absolute creep of the valves.

The Instron test covers the determination of the force needed to mechanically open the valves, defining the snappiness of the valve. The snappiness of the valve is a designation for the easy opening of the valve simultaneously with the return of the valve to its initial position. Tilt valves opening forces ($\approx 50\ N$) are much lower than gun ones ($\approx 200\ N$) because tilt valves have to "break" only part of the polyurea union between the stem and grommet to be activated, while gun valves need to "break" this union in all the stem-grommet contact surface.

Diffusion of water vapour through the valve grommet or existence of water already in the foam raw materials causes serious problems in the valves behaviour. The water reacts with free functional "$R - N = C = O$" groups (Isocyanate) of the foam, resulting in the formation of a harder compound (polyurea) that grows near the valve (sticked valve) and in the grommet's pores, increasing its hardness (stucked valve); this will difficult the opening of the valve. Sticking and stucking behaviours usually increase with similar rates; sticking behaviour is important for both gun and tilting valves, while stucking problems are more important for the tilt valves. Cans are recommended to be vertically stored, so the isocyanate free functional groups are not in contact with the bottom part of the valve to avoid the sticking/stucking behaviour.

Sticking/stucking behaviour and valves opening forces increment with time, especially when cans are stored horizontally at aging conditions. The increment of the sticking/stucking behaviour causes a decreasing general tendency for the valves flows (outputs).

The main incidents that can happen to the final product, their explanations and recommendations are shown in Table 15 (pgs. 42-43); this table can be used to make conclusions for any of the projects developed in Altachem R&D department.

5.2 Benchmarking Project Conclusions

After performing the benchmarking and quality control of the different valves, it is possible to conclude which valves have a better behaviour as well as some carachteristics of the foams involved.

5.2.1 Gas Loss Analysis

- Foams 2, 3, 5, 6 and 8 have larger blowing agent's quantities and therefore higher can internal pressure and gas looses ($6 - 12\ g/year$ at normal storing conditions) than foams 1 and 7 (less than $6\ g/year$ at normal storing conditions).
- Making an average for all the foams involved, "Competitor A" valve is the one with lower gas looses (almost inexistent); followed by Altachem and "Competitor C" valves, which perform a similar behaviour ($6 - 10\ g/year$ at normal storing conditions). "Competitor B" valves perform slightly higher gas losses comparing with the rest of valves, reaching values of $12\ g/year$ at normal storing conditions for some of the foams involved.

5.2.2 Creep Analysis

- At normal storing conditions, the general creep results for the "Competitor C" and Altachem valves are similar (around $5\ mm$ after 8 weeks at normal storing conditions), suffering little variations depending on the type of foam.
- C.B PU 55 gun valve is more affected by the high temperature and humidity than the rest of the valves, so these valves perform slightly higher creep values at aging conditions. Any of the blowing agents used in the foams 1 and 8 has important repercussions in the stem and/or grommet materials of this valve, increasing its creep.
- C.B PU 784 tilt valve's materials show a low interaction with the blowing agents of the foam 3 (creep remains stable).

- The storing position of the cans affects to the C.C 970 valve. When cans are stored vertical, the C.C 970 valve creep increases, but when cans are stored horizontal the behavior is just the opposite.

5.2.3 Opening Forces and Output Analysis

- Foams 1 and 6 behave better (lower opening forces and higher output values) than foams 5 and 7 due to a lower MDI quantity in their formulations; foams 5 and 7 perform lower outputs as a result of a high density of the pre-polymers involved.
- Tilt valves perform less regular flows comparing with the gun ones, due to a larger quantity of “Incidents”[1].
- All the valves (excepting the C.A one) show sticking/stucking behaviour since the 4th week.
- C.B PU 55 valve requires a larger force to be opened than the rest of the valves, with maximums that reach $400 - 500\ N$ for the foam 5.

5.2.4 Valves analysis[2]

Taking into account all the characteristics of the valves, the three following statements can be assumed:

- C.A valve is clearly superior to the rest of gun valves due to its more expensive design and materials.
- Altachem valves can clearly compete with competitors B and C; performing good outputs results till the 26th week at aging conditions. The results for these three producers demonstrate similar designs and materials in Altachem and “competitor C” valves. “Competitor B” valves show a slightly low quality compared with the rest of valves.
- Altachem client will need to make a balance taking into account the expenses and the quality of the valves; the most important characteristic to take into account is the output[3].

Table 14 (p. 41) represents an evaluation for each valve in each aspect analysed[4], in a scale from 1-4 for the gun valves and 1-3 for tilting valves. Performing the sum of the notes

[1] *Main incidents for each valve and the recommendation for each type of incident are showed in Table 16 (p. 44).*
[2] *The technical data sheets and drawings for the Altachem valves analysed can be found in Annex 7 (p. 81).*
[3] *After checking the results, the company which ordered the benchmarking analysis ended being an Altachem client.*
[4] *For the GL and C aspects, an average has been performed for the both environments tested.*

multiplied for a symbolic importance percentage[1] of each aspect, and dividing each result by the highest value, a general note can be assigned to each valve. For the final decision, the same type of table can be done with two aspects: general behaviour and economic feature[2].

Table 14 – Behaviour Evaluation for the Benchmarking Project (scale from 1 to 4 for the gun valves and 1 to 3 for the tilting valves in each aspect and 1 to 10 for the global evaluation)[3]

	Aspect	Creep	Gas Loss	Opening Forces	Output	Global Evaluation
	Importance Percentage	$6.25\ \%$	$37.5\ \%$	$6.25\ \%$	$50\ \%$	$100\ \%$
Gun Valve Notes	**C.B PU 55**	1	1	1	2,5	**5,4**
	C.C 961	2	2,5	2,5	2,5	**7,6**
	A3105	3	2,5	2,5	2,5	**7,8**
	C.A	4	4	4	2,5	**10**
Tilt Valve Notes	**C.B PU 784**	3	1	1	2	**7,3**
	C.C 970	1	2,5	2,5	2	**9,7**
	A4105	2	2,5	2,5	2	**10**

After checking the table results, it is possible to observe that Altachem valves perform slightly better results than "Competitor C", followed by "Competitor B". "Competitor A" valve behaves better than the Altachem standard gun valve but is also much more expensive.

Observing the main incidents showed in Annex 5 (p. 64), it is possible to determinate some typical problems for each valve (the ones which repeated frequently) (Table 16, p. 44). The reasons to these problems and some recommendations can be checked using the table 15 (pgs. 42-43); this way is possible to improve the new valve generations, taking into account these clews.

Further studies involving additional types of valves and foams and including quality/expenses comparisons can be performed, in order to improve the benchmarking range.

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[1] *The output represents the* $50\ \%$ *of the percentage because of being the most important characteristic for an aerosol valve, followed by the gas loss (*$37.5\ \%$*) because this problem cause a worsening of the foam quality; opening forces and creep are less important characteristics comparing with the output and gas loss (*$6.25\ \%$*).*

[2] *This table is not performed because there is no information provided by the client about the economic aspect.*

[3] *The following calculations show an example of how the evaluation was performed (a value of 10 was assigned to the better valve of each type, and rest of valves were evaluated keeping the relationship existent):*

$$\boldsymbol{Global\ Note}_{C.A\ Valve} = \frac{4 \cdot 6.25 + 4 \cdot 37.5 + 4 \cdot 6.25 + 2.5 \cdot 50}{4 \cdot 6.25 + 4 \cdot 37.5 + 4 \cdot 6.25 + 2.5 \cdot 50} \cdot 10 = \mathbf{10}$$

$$\boldsymbol{Global\ Note}_{A3105\ Valve} = \frac{3 \cdot 6.25 + 2.5 \cdot 37{,}5 + 2.5 \cdot 6.25 + 2.5 \cdot 50}{4 \cdot 6.25 + 4 \cdot 37.5 + 4 \cdot 6.25 + 2.5 \cdot 50} \cdot 10 = \mathbf{7.8}$$

Etc…

Table 15, a - Main Incidents occurred during the valve's Testing

<table>
<tr><th>Incident</th><th>Picture detail</th><th>Possible reasons</th><th>Recommendations</th></tr>
<tr><td>Valve does not close after the Instron test</td><td rowspan="3">
</td><td rowspan="3">Stem does not return to its initial position once the valve is open because:
The grommet is damaged due to the polyurea formation inside its pores, or
Some hard fragments of the polyurea "crunch" stay in the space left between the grommet and the stem when the valve is activated.</td><td rowspan="3">Improve grommet material trying to decrease its permeability without decreasing its flexibility, this way polyurea formation will decrease.</td></tr>
<tr><td>Valve does not close after testing output</td></tr>
<tr><td>Valve does not close after mounting the adaptor</td></tr>
<tr><td>Foam releasing between the grommet and the cup after the Instron test</td><td rowspan="3"></td><td rowspan="3">There is some space left between grommet and cup because of:
- Bad assembling between grommet and cup, or
- Dilatation of stem and grommet.</td><td rowspan="3">When mounting the valves, take care about assembling properly the cup.
Improve grommet and stem materials adding reinforcing particles to decrease dilatation.</td></tr>
<tr><td>Foam releasing between the grommet and the cup after testing output</td></tr>
<tr><td>Foam released between the grommet and the cup while storing</td></tr>
<tr><td>Foam releasing between the stem and the grommet after testing output</td><td rowspan="2"></td><td rowspan="2">There is some space left between stem and grommet because of:
- Bad assembling between stem and grommet, or
- Stem positive creeping</td><td rowspan="2">When mounting the valves, take care about assembling properly the stem and grommet.
Improve stem materials adding reinforcing particles to decrease its creeping.</td></tr>
<tr><td>Foam releasing between the stem and the grommet after the Instron test</td></tr>
</table>

Table 15, b - Main Incidents occurred during the valve's Testing

Incident	Picture detail	Possible reasons	Recommendations
Stem broken during the Instron test (tilt valves)		Stucked grommet that not allows the stem movement. Stem damaged material because of high temperature and humidity.	Improve grommet materials to decrease stucking behaviour. Improve stem materials adding reinforcing particles to increase its resistance.
Stem broken during the output test (tilt valves)			
Aged foam (high density = low output result), bad shake ability		Bad valve sealing, which allows humidity to enter inside the can. H_2O molecules react with the free MDI to form polyurea increasing the foam density.	Improve the valve sealing by modifying materials and designs.
Foam in bad state		Bad formulation.	Take care when formulating the foam, being sure the components amounts are the correct ones.
Output result under the acceptable minimum (valve is taken as blocked)	No picture needed for this incident	Aged foam. Polyurea formation between stem and grommet impeding the valve to open properly.	Improve the valve sealing by modifying materials and designs so humidity does not get inside the can and polyurea formation decreases.
Output result close to the acceptable minimum	No picture needed for this incident		

Table 16 - Benchmarking Project Main Incidents and Recommendations

	Valve name	Main incidents	Recommendations
GUN	C.B PU 55	Valve does not close after testing output	Improve grommet material trying to decrease its permeability without decreasing its flexibility, this way polyurea formation will decrease.
		Foam releasing between the grommet and the cup after testing output	When mounting the valves, take care about assembling properly the cup. Improve grommet and stem materials adding reinforcing particles to decrease dilatation.
		Aged foam (high density = low output result), bad shake ability	Improve the valve sealing by modifying materials and designs.
	C.C 961	Aged foam (high density = low output result), bad shake ability	Improve the valve sealing by modifying materials and designs.
	A3105	Foam releasing between the grommet and the cup after testing output	When mounting the valves, take care about assembling properly the cup. Improve grommet and stem materials adding reinforcing particles to decrease dilatation.
	C.A	Aged foam (high density = low output result), bad shake ability	Improve the valve sealing by modifying materials and designs.
TILT	C.B PU 784	Stem broken during the Instron or the output test	Improve grommet materials to decrease stucking behaviour. Improve stem materials adding reinforcing particles to increase its resistance.
	C.C 970	Valve does not close once is activated	Improve grommet material trying to decrease its permeability without decreasing its flexibility, this way polyurea formation will decrease.
	A4105	Valve does not close once is activated	

6 Evaluation of the Work

6.1 Objectives Accomplished

As it was explained in the thesis introduction, there were two main objectives to accomplish after this six months internship:

1) To perform a benchmarking study of some of the valves available in the market, in order to demonstrate a possible new customer that Altachem valves are a competitive solution for their necessities.
2) To achieve competences in the aerosol valves for polyurethane foams development area.

The first objective has been totally accomplished, and the customer ended being an Altachem client. The second objective has been also performed, but a further investigation about the foams behaviour and materials properties can be done in order to achieve a better understanding of the final product problems.

6.2 Other Projects Performed

Apart from the benchmarking project performed for this thesis, I had the opportunity to participate in many other projects[1]:

- **A1000 Project -** Descriptive study focused in a new type of valve for Altachem.
- **A4005 Project** – Cross test between A4005 series valves using the two main Altachem formulations.
- **Analysis of recent competitor valves (2009)** – Large benchmarking of all the valves available on the market during the year 2009, using standard Altachem formulations.
- **Cross test HDPEGF + different grommet "Competitor C" vs. Altachem -** Large project involving different aging conditions and the two standard formulations that cross the stems series reinforced with "Reinforcing Material" with different types of grommets.
- **Developing an ABS valve with high performance** – GL/C, SS and DOT test for two new stems developed by Altachem.
- **Development of A2(1)005** – Analysis of 4 new types of tilt stems from one of Altachem suppliers.

[1] *The description of the entire different test referred in these projects can be found between Chapter 3 (p. 13) and Annex 3 (p. 57).*

- **Development of a better dosable and stronger tilting valve** – Descriptive study focused in a new stem for one of Altachem clients[1].
- **Dow Project** – Cross test between different valves and foams.
- **Evaluation of thinner cups 0.35mm** – Comparison analysis for thinner and therefore cheaper cups.
- **Reproducibility Sticking & Stucking Test** – Viability study focused in a new type of SS Test with harder aging conditions.
- **Research for a cheaper alternative for the neoprene grommet** – Comparison between different grommets supplied to Altachem.
- **Research for HDPE with long GF** – Large project involving different aging conditions and the two standard formulations, focused on the stems series reinforced with "Reinforcing Material"; GL/C, SS, DOT and Bending Force of the Stem tests performed.
- **"Supplier A" vs. "Supplier B" Project** – Swelling and SS tests comparing the two main suppliers from Altachem[2].
- **"Supplier C" Cross test A3004 A3105 A4004 A4105** – Cross test between the first and second Altachem valve generations (tilt and gun valve) using "Supplier C" grommets.
- **Testing ABS grommets "Supplier D" vs. "Supplier E"** – Study including GL/C, SS, Cycling and Radial Tear tests to compare two Altachem suppliers.

[1] *A discussion for this Project can be found in Annex 6 (p. 61).*
[2] *A discussion for this Project can be found in Annex 6 (p. 77).*

6.3 Limitations and Future Work

The benchmarking study realized could have been more complete if more types of valves/foams were tested; also a deeper analysis of the materials involved would have helped to understand the valves behavior (in particular a Swelling Test involving stems, grommets and the raw materials of the foams used[1]). A description of the formulations used and information about the client production could have helped to perform a better comparison between the foams and an economic balance, but the client keeps these data as confidential.

To improve the Benchmarking study, it is possible to calculate mathematical correlations between the variables analyzed, for each valve and foam, in particular:

- *GL & Time*
- *GL & C*
- *GL & OP*
- *GL & Maximum Load*[2]
- *C & Time*
- *C & OP*
- *C & Maximum Load*[1]
- *C & Peak Point Extension*[2]
- *Maximum Load*[1] *& Time*
- *Maximum Load*[1] *& Peak Point Extension*[2]
- *Peak Point Extension*[2] *& Time*
- *Peak Point Extension*[3] *& GL*
- *OP & Time*
- *OP & Maximum Load*[1]
- *OP & Peak Point Extension*[2]

To perform all these correlations, the method would represent the graphs adding a "trend line" which would include an equation relating the two variables and the error involved in the equation estimation[4]. This method will result in a 6 independent equations mathematical system with 6 variables, useful to calculate fast and easily the estimated value of one of the variables and its error, once some of the other variables are known.

In order to perform clearer general conclusions about how each foam affect the valves, without taking into account the valve model, graphs with the averages of the different valves for each variable can be done in a further investigation. Also, it would be possible to make graphs with the averages of the different foams for each variable, so clearer general conclusions for the valves can be made without taking into account the foam formulation[5].

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[1] *This test is described in Annex 3 (p. 57).*

[2] *This maximum load refers to the maximum load performed by the Instron machine to open the valves (See Figure 10, p. 19).*

[3] *This peak point extension refers to the corresponding extension for the maximum load performed by the Instron machine to open the valves (See Figure 10, p. 19).*

[4] *This can be done using any of the software available in the market, such as Microsoft Office Excel®.*

[5] *The performance of these two methods will carry an error so the conclusions will have to be made taken into account some tolerance.*

6.4 Final Assessment

A thesis is an academic work which is intended to evaluate the author. For me, this thesis was much more than that. It made it possible for me to discover the world of chemical companies and increase my knowledge in the polyurethane foams and aerosol valves scientific field. Moreover, it gave me the opportunity to meet interesting people with related interests and to live in a different and beautiful country.

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Annex 1 Brief Definitions of Terms

- *Acetone* — Acetone is the organic compound with the formula "$OC-(CH_3)_2$". This colorless, mobile, flammable liquid is the simplest example of the ketones. Owing to the fact that acetone is miscible with water; it serves as an important solvent in its own right, typically as the solvent of choice for cleaning purposes in the laboratory.

- *Additives* — Something that is added, as one substance to another, to alter or improve the general quality or to counteract undesirable properties.

- *Blowing agents* — Blowing agent is a substance which is capable of producing a cellular structure in a variety of materials that undergo hardening or phase transition (such as polymers, plastics and metals). They are applied when the blown material is in liquid stage.

- *Butane* — Butane, also called n-butane, is the unbranched alkane with four carbon atoms, $CH_3-CH_2-CH_2-CH_3$. Butane is also used as a collective term for n-butane together with its only other isomer, isobutene (also called methyl propane), $CH-(CH_3)_3$. Butanes are highly flammable, colorless, odorless, easily liquefied gases.

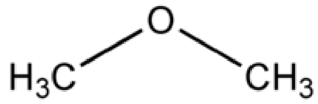
- *Catalysts* — A substance that causes or accelerates a chemical reaction without itself being affected.

- *Copolymer* — A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used.

- *Copolymerization* — Copolymerization refers to methods used to chemically synthesize a copolymer.

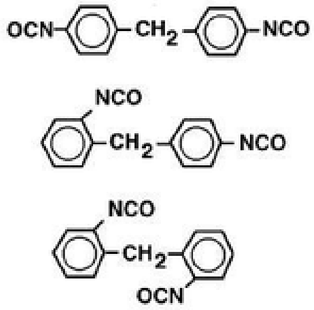
- *Diisocyanate* — An isocyanate that has two isocyanate groups is known as a diisocyanate. Diisocyanates are manufactured for reaction with polyols in the production of polyurethanes.

- *Dimethyl ether (DME)* — Dimethyl ether (DME) is the organic compound with the formula $CH_3 - O - CH_3$. It is the simplest ether, a colorless gas that is a useful precursor to other organic compounds and an aerosol propellant.

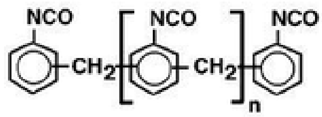


- *Diol* — Any of a group of alcohols containing two hydroxyl groups.

- *Diphenylmethane diisocyanate (MDI)* — Diphenylmethane diisocyanate (MDI) has three isomers: 4,4'-MDI, 2,4'-MDI, and 2,2'-MDI; and is also polymerized to provide oligomers of functionality three and higher.



Pure MDI's



Polymeric MDI's

- *Ethylene oxide* — Ethylene oxide, also called oxirane, is the organic compound with the formula $C_2 - H_4O$. This colorless flammable gas with a faintly sweet odor is the simplest epoxide, a three-membered ring consisting of two carbons and one oxygen atom.

- *Freon* — Freon is DuPont's trade name for chlorofluorocarbon and hydro chlorofluorocarbons.

- *Functionalities* — In organic chemistry, functional groups are specific groups of atoms within molecules that are responsible for the characteristic chemical reactions of those molecules. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule. However, its relative reactivity can be modified by nearby functional groups.

- *Glycol* — A diol or glycol is a chemical compound containing two hydroxyl groups ($-OH$ groups)

- *Grommet* — An insulated washer of rubber or plastic, inserted in a hole in a metal part to prevent grounding of a wire passing through the hole.

- *Hydroxyl groups* — The univalent group $-OH$, as in inorganic compounds, such as sodium hydroxide, NaOH, or as in organic compounds, such as ethyl alcohol, C_2H_6O. Also called hydroxyl radical.

- *Instron* — Instron (an ITW company) is a manufacturer of test equipment designed to evaluate the mechanical properties of materials and components.

- *Liquefied Petroleum Gas (LPG)* — Also called GPL, LP Gas, or autogas, LPG is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles, and increasingly replacing chlorofluorocarbons as an aerosol propellant and a refrigerant to reduce damage to the ozone layer, inferring that it is flammable.

- *Neoprene®* — Neoprene® is an oil-resistant synthetic rubber: used chiefly in paints, putties, linings for tanks and chemical apparatus, and in crepe soles for shoes.

- *Polyaddition* — Chain growth polymerization is a polymerization technique where unsaturated monomer molecules add on to a growing polymer chain one at a time. It can be represented with the chemical equation:

$$nM(monomer) \rightarrow (-M-)_n(polymer)$$

Where n is the degree of polymerization.

- *Polyhydric alcohols* — A sugar alcohol (also known as a polyol, polyhydric alcohol, or polyalcohol) is a hydrogenated form of carbohydrate, whose carbonyl group has been reduced to a primary or secondary hydroxyl group (hence the alcohol). Sugar alcohols have the general formula $H(HCHO)_n + 1H$.

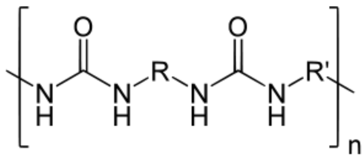
- *Polymer* — A polymer is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. While polymer in popular usage suggests plastic, the term actually refers to a large class of natural and synthetic materials with a variety of properties.

- *Polymerization* — Combination of many like or unlike molecules to form a more complex product of higher molecular weight.

- *Polyol* — An alcohol containing three or more hydroxyl groups; a polyhydric alcohol, also called polyalcohol. Molecular weights ranging from $200 - 8000$ and functionalities ranging from 2 and 8.

- *Polypropylene glycol* — Polypropylene glycol or polypropylene oxide is the polymer of propylene glycol. Chemically it is a polyether. The term polypropylene glycol, or PPG, is reserved for low to medium range molar mass polymer when the nature of the end-group, which is usually a hydroxyl group, still matters.

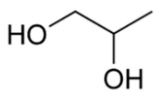
- *Polyurea* — Polyurea is a type of elastomer that is derived from the reaction product of an isocyanate component and a synthetic resin blend component, through step-growth polymerization.



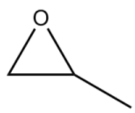
- *Polyurethane* — A thermoplastic polymer containing the group $NH - COO$: used for padding and insulation in furniture, clothing, and packaging, and in the manufacture of resins for adhesives, elastomers, and fillers.

- *Propylene* — Propene, also known as propylene, is an unsaturated organic compound having the chemical formula $C_3\,H_6$. It has one double bond, and is the second simplest member of the alkene class of hydrocarbons.

- *Propylene glycol* — Propylene glycol, known also by the systematic name propane-1,2-diol, is an organic compound (a diol alcohol), with a faintly sweet taste, and is a colorless, nearly odorless, clear, viscous liquid that is hygroscopic and miscible with water, acetone, and chloroform.



- *Propylene oxide* — Propylene oxide is an organic compound with the molecular formula CH_3CHCH_2O. This colorless volatile liquid is produced on a large scale industrially, its major application being its use for the production of polyether polyols for use in making polyurethane plastics.



- *Raw materials* Material before being processed or manufactured into a final form.
- *Relative humidity* Relative humidity is a term used to describe the amount of water vapor that exists in a gaseous mixture of air and water vapor. It is very nearly a property of the water vapor alone, that is, it very nearly does not depend on what other gases (nitrogen, oxygen, etc.) are present and in what amounts.
- *Sticked* Referring to an aerosol can valve: A valve is “sticked” when existing formation of polyurea between stem and grommet. This polyurea acts “as a glue”, making more difficult to open the valve.
- *Stucked* Referring to an aerosol can valve: A valve is “stucked” when its grommet gets hard because of formation of polyurea inside the grommet material pores, making more difficult to open the valve. This phenomenon is especially important in “tilting valves”.
- *Surfactants* Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower interfacial tension between two liquids.
- *Thermoplastic elastomers (TPE)* Thermoplastic elastomers (TPE), sometimes referred to as thermoplastic rubbers, are a class of copolymers or a physical mix of polymers (usually a plastic and a rubber) which consist of materials with both thermoplastic and elastomeric properties.
- *Urea* Urea or carbamide is an organic compound with the chemical formula $(NH_2)_2CO$. The molecule has two amine ($-NH_2$) residues joined by a carbonyl ($-CO-$) functional group.
- *Urethane* Any derivative of carbamic acid having the formula CH_2NO_2R.

Annex 2 Description of the Coding of Altachem Valves in Development and Production

The names that Altachem uses for the valves in development consist of:

- 1-3 letters followed by 4 digits:
  - first 2 digits indicating the design of the valve;
  - second 2 digits indicating the main difference in raw material (RM) used for the stem;
- Then, 2 digits indicating differences in color, rubber hardness, minor design changes, etc…

The definition of the letters and numbers is described at the Tables 17-19:

Table 17 - First letters code description[1]

First Letter	Description
A	Altachem Valve
ABS	Altachem B.S. Valve[2]
EXP	Experimental Product Code

Table 18 - Design of stem code description

First 2 digits - Design of stem	Description
10 - 19	“Competitor A” Copy[3]
20 - 29	Adaptor Valve - thin stem
30 - 39	Gun Valve
40 - 49	Adaptor Valve - thick stem
50 - 59	A5000 - Non-sticking valve
60 - 69	A6000 - A&S valve[4]
70 - 79	360° Valve
80 - 89	AF Valve[4]
90 - 99	…

[1] *Once a valve is approved, the EXP number will be converted into an A or ABS number.*

[2] *Anti-Block System valve.*

[3] *Competitor names are omitted due to Altachem confidentiality norms.*

[4] *Altachem and supplier cooperation valve (Supplier name omitted due to Altachem Confidentiality Norms).*

Table 19 - Raw material of stem code description

Second 2 digits: ***Raw Material of stem***	***Description***
00	Polypropylene (PP)
04	Polypropylene + "Reinforcing Material"[1] (PPGF)
05	Polyethylene + "Reinforcing Material" (PEGF)
06	Polyethylene + long quantity of "Reinforcing Material" (PELGF)
07	Mixture of 20% "Reinforcing Material" + 40%PP + 60%PE (Supplier A)
08	Mixture of 20% "Reinforcing Material" + 40%PP + 60%PE (Supplier B)

[1] *Reinforcing Material name omitted due to Altachem Confidentiality Norms.*

Annex 3 Chemical and Mechanical Tests

3.1 Swelling Test – Materials Selection

Altachem performs this test to study the resistance behaviour or swelling of the new materials in diverse environments the valve will be in contact with during its shelf-life.

In order to study the swelling effect and changes in the valve materials properties, volume and weight variations of the stems and grommets in contact with different substances are calculated.

The bottom part of a general polyurethane aerosol valve will be in contact with the blowing agents of the foam (gases like Freon* 134a, Freon 22 (F22), DME (Dimethyl Ether) and LPG (Liquefied Petroleum Gases)). The top part of the valve can be also in contact with acetone* because acetone is the solvent recommended for the clients to clean the valve. Cans are recommended to being vertically stored, so the polyol and the MDI are not in contact with the bottom part of the valve, but Altachem also perform swelling test with these substances because, if cans are stored by mistake horizontally or on head, a direct contact will exist. Therefore, is important to study the performance of the stem and grommet with these chemicals, to guarantee that valve materials will not be destroyed or modified during its use.

The initial weight and dimension of a test sample are measured. Afterwards, each sample is immersed in the chosen substances for seven days. At the end of this period, the test piece is taken out and the adhered liquid is quickly removed blotting with laboratory paper. Afterwards, the swollen weight and dimensions are measured again. With these results the chemical compatibility is evaluated. After three days, the samples are dried in a $23\ ^{\circ}C$ room with 50% Relative Humidity (RH), and the desorbed weight is measured, as well as the dimensions. The results obtained illustrate the chemical resistance of the new materials, when in contact with these chemicals.

The weight measurements are performed with an $0.001\ g$ absolute error balance; and the dimensions are measured with a thickness gauge or an optical microscope (Nikon), depending on the piece model.

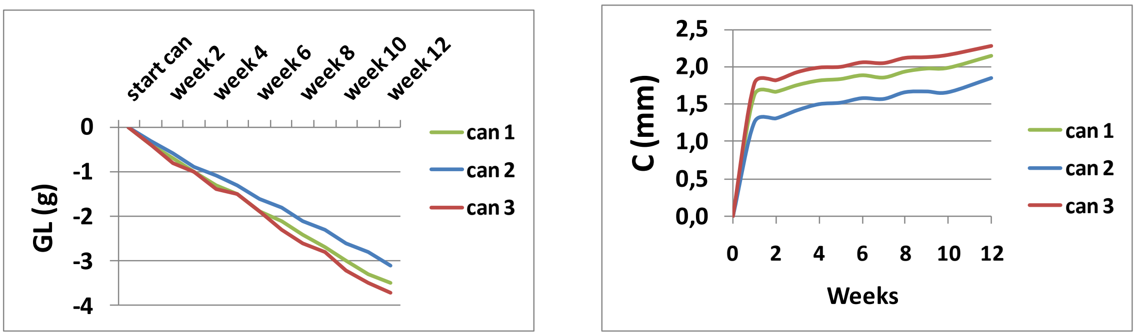
A discussion of this test for a real project can be found in Annex 6 (p. 77), alongside with the graphic results.

* *A brief definition of this term is performed in Annex 1, p. 50.*

3.2 DOT Test

DOT means "Department Of Transportation", and is a test that is performed to guarantee that the can will not explode during transportation. Passing this test is necessary to export this type of products to the United States.

So, 3 cans of each valve are filled with Freon 22 and Butane[1] to promote the pressure required in the can ($14\ bar$). The cans are stored vertically in an oven at $55\ ^{\circ}\mathrm{C}$ during 12 weeks. The gas loss and the creep are measured weekly (Figure 13) and the valve is checked visually to see if it is broken or not.



(a) (b)

Figure 13 – DOT Test Example Results: a) Gas Loss; b) Creep

3.3 Cycling Test

The cycling test is a way to simulate the injection of gas in the can through the valve. It covers the determination of the force needed to mechanically open the valves, defining its snappiness (term described in Chapter 3.2, p. 17).

This method is used for gun and adapter aerosol valves. INSTRON and associated software MERLIN are used (Figure 14).

Figure 14 - Cycling test of a valve.

[1] *A brief definition of this term is performed in Annex 1, p. 50.*

In this test, extensions of $1\,mm$ and $2.8\,mm$ with a rate of $100\,mm \cdot min^{-1}$ are used. Each valve is submitted to 5 cycles of opening-closing. The results are presented by a graph of Load (N) vs. Extension (mm) (Figure 15).

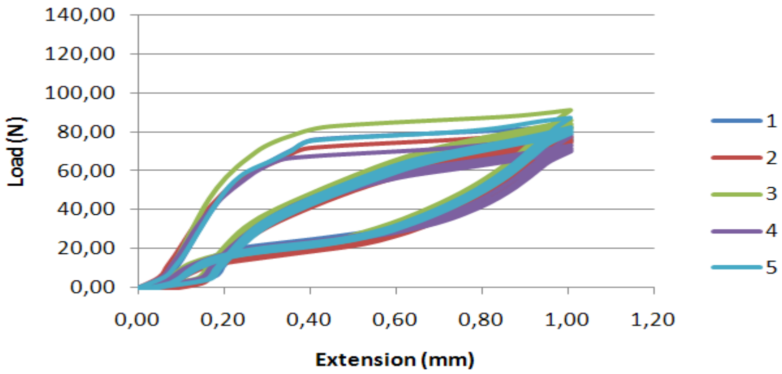


Figure 15 - Example of Cycling Test results.

3.4 Radial Tear Strength Test

This test method covers the determination of the radial tear strength of rubber grommets. The radial tear strength test is a way to simulate the conditions under which the grommet is assembled on a valve and the effect of the tilting movement for the tilt valves. Testing the radial tear strength is a way to determine the effects that a specified extension produces over the grommet and is essential to approve a new rubber material (Aster De Schrijver, 2001).

The test specimen support consists of two identical pieces, both composed by a cylindrical part which allows fitting to the INSTRON and a moving arm by which the grommet will be held (Figure 16).

Figure 16 - Radial tear strength tool performed with INSTRON equipment.

Fifty rubber grommets samples are tested in the INSTRON machine with a maximum extension of $15\,mm$ and a rate of $150\,mm \cdot min^{-1}$ for the movement of the adjusted pieces. The results are presented in a Load (N) vs. Extension (mm) graph. Is expectable that the number of teared is lower than 5%. This test should be performed on grommets that were not submitted to any kind of deformation or previous test (Aster De Schijver, 2001).

Below is represented the load applied and the representative picture illustrating the percentage of rubber failure during tearing (Figures 17 and 18).

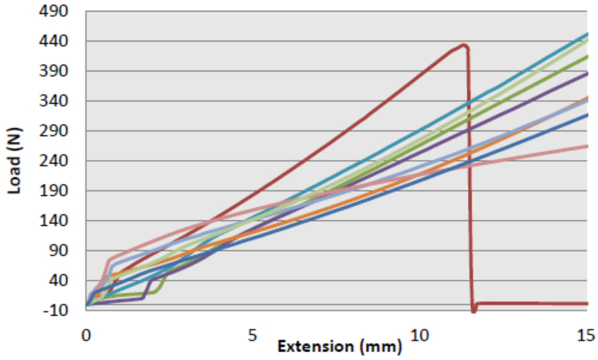


Figure 17 - Radial Tear Test showing the necessary load applied until $15\ mm$ of extension.

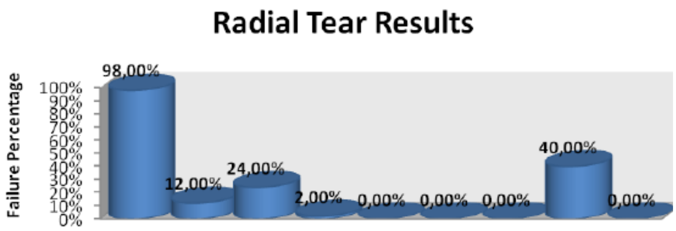


Figure 18 - Tearing results from all rubbers radial tear test for different grommets (model names omitted due to Altachem confidentiality norms).

3.5 Standard test method for measuring the bending force of the stem

The bending test is a way to determine the maximum bending or tilting load for a specified extension of a rigid plastic tilting valve stem. Testing the bending force of the stem is an indirect measurement of the accurate tilting of the valve.

Three stem samples are tested in the INSTRON machine with a maximum extension of $100\ mm$ and a rate of $100\ mm \cdot min^{-1}$ for the movement of the loading edge. The results are presented by a graph of load (N) versus extension (mm) and the maximum load value is recorded.

Instron and associated software Merlin are used to perform this test. The specimen support consists of a two parts apparatus:

- One cylindrical flat part which allows fitting to the INSTRON and a cubic part which supports the stem (Figure 19, a).

- The loading edge, which is the part used to apply force on the stem and must be located on the edge of the stem and parallel to the support edge (Figure 19, b).

(a) (b)

Figure 19 – a) Specimen support; b) loading edge used in the bending test.

This test shall be performed on stems that weren't submitted to any kind of deformation or previous test.

The test specimen must be placed in the support edges so that the direction of loading is perpendicular to the longitudinal axis of the specimen (Figure 20).

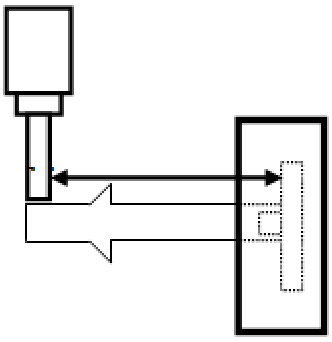


Figure 20 - Schematic representation of the stem in the support.

3.6 Test method to check the "Reinforcing Material" of the stems

To perform this test, the weight of 8 stem samples is measured before and after heating them until $450\ °C$ during $100\ min$.

Stems are usually made of PP (Polypropylene) material, sometimes reinforced with other types of materials to improve their characteristics (strength, etc…). All the PP material is vaporized during the heating. This way, it is possible to weight the ashes after the heating. This weight corresponds to the reinforcing material. The results of this test check if the reinforced material percentage (in weight) is correct, availing Altachem to accept or not the new stems from the suppliers.

(a) (b)

Figure 21 – a) Oven; b) scale used in "Reinforcing Material" Percentage Determination Test.

It is important not to stand too close to the muffle oven when opening after the test because the smoke of the burned ash residue is dangerous for the health.

The equation 4.1 explains the calculation of the reinforcing material percentage:

$$\%_{REINFORCING\ MATERIAL} = \frac{M_2 - M_3}{M_1} \cdot 100 \tag{4.1}$$

- $M_1\ (g)$: Crucible weight
- $M_2\ (g)$: Crucible + sample weight
- $M_3\ (g)$: Crucible + material not burned weight

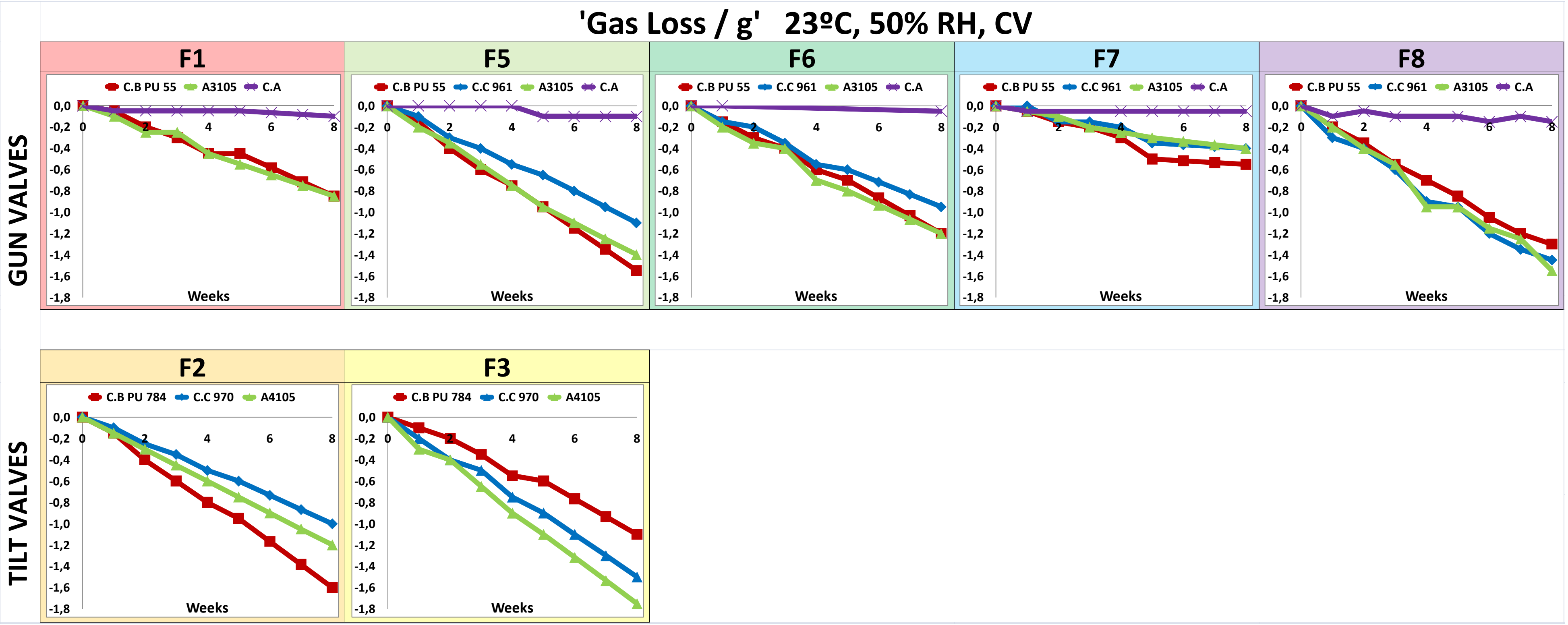
3.7 Vacuum Test

This test covers the evaluation of aerosol's valves sealing properties submitted to vacuum. 12 assembled valves are simultaneously vacuum tested ($\Delta P = -0.6\ bar$) to verify their sealing performance and to check if they show gas leakage. The global vacuum leak of this set of 12 valves should not exceed $13\ mbar$ in $1\ min$.

Figure 22 - Vacuum Test machine.

Annex 4 Benchmarking Project - GL/C Test at 23 °C, 50% RH, CV: Gas Loss vs. Time

Table 20 - Gas Loss Time Evolution for the GL/C Test



Annex 5 Benchmarking Project – Incidents Detailed Results

Table 21 – C.B PU 55 Gun Valve – Incidents Detailed Results

VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS				
C.B PU 55	F1	16	NO						
		20	NO						
	F5	14	NO	Valve does not close after testing output					
		16	NO	Aged foam (hight density = low output result), bad shake ability					
		18	NO	Foam releasing between the grommet and the cup after testing output					
		22	YES	Foam releasing between the grommet and the cup after testing output					
		24	YES	Foam releasing between the grommet and the cup after testing output					
				Aged foam (hight density = low output result), bad shake ability					
		26	YES	Foam releasing between the grommet and the cup after testing output					
				Aged foam (hight density = low output result), bad shake ability					
	F6	14	NO	Aged foam (hight density = low output result), bad shake ability					
		16	NO	Aged foam (hight density = low output result), bad shake ability					
		18	YES	Aged foam (hight density = low output result), bad shake ability					
		22	NO	Valve does not close after testing output					
		24	NO	Valve does not close after testing output					
	F7	14	NO	Valve does not close after testing output					
		18	NO						

Table 22 – C.C 961 Gun Valve – Incidents Detailed Results

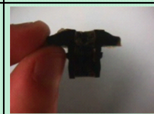
VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS				
C.C 961	F5	26	YES	Aged foam (hight density = low output result), bad shake ability					
	F6	5	NO	Valve does not close after testing output Foam in bad state					
		14	NO	Valve does not close after testing output Aged foam (hight density = low output result), bad shake ability					
		16	NO	Aged foam (hight density = low output result), bad shake ability					
		18	NO	Aged foam (hight density = low output result), bad shake ability					
		20	NO	Valve does not close after testing output					
	F7	5	NO	Valve does not close after the Instron test					

Table 23 – A3105 and C.A Gun Valves – Incidents Detailed Results

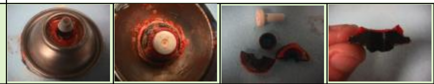
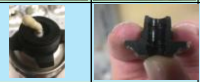
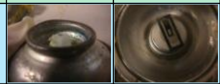
VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS
A3105	F5	18	NO	Foam releasing between the grommet and the cup after testing output	
		20	NO	Foam releasing between the grommet and the cup after testing output	
		22	YES	Foam releasing between the grommet and the cup after testing output	
		24	YES	Foam releasing between the grommet and the cup after testing output	
		26	YES	Foam releasing between the grommet and the cup after testing output	
	F6	10	NO	Valve does not close after testing output	
		14	NO	Aged foam (hight density = low output result), bad shake ability	
		16	NO	Aged foam (hight density = low output result), bad shake ability	
		18	NO	Aged foam (hight density = low output result), bad shake ability	
		20	NO	Valve does not close after testing output	
	F7	5	NO	Valve does not close after the Instron test	
C.A	F5	10	NO	Valve does not close after testing output	
		14	NO	Valve does not close after testing output	
		18	YES		
		22	NO	Output result under the acceptable minimum	
		26	YES	Aged foam (hight density = low output result), bad shake ability	
	F6	14	NO	Aged foam (hight density = low output result), bad shake ability	
		16	NO	Aged foam (hight density = low output result), bad shake ability	
	F7	16	NO		
		18	NO		
		20	NO	Output result close to the acceptable minimum	

Table 24 – C.B PU 784 Tilting Valve – Incidents Detailed Results

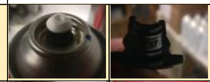
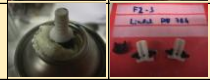
VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS
C.B PU 784	F2	6	YES	Stem broken during the Instron test	
		8	YES	Foam releasing between the grommet and the cup after testing output	
		12	YES	Gas releasing between the grommet and the cup after the Instron test Foam releasing between the grommet and the cup after testing output	
		14	YES	Stem broken during the Instron test	
		16	NO	Foam releasing between the grommet and the cup after testing output Valve does not close after testing output	
		18	YES	Stem broken during the Instron test	
		20	YES	Stem broken during the output test	
		22	YES	Stem broken during the output test Foam releasing between the grommet and the cup after testing output	
	F3	6	YES	Foam releasing between the grommet and the cup after testing output	
		8	YES		
		10	NO	Great force needed to open the valve	
		12	YES	Stem broken during the output test	
		18	YES	Foam releasing between the grommet and the cup after testing output	
		20	NO	Foam released between the grommet and the cup while storing	
		22	YES	Foam releasing between the grommet and the cup after testing output	

Table 25 – C.C 970 Tilting Valve – Incidents Detailed Results

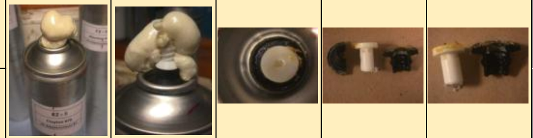
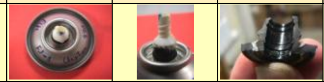
VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS
C.C 970	F2	8	NO	Foam releasing between the stem and the grommet after testing output	
		12	NO	Valve does not close after mounting the adaptor Valve does not close after testing output	
		16	YES	Foam released between the grommet and the cup while storing	
		18	NO	Valve does not close after the Instron test	
		20	NO	Valve does not close after the Instron test	
		22	NO	Valve does not close after the Instron test	
	F3	4	NO		
		6	NO	Valve does not close after testing output	
		10	NO	Foam releasing between the stem and the grommet after testing output	
		12	NO	Valve does not close after the Instron test	
		14	NO	Foam releasing between the stem and the grommet after testing output	
		16	NO	Foam releasing between the stem and the grommet after the Instron test Valve does not close after the Instron test	
		18	YES	Stem broken during the output test	
		20	NO	Valve does not close after the Instron test	
		22	NO	Valve does not close after the Instron test	

Table 26 – A4105 Tilting Valve – Incidents Detailed Results

VALVE	FOAM	WEEK	VALVE BLOCKED?	REMARKS	DETAILLED PHOTOS
A4105	F2	10	NO	Valve does not close after testing output	
		12	NO	Valve does not close after the Instron test	
		14	NO	Aged foam (hight density = low output result), bad shake ability Valve does not close after testing output	
		16	NO	Valve does not close after the Instron test	
		18	NO	Valve does not close after the Instron test	
		20	NO	Valve does not close after the Instron test	
		22	YES	Stem broken during the output test Foam releasing between the grommet and the cup after testing output	
	F3	6	NO	Valve does not close after testing output	
		8	NO	Valve does not close after testing output	
		10	NO	Valve does not close after testing output	
		12	NO	Foam releasing between the stem and the grommet after testing output Valve does not close after testing output	
		14	NO	Foam releasing between the stem and the grommet after testing output	
		16	NO	Valve does not close after the Instron test	
		18	NO	Valve does not close after the Instron test Stem broken during the output test	
		20	NO	Valve does not close after the Instron test	

Table 27 – Other Incidents occurred during the performance of the Benchmarking Project

 Example of valves arrived in bad state	 Example of foam released during the storage from a valve in bad state	 Example of oxide can due to high humidity and temperature
 Picture comparing the three tilting valves for the foam 2, week 20: The stem of the can on the left was broken due to the hardening of the grommet, while the two valves on the right did not close properly once they were activated.	 Picture comparing the three tilting valves for the foam 3, week 20: There is foam releasing between the stem and the grommet of the can on the left, while the two valves on the right did not close properly once they were activated.	 Picture showing an output of foam in bad state: outflow foam (low density).

Annex 6 Other Projects Discussed

6.1 Development of a stronger better dosable tilting valve - A2000 Green Stem

This project is performed to learn about the characteristics of a new Altachem type of tilting stem which will be used by one of our clients: the A2000 Green Stem. It is a descriptive project, without comparisons with any other kind of stem.

Samples of this stem where mounted with the standards grommets and cups from Altachem, and standard formulation 4230 was used to fill the cans. GL/C and SS tests were performed at $23\ °C, 50\%\ RH$ and $45\ °C, 80\%\ RH$.

6.1.1 Gas Loss and Creep Tests at $23\ °C, 50\%\ RH$ and $45\ °C, 80\%\ RH$, Cans Vertical

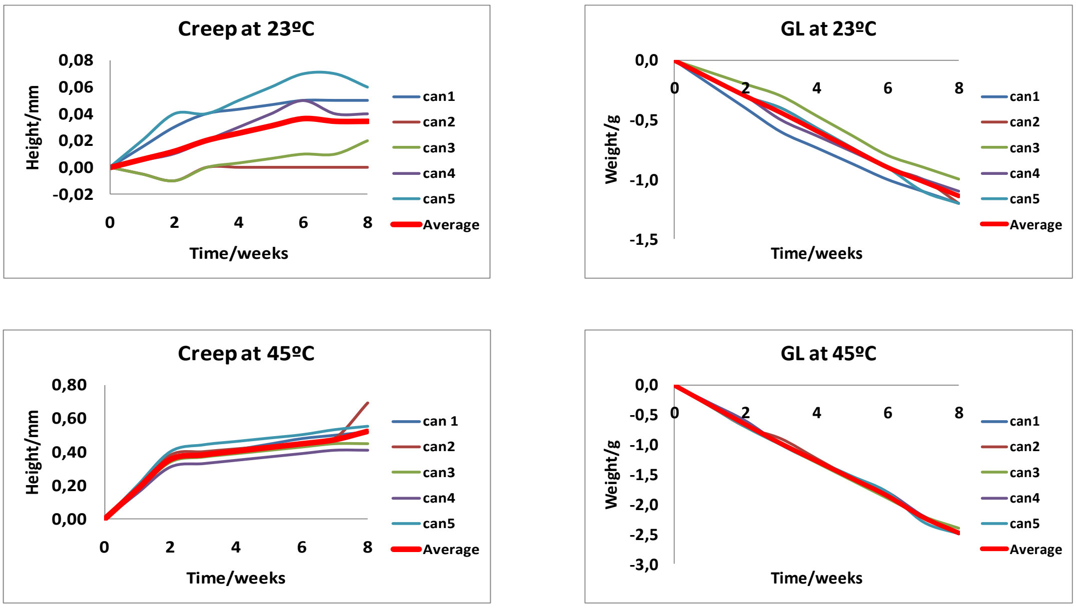


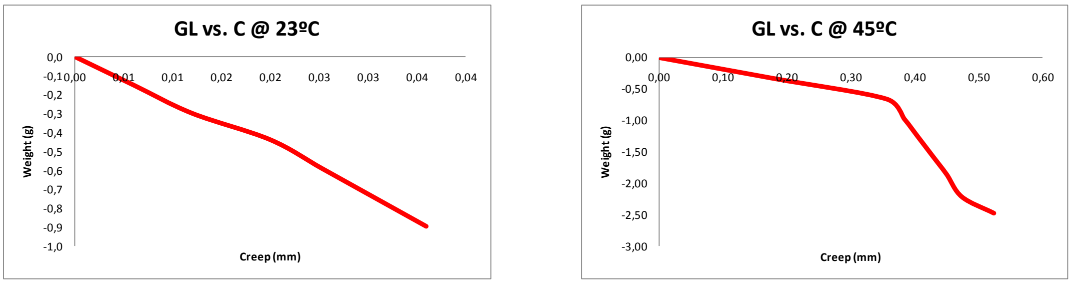
Figure 23 - GL/C Test Results for the A2004 Stem

It can be observed that the average of the A2000 stems reaches a maximum of $0.04\ mm$ creep at week six; after this stays stable. Cans loss around $1.1\ g$ of gas (blowing agents) after 8 weeks at $23\ °C, 50\%\ RH$.

The test at $45\ °C, 80\%\ RH$ provides information about what will happen under bad storing conditions. The average represents a creep rate of $0.2\ mm \cdot week^{-1}$ until the second week. After the second week, this rate decreases to $0.025\ mm \cdot week^{-1}$. Cans loss around $2.5\ g$ of gas in eight weeks at $45\ °C, 80\%\ RH$.

Figure 23 graphs show that the creep results average has a minor error at the $45\,°C, 80\%\,RH$ test, so this test is considered more reliable.

To end the GL/C Test analysis, is possible to try to make correlations between the averages of gas losses and creeps. The correlation equation is not needed by Altachem, so just the graphs are represented, to have a general idea of the relation between GL & C variables (Figure 24).



(a) (b)

Figure 24 - GL vs. C Graphs - a) $23\,°C, 50\%\,RH$; *b)* $45\,°C, 80\%\,RH$.

A proportional relation between the gas loss and the creep is observed as a general tendency.

As it is said before, GL results at $45\,°C, 80\%\,RH$ are more reliable than at $23\,°C, 50\%\,RH$ for this project, so the Figure 24 discussion will only be performed for the graph b): At $45\,°C, 80\%\,RH$, can's gas loss reaches $0.6\,g$ until the creep increases its valor to $0.38\,mm$. After this, gas loss increases until reaching a $2.5\,g$ value, corresponding to a $0.5\,mm$ creep.

6.1.2 SS Test at $45\,°C, 80\%$ RH, Cans Horizontal

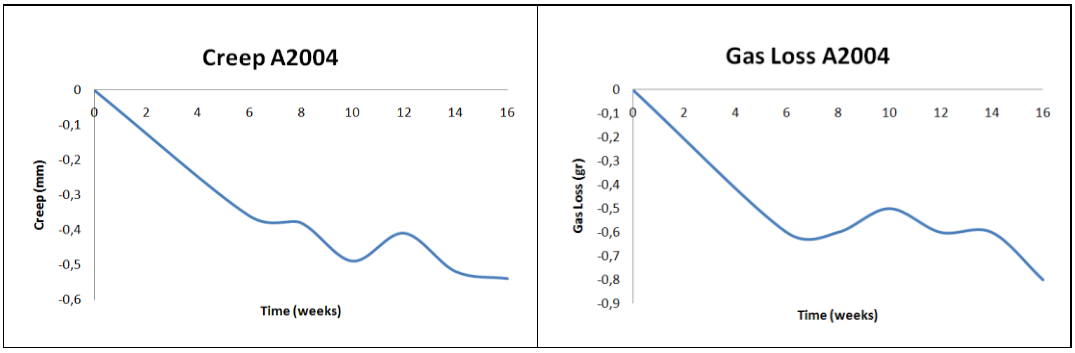


Figure 25 - SS Test for the A2004 stem, GL/C Results

It is proved that, for the SS tests purpose, one day at $45\,°C, 80\%\,RH$ equals a week at $23\,°C, 50\%\,RH$, so 16 weeks at $45\,°C, 80\%\,RH$ equals to two years at $23\,°C, 50\%\,RH$.

In this case, stems creep is decreasing with time, the opposite to the Gas Loss and Creep Test showed before. It is possible to conclude that the storing position of the cans affects to this stem. When cans are stored vertical (CV), the stems creep increases, but when cans are stored horizontal (CH) the behavior is just the opposite.

Valves creep behavior depends on the stress forces suffered by the stems and/or the chemicals in contact with the stem and grommet. For cans stored vertical (CV), the chemicals in contact with the bottom part of the valve are the blowing agents. For cans stored horizontal (CH) the bottom part of the stem and grommet is in contact not only with gases, but also with the polyol and the MDI (Methylene Diphenyl Diisocyanate). It is possible to explain why creep increases when cans are stored vertical but decreases when stored horizontal: As seen in previous experiences, the DME from the blowing agents is usually absorbed by stems material, increasing the size of the bottom part of the stem. If the grommet is not hardened due to polyurea formation, it allows the stem to go up because of the internal can pressure; but when the grommet is hardened (as happens when cans are stored horizontal), the stem goes down because the hardened grommet does not allow it to rise, decreasing the valves creep.

For further investigation, it would be desirable to perform a DOT Test to study the pressure impact over the stem. A Swelling Test would be also desirable, to learn how the chemicals interact with the stems material.

The gas loss also decreases when cans are stored horizontal, but in a lower rate. Usually storing cans vertical is recommended to the customers; but, taking just into account the gas loss results, maybe for this stems the recommendation could be to store them horizontally (usually storing cans horizontal would carry associated problems like sticking/stucking valves).

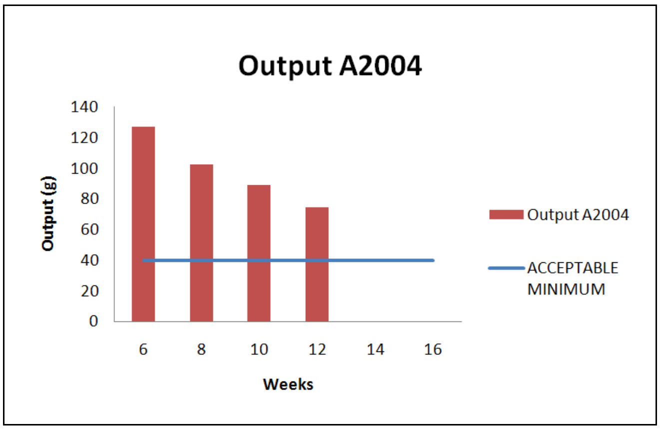


Figure 26 - SS Test for the A2004 stem, Output Results

The output for the A2004 stem decreases progressively from $120\ to\ 80\ g/10s$ from the 6th until the 12th week at $45\ °C, 80\%\ RH$. After this moment, equivalent to one year and a half at $23\ °C, 50\%\ RH$ approximately, valves are blocked and no output is performed. Because of this, the storage time recommended to Altachem client for this type of stem should not be more than one year and a half.

More details about the 12th week valve are showed at Figure 27. The valve did not close properly so gas and foam were releasing by the stem and between the stem and the grommet (Figure ‘27-a’ & ’27-b’). One possible reason can be the formation of polyurea between the stem and grommet (see sticked valve, showed in Figure ’27-c’ and “Instron Graph” (Figure 28, p. 75)). The grommet seems to be hardened at the bottom part, because of the polyurea formation at the interior of its pores (Figure ’27-f’).

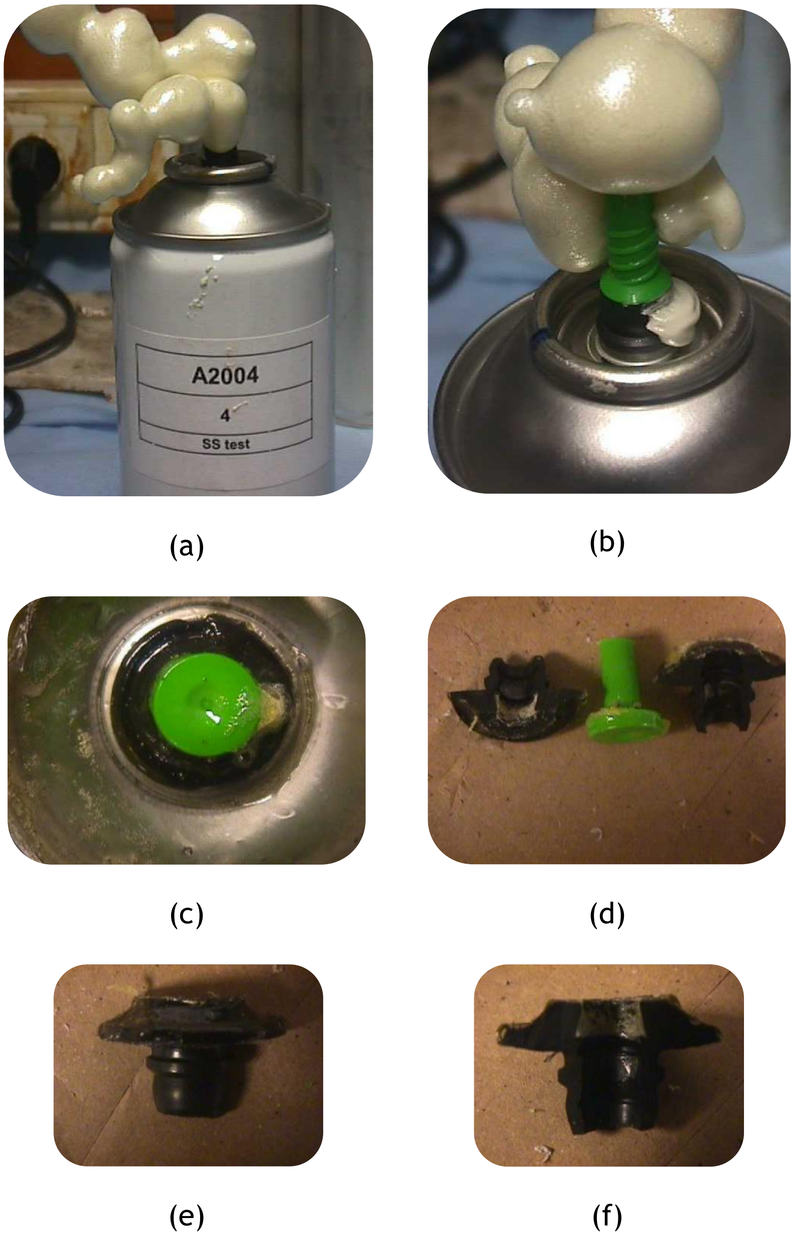


Figure 27 - a) & b) Foam releasing by stem and between stem and grommet; c) Polyurea formation; d) Polyurea formation, closer view of stem and grommet; e) & f) Polyurea formation, grommet’s closer view.

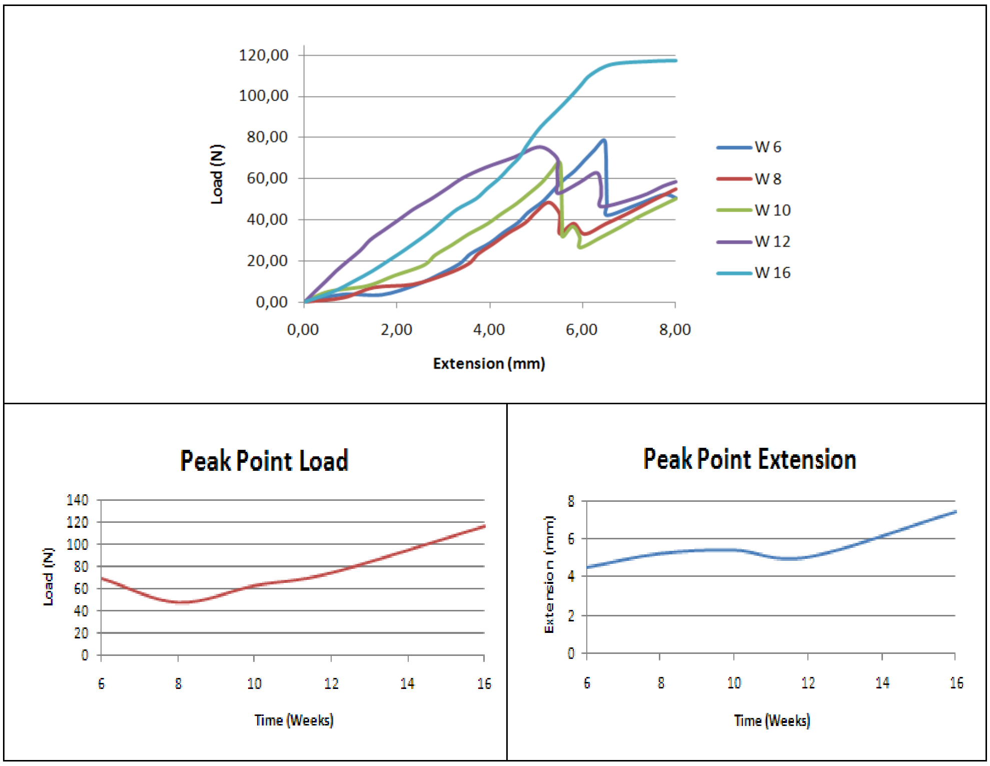


Figure 28 - Instron Graphs

The load necessary to push the stem an $8\,mm$ extension increases with time (Figure 28). The sticking behavior increases too, as is showed at the peak points around $6\,mm$ extension. After 12th week, the stems where broken during the test due to their bad state; only the stem of the 16th week resisted, but it was so sticked that it did not open (if a valve opens the gas releasing is audible), so the graph for this week only shows an increasing force without stucking behavior. This can did not had output because of being blocked even if the stem resisted the INSTRON test.

It is also observed that the load peak point which corresponds to the sticking behavior increases with time, as polyurea formation advances. The same happens for the extension peak point.

To end the SS Test analysis, is possible to try to make correlations between:

- GL & C
- GL & OP (Without useful correlation for this project after checking the graph)
- GL & Maximum Load (Without useful correlation for this project after checking the graph)

- GL & Peak Point Extension (Without useful correlation for this project after checking the graph)
- C & OP
- C & Maximum Load
- C & Peak Point Extension
- OP & Maximum Load
- OP & Peak Point Extension

Graphs have been done without involving creep because of the contradictory data showed before. It is observed that the OP decreases with the peak point load and extension increasing (Figure 29).

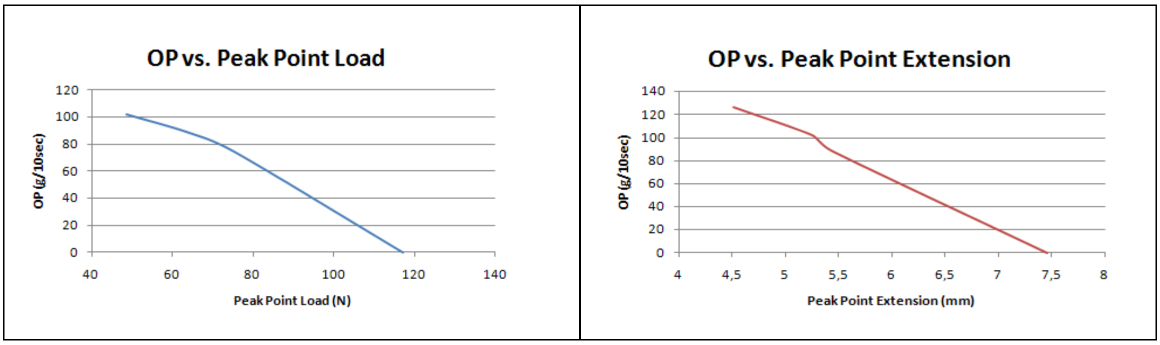


Figure 29 - Variables study for the A2004 SS Test

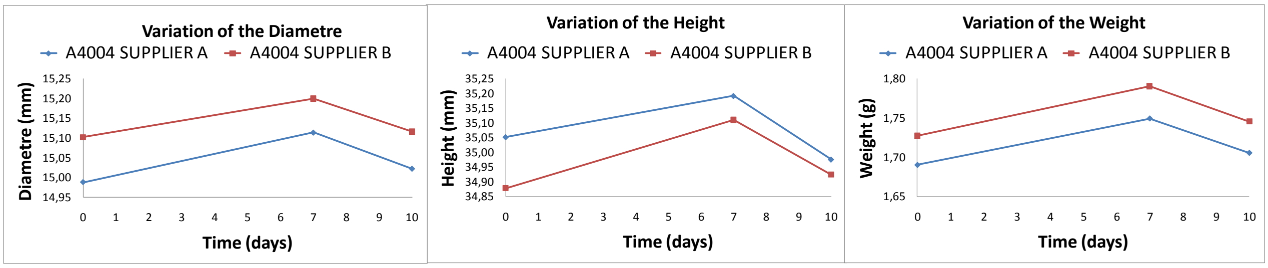
There are no more tests running at this moment for this valve. For further studies DOT and Swelling test could be performed, as well as a new "SS Test" modified with cans horizontal to compare and decide which storing position is better. Also one GL/C Test at $-20\,°C$ would explain about the stem behavior at low temperatures, so Altachem knows if the product can be exported to cold countries.

6.2 "Supplier A" vs. "Supplier B" Project

This project is made to compare the stems of Altachem two main stem suppliers (They will be called supplier A and B due to confidentiality norms). At this moment, SS Test at 45ºC and Swelling Test are finished, but SS Test at 23ºC is still running so, for this test, it is not possible to make conclusions yet.

6.2.1 Swelling Test

Five A4004 stems of each supplier where immersed in a mixture of gas 40/10 (vol.) LPG/DME; the results represent the average dimensions and weight of these five stems (Figure 30).



(a) (b) (c)

Figure 30 – Swelling Test Results for the A4004 stem, immersed in a mixture 40/10 (vol.) LPG/DME, comparing two Altachem suppliers.

As graphs show, Supplier B stem has a larger diameter and weight, but smaller height.

It is observed that both of the type of stems adsorbed gas particles after one week of immersion, increasing their dimensions and weight. After three days without immersion, supplier A and B stems recover practically its dimensions and weight ("Supplier A" stem's height even decreases a little bit from its first measure). Both stem's behaviours are almost the same for the two suppliers, so it is not possible to discriminate any of the suppliers with this test. Additional Swelling test with other substances can be performed to know more about the stems, in order to discriminate one of the two suppliers.

6.2.2 SS Test at 45 °C, 80% RH

Three types of stems for Supplier A (A3004, A3104 and A4004)[1] where compared with two types of Supplier B stems (A3004 and A4004). Standard formulation 4230 was used to fill the cans.

[1] *The difference between A3004 and A3104 is in the stems design. A3004 and A3104 are gun stems while A4004 is a tilting stem.*

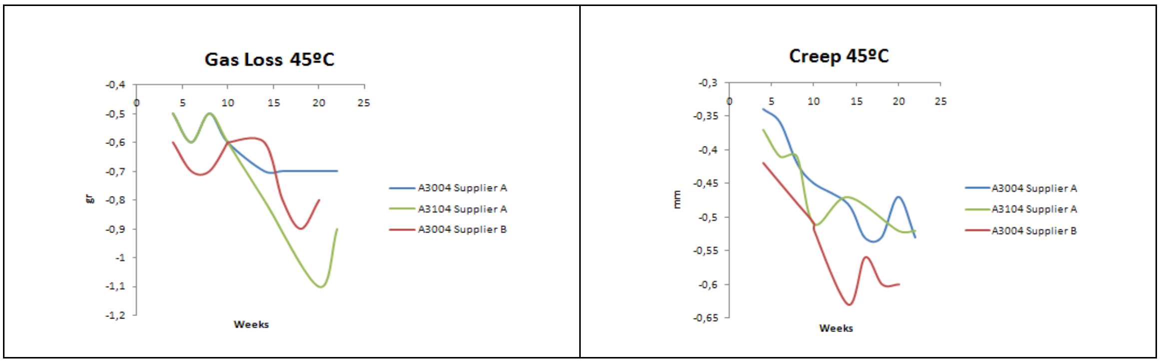


Figure 31 - GL/C Results for the gun stems.

After 22 weeks at $45\ °C, 80\%\ RH$ (equivalent to almost three years of shelf life at $23\ °C, 50\%\ RH$), the stem A3004 from "Supplier A" is the one who suffers less gas loss (around $0.7\ g$). It is also observed that the creep and the gas loss are directly proportional. Taking into account this data, "Supplier A" A3004 stem has to be chosen to mount Altachem valves, better than the other two stems.

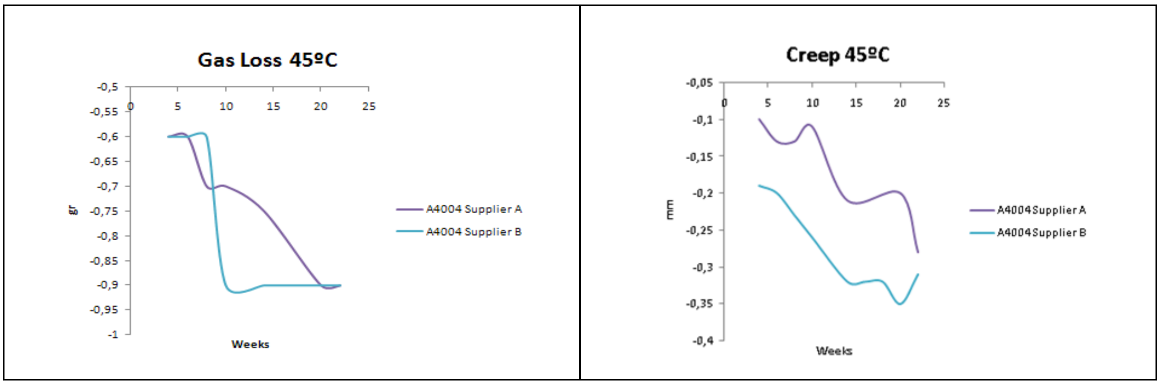


Figure 32 - GL/C Results for the tilting stems

Looking at the GL/C results for the tilting stems (Figure 32), it is possible to conclude that both of the stem types reach $0.9\ g$ of gas loss after 25 weeks at $45\ °C, 80\%\ RH$, but "Supplier B" stem reaches this point almost 15 weeks before, so "Supplier A" stem must be chosen. Creep results correspond with gas loss results, as "Supplier B" stem has a larger creep, having increasing consequences in the gas loss.

Comparing gun stems with tilting stems, gas losses are similar but gun stems suffer a slightly larger creep than the tilting ones.

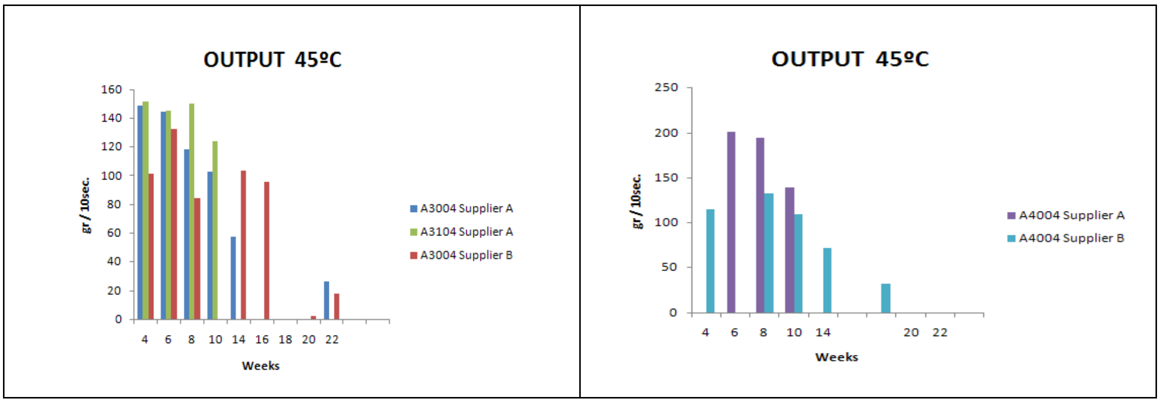


Figure 33 - OP Results

For the gun stems, "Supplier A" stems behave better (larger OP) than "Supplier B" stems until week 10 at $45\,°C, 80\%\,RH$ (which corresponds to 70 weeks at $23\,°C, 50\%\,RH$). It is also observed that A3104 stem has larger OP than A3004, so the efficiency of the reinforcing material is proved. "Supplier B" stem has less OP but it keeps working around five weeks more than the "Supplier A" stems. 22^{nd} week OP are not considered because of escaping from the general trend.

For the tilting stems, the same conclusion is made: "Supplier A" stems have larger outputs but "Supplier B" stems keep working longer.

After checking the OP results, it is necessary to choose between larger OP and longer shelf life in order to discriminate one of the suppliers. Taking into account GL/C Test results "Supplier A" A3004 stem will be chosen (It is necessary to remember that the gas loss will affect the foam quality).

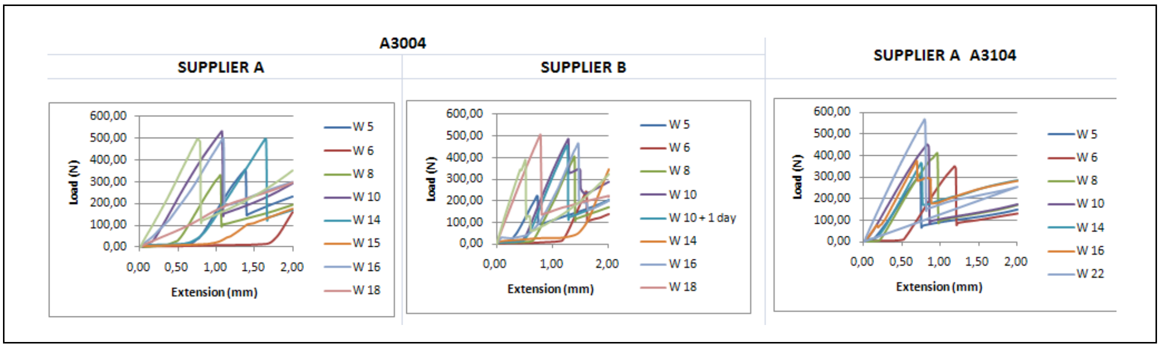


Figure 34 - Instron Graphs, gun stems.

In these three graphs, the sticking behavior is observed, also the increasing of the sticking behavior peak point with time. The load necessary to open the three stems is similar after 20 weeks at aging conditions (around $500\,N$). The peak point extension for the A3004 series differs; while, for the A3104 stem, is around $0.75\,mm$.

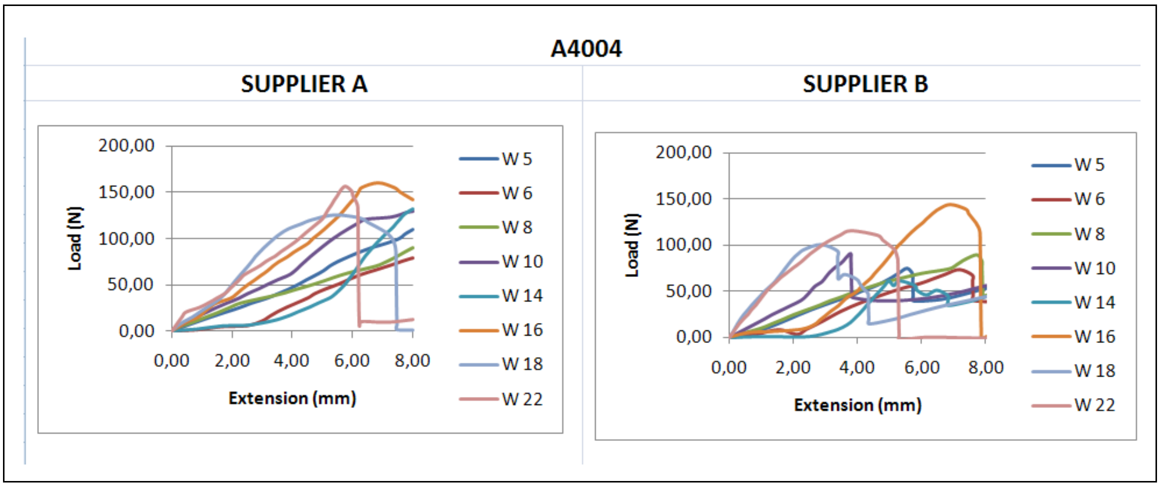


Figure 35 - Instron Graphs, tilting stems.

Stucking behavior for "Supplier B" is observed. "Supplier A" valves are only sticked at the last weeks of the test, so they have a better behavior. This is confirmed by the OP results. The load necessary to open the valves increases with time till a maximum of $150\ N$ approximately (less than for the gun valves) for both suppliers.

The objective of this project is to compare the two suppliers, so other graphs relating the variables are not useful. It is possible to conclude that gun and tilting "Supplier A" stems behave better. So they must be chosen if the prices from both suppliers are similar. The reinforcing material of the A3105 stem has not positive effects on the cans shelf life, so "Supplier A" A3004 stem has to be chosen. Final conclusions can be made when the SS Test at $23\ °C, 50\%\ RH$ will be finished.

Annex 7 Technical Data Sheets and Drawings of the Altachem Valves Involved in the Benchmarking Project

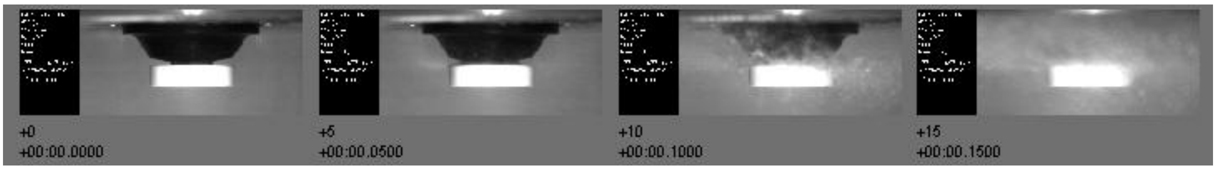
Technical Datasheet of A3105

<u>Mechanical opening in mm</u>

Years of experience has proven that most of our customers are using +/- 1 mm as "a mechanical starting opening" and then check after some hours of filling if any backsplash is noted or if the lip seal is leaking gas through (mechanical opening too low) which is noticed by bowling of the upper part of the grommet.

Technical Data	**A3105 Gun Valve**
Valve Stem:	High modulus polyolefin alloy
Mounting Cup:	Tinplated; thickness: 0,4 mm ; Low Rim
Grommet:	Vulcanized rubber Shore M 70 with improved swell resistance
Laid in Gasket:	Buna
Crimp Depth:	5,3 +/- 0,10 mm
Crimp Diameter:	27 +/- 0,10 mm
Filling Head & Nozzle:	Filling Nozzle Pamasol recommended : 2003-433_001 Filling Nozzle Pamasol recommended : 2003-465/002 (not opening mechanically)
Packaging:	2.500 pcs per carton; 60.000 pcs or 80.000 pcs per pallet

But in some cases at the cessation of the filling pressure the valve closes not fast enough and it results in pollutions (= backsplash). For this reason we recommend not to open the valve anymore mechanical wise.



Gas filling movie shots

Crimp diameter in mm

Is depending on the valve cup thickness. A3105 valve cups have 0,40 mm which gives a crimp diameter of 27 mm.

Crimp height in mm

Depending on the contact height of the can rim, thickness of squeezed valve gasket and thickness of valve cup, the crimp height varies from 5,20 mm to 5,40 mm. Crimp height of can is given by the can producer. In Europe for our valves we use in general a crimp height of 5,3 mm.

(Contact height of can + thickness of valve cup + thickness of squeezed gasket = crimp height to be set)

Contact pressure in daN (10 x Newton)

The valve and container are sealed well if the valve seal has been compressed before crimping.

On a Pamasol machine the compression is achieved with the air pressure in the slave cylinder and can be set with the pressure regulator.

Normal contact pressure in daN is 70 à 100.

Please feel free to contact us for any further information or experience exchange :

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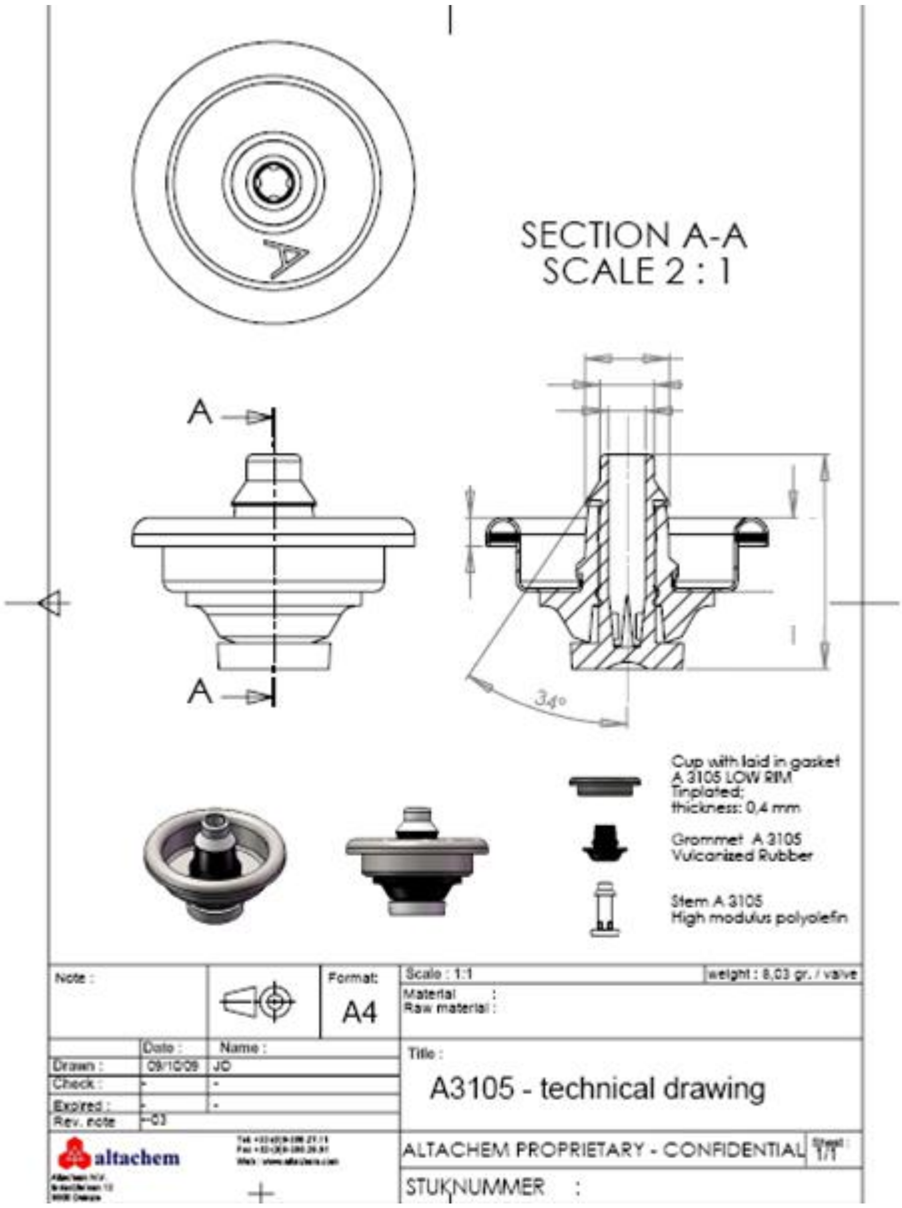
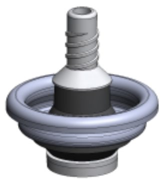
Jordi Demey,
Product Development,
jd@altachem.com

www.altachem.com



(Dimensions omitted due to Altachem Confidentiality Norms)

Technical Datasheet of A4105



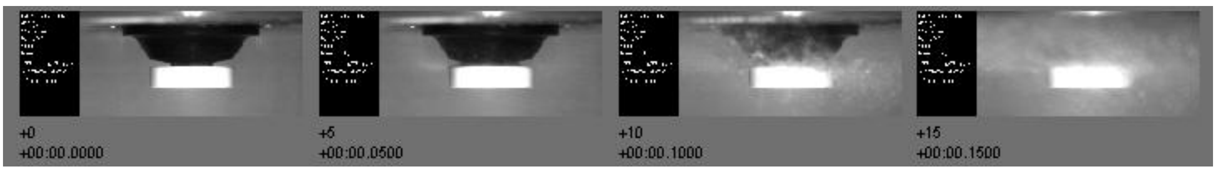
Mechanical opening in mm

Years of experience has proven that most of our customers are using +/- 1 mm as "a mechanical starting opening" and then check after some hours of filling if any backsplash is noted or if the lip seal is leaking

Technical Data	**A4105 Tilting Valve**
Valve Stem:	High modulus polyolefin alloy
Mounting Cup:	Tinplated; thickness: 0,4 mm
Grommet:	Vulcanized rubber Shore M 70 with improved swell resistance
Laid in Gasket:	Buna
Crimp Depth:	5,3 +/- 0,10 mm
Crimp Diameter:	27 +/- 0,10 mm
Filling Head & Nozzle:	Filling Nozzle Pamasol recommended : 2003-367_001
	Filling Nozzle Pamasol recommended : 2003-253/002 (not opening mechanically)
Packaging:	2.500 pcs per carton; 60.000 pcs or 80.000 pcs per pallet

gas through (mechanical opening too low) which is noticed by bowling of the upper part of the rubber grommet.

But in some cases at the cessation of the filling pressure the valve closes not fast enough and it results in pollutions (= backsplash). For this reason we recommend not to open the valve anymore mechanical wise.



Gas filling movie shots

Crimp diameter in mm

Is depending on the valve cup thickness. A4105 valve cups have 0,40 mm which gives a crimp diameter of 27 mm.

Crimp height in mm

Depending on the contact height of the can rim, thickness of squeezed valve gasket and thickness of valve cup, the crimp height varies from 5,20 mm to 5,40 mm. Crimp height of can is given by the can producer. In Europe for our valves we use in general a crimp height of 5,3 mm.

(Contact height of can + thickness of valve cup + thickness of squeezed gasket = crimp height to be set)

Contact pressure in daN (10 x Newton)

The valve and container are sealed well if the valve seal has been compressed before crimping.

On a Pamasol machine the compression is achieved with the air pressure in the slave cylinder and can be set with the pressure regulator.

Normal contact pressure in daN is 70 à 100.

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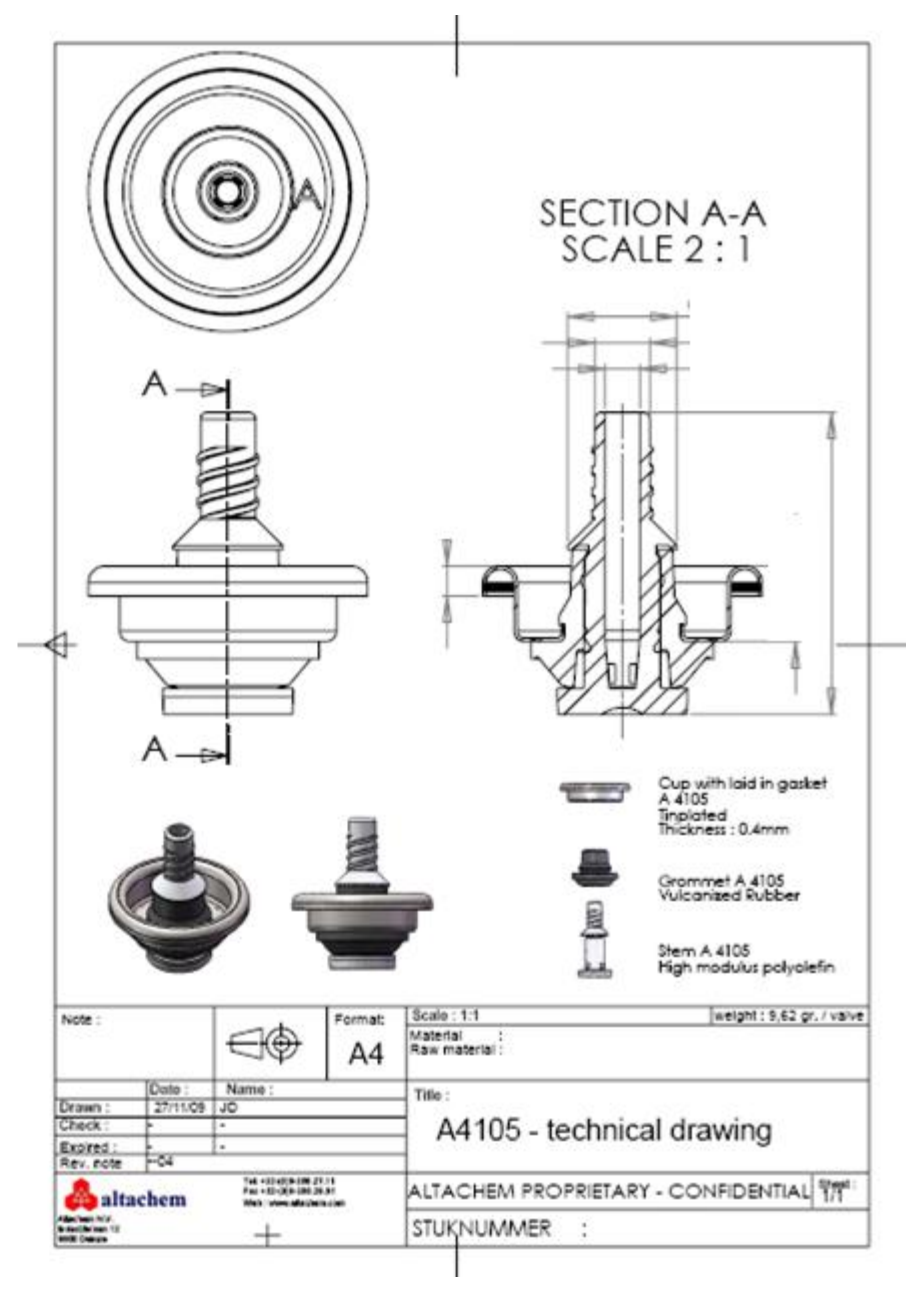

(Dimensions omitted due to Altachem Confidentiality Norms)

Annex 8 Lists of Figures, Schemes and Tables

8.1 List of Figures

8.2 List of Schemes

8.3 List of Tables

Some Remarks after the Thesis Discussion

- Cans are usually made at Altachem Laboratory, measuring the quantities of raw materials, “clinching” the valves (which are usually mounted at Altachem also), and finally filling in with the blowing agents.
- To contra rest the big variability at the different test, Altachem tries to test as much samples as possible. This variability is due, for example, to liger’s different positions of the cans when stored at the oven, different temperature and humidity zones at the oven, etc…
- As a chemical engineer, the possible work at Altachem would be to improve valve materials and/or develop new foams.
- The cans must be shacked before using them, so a mixture of raw materials is dispensed. If they are not sacked the mixture won’t be homogeneous and, depending on the orientation while dispensing, some raw materials will be dispensed more than the rest.
- The pre-polymerization reaction is performed completely because the isocyanate is presented in excess. It forms polyurethane with not rigid cells. When sprayed, the second reaction is performed between the isocyanate in excess and the water, to form polyurea which is a hard substance. This hardness, alongside with the vaporization of the blowing agents and the carbon dioxide, forms rigid dodecahedral cells.
- The title of this thesis could have been changed for “Becnmarcking of New Aerosol Valve Generations” because of being focused in a comparison of different valves and not in the development of new models of valves.