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OPTIMIZACIÓN DE UN PROCESO DE RECOCIDO: UNA APROXIMACIÓN DESDE LA ESTADÍSTICA Y LA CIENCIA DE MATERIALES A UN CASO DE APLICACIÓN EN LA MANUFACTURA DE ENVASES DE VIDRIO

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RESUMEN

El recocido es uno de los procesos más importantes en la manufactura del vidrio ya que proporciona la relajación de la red vítrea de SiO_2 y por ende define importantes propiedades mecánicas requeridas para hacer a este material útil. Sin embargo, dicho proceso también es costoso debido a las grandes cantidades de energía y tiempo involucradas para llevarlo a cabo, razón por la cual hay al interior de la industria del vidrio un paradigma concerniente a los posibles problemas involucrados con el cambio de variables para mejorar el proceso a nivel técnico sin afectar la calidad del vidrio. En este orden de ideas, disminuciones progresivas de temperatura y tiempo fueron llevadas a cabo al interior de un archa de recocido real pretendiendo así medir, analizar y comparar los valores de esfuerzo obtenidos con el proceso actual contra los valores obtenidos con los procesos propuestos. Todo lo anterior siguiendo las normas ASTM C336-71 y ASTM C148-14, así como haciendo uso de herramientas estadísticas tales como: Diseño de Experimentos (DOE) y Análisis de Varianza (ANOVA). Como resultados fueron obtenidos cambios estadísticamente no significativos entre los valores de esfuerzo obtenidos para la mayoría de las disminuciones efectuadas, lo cual permite pensar en dichas disminuciones como una opción para los altos costos de la industria del vidrio.

***Palabras claves**:* Archa, punto de recocido, punto de ablandamiento, retraso óptico, birrefrigencia y luz polarizada.

OPTIMIZATION OF A GLASS ANNEALING PROCESS: A STATISTICAL AND MATERIALS SCIENCE APPROACH TO A GLASS CONTAINERS MANUFACTURING CASE APPLICATION.

ABSTRACT

Annealing is one of the most important processes to manufacture glass since it provides relaxation to the SiO_2 vitreous network and therefore it determines important mechanical properties required for doing this material useful. However, this process is also expensive due to there are involved high quantities of energy and time to carry it out, and for these reasons there is into the glass industry a paradigm regarding possible issues involved with the changing of variables to improve the process at the technical level without affecting the glass quality. In this order of ideas, progressive decreases of both, temperature and time were performed into an actual lehr, aiming to measure, to analyze and to compare the values of stress obtained from the actual and the proposed processes, all of this using the ASTM C336-71 and the ASTM C148-14 standards, as well as using statistical tools such as: Design of Experiments (DOE) and Analysis of Variance (ANOVA). As results were obtained non-significant statistical changes between the values of stress obtained for the majority of decreases performed, which allows to think about these decreases as an option for the high glass industry costs.

***Keywords**:* Lehr, annealing point, softening point, optical delay, birefringence and polarized light.

1. INTRODUCTION

Soda-lime-silica glasses have been the most common type of glass used for both, conventional applications (glass containers and windows panels) and special applications (lasers and optical devices) mainly due to the high availability and low cost of the ores necessary to manufacture products in this material, as well as the facility and versatility of the processes involved such as: glassblowing for glass containers, precision glass molding for lenses and float for glass sheets among others. In addition, glass stands out mainly due to properties such as: its low chemical reactivity, its transparency and its low resistance to brittle fracture, being these two last ones strongly dependent of the residual stresses into the glass and hence of the annealing degree. Specifically, the transparency and the brittle fracture are controlled by the viscosity at the glass transition temperature region [1,2]. When the glass is cooled from temperatures above the glass transition region during the thermo-mechanical manufacturing process, the viscosity of glass drastically increases, which does not allow the rearranging of atoms and therefore it does not allow the crystallization (or also called 'being frozen'), making the glass amorphous, transparent and brittle at the end [1–3].

All substances when are cooled from a softened to a hardened state are likely to acquire internal stresses. This behavior is more familiar in the case of glass because it is transparent and the stress can be readily detected [4]. In general terms, while the glass is in the plastic-viscous state, it can be cooled to the desired rate [2], however, from the softening point, and particularly in the relaxation interval, the cooling must be done in a very slow way aiming not generate tensions, which in turn are generated due to the low caloric conductivity of the glass, since when the cooling of glass begins, the thermal dissipation does not have the same velocity on the surface of the mass that in its interior, which produces temperature gradients and therefore stresses. Naturally, the outer layers cool, stiffen and contract faster than the inner layers still hot and plastic state. However, as the thermal gradient decreases, the interior also begins to cool, to stiffen and to contract, but it is not possible to do it freely given that the

rigid state of the surface and for this reason the interior of glass is subject to compression stresses and the surface is subjected to tension stresses, but when the thermal gradient is minimized and controlled by processes such as annealing and/or tempering, the signs of stresses are reversed leaving the surface subjected to compression stresses and the interior subjected to tension stresses (Figure 1). As a result, the physical key principle for an optimal annealing and/or tempering is to produce compressive stresses in the surface and to solve this issue, processes such as: tempering and annealing have been developed, nevertheless always there is remained a residual stress that it is necessary to control.

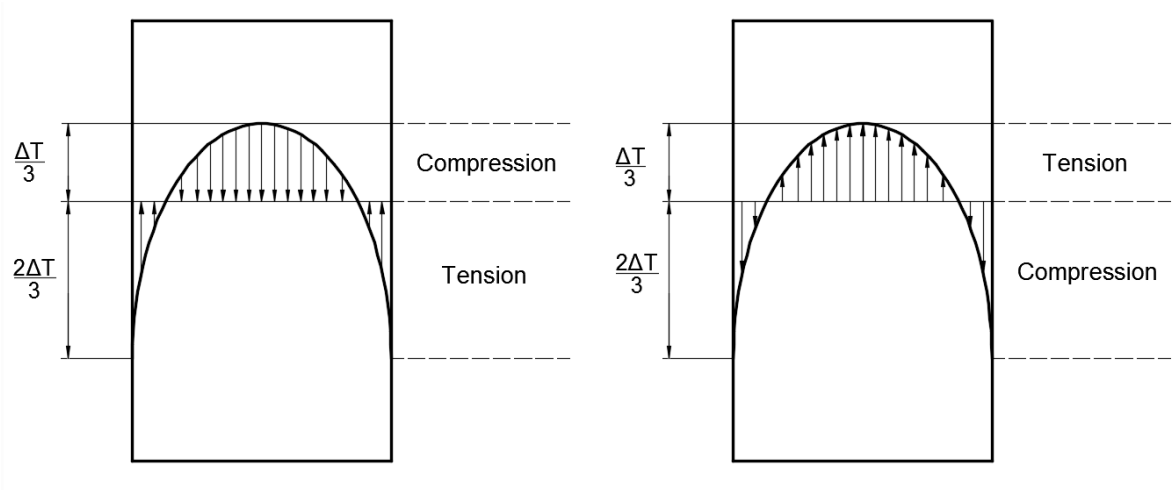


Figure 1. *Thermal gradient and stress generation. a) Core of glass hot and b) Core of glass cool [2].*

The annealing range is defined as the set of temperatures in which stresses in glass articles can be relieved at commercially desirable rates [1–2]. However, aiming to compare different glasses, the annealing range is normally assumed as the temperatures between the annealing point and the strain point [5-8]. Specifically, the annealing point is defined as the temperature at which internal stresses in a glass are substantially relieved in a matter of minutes, or in more formal terms, when the viscosity is $10^{13.0}$ Poises [2,6–7], while the strain point is defined as the temperature at which the internal stresses in a glass are substantially relieved in a matter of hours, or in more formal terms, when the viscosity is $10^{14.5}$ Poises [2,6–7].

An ideal annealing curve requires both, temperature and time, however at the industrial level this is often not feasible and for this reason, two different paths can be taken. Firstly, it is possible to opt for a brief heating above of the higher annealing temperature followed by a prolonged cooling time, or secondly it is possible to opt for keeping the glass at a temperature slightly above of the lower annealing temperature during a long period of time and then to cool quickly, nevertheless the disadvantage with the first form is based on the risk of producing deformations due to the subjection of glass to temperatures higher than the upper annealing temperature. For its part, the second case requires a high quantity of time. It is important to notice that at industrial level, it is more used the second process in order to avoid deformations of the glass products. In detail, the industrial annealing process is commonly divided into three stages, which are: *1) Thermal stabilization*, *2) Slow cooling* and *3) Fast cooling*. The first stage is done in order to relax and to eliminate the stresses cooling the glass from the upper temperature of annealing. The second stage is done in order to avoid creating new stresses and it consists basically of a very slow cooling of glass from to upper temperature to the lower temperature of annealing. Finally, the third stage consists in drastically decrease the temperature of the glass to the room temperature aiming to be able to manipulate it.

The main goal of this paper is to investigate the effect of decrease at the same time both, temperature and velocity of lehrs used in the annealing process of soda-lime-silica glasses for glass containers and flat glass industries, aiming to keep properties such as: toughness, thermal shock resistance and transparency, as unaltered as possible in order to mitigate the paradigm that exists into this business concerning the productivity issues involved with the decreasing of these variables. For this purpose, annealing measurements and statistical analysis were performed according with lehr movements guided by a Design of Experiments DOE.

2. METHODOLOGY

2.1 Design of experiments (DOE)

For optimizing the actual annealing curves was necessary to modify slightly and systematically the actual temperatures and times of lehr according to a factorial design of experiments (DOE) with 4 factors *(A: Temperature of zone 1, B: Temperature of zone 2, C: Temperature of zone 3* and *D: Time of annealing)*, with 2 levels (*"High"* and *"Low"*) and with 2 replicas as it is summarized in Table 1 and Figure 2. Regarding the sampling, it is important to notice that were used bottles of the extremes and the middle of lehr, randomly selected and taken 30min after the parameter changes in order to guarantee the process stability. In addition, the thickness values varied in the range 0.0700 ± 0.0084 in.

Table 1. *DOE details.*

Factors	Levels	
	Low	High
Temperature of zone 1 [°C]	550	560
Temperature of zone 2 [°C]	530	540
Temperature of zone 3 [°C]	520	530
Time of annealing [min]	19	22

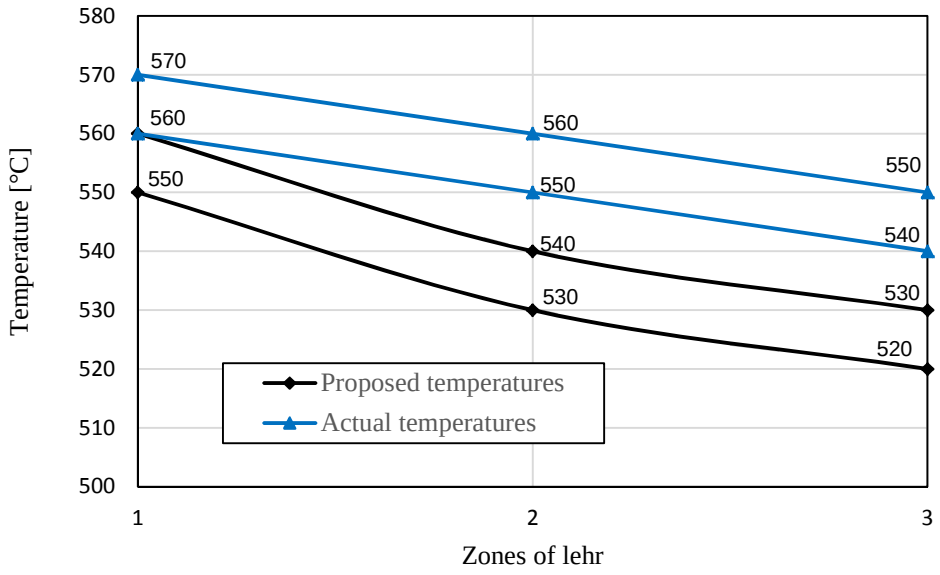


Figure 2. *Comparison between actual curves of temperatures used and the new one curves tested.*

2.2 Determination of the annealing degree

To determine the degree of annealing of samples, in the first place the optical delays were measured through the ASTM C 148-14 [10] standard. Specifically, to determine the optical delay, it is necessary to obtain the apparent degree of annealing through a set of calibrated and standardized disks, overlaying a disc on other one until to reach the color of the sample subjected to polarized light. It is important to notice that the use of these standard disks allows obtaining a qualitative measurement of annealing degree giving to each disk a numerical value located between 1 and 5, where 1 corresponds with a high level of annealing and 5 corresponds with a poor level of annealing. In addition, each disk corresponds with an optical delay of 22.8nm which in turn corresponds with a known and determined level of stress. For its part, the actual degree of annealing is computed through the equations (1) and (2) shown below:

$$T_R = T_A\left(\frac{4.06}{t}\right) \tag{1}$$

$$T_R = T_A\left(\frac{0.16}{t}\right) \tag{2}$$

Where T_R is the actual degree of annealing, T_A is the apparent degree of annealing, t is the thickness of the glass, 4.06 is the thickness constant measured by The International System of Units, and 0.160 is the thickness constant measured by The English System of Units. Then, the values of stress were determined by the equation (3):

$$\sigma = \frac{\Delta}{Ke} \tag{3}$$

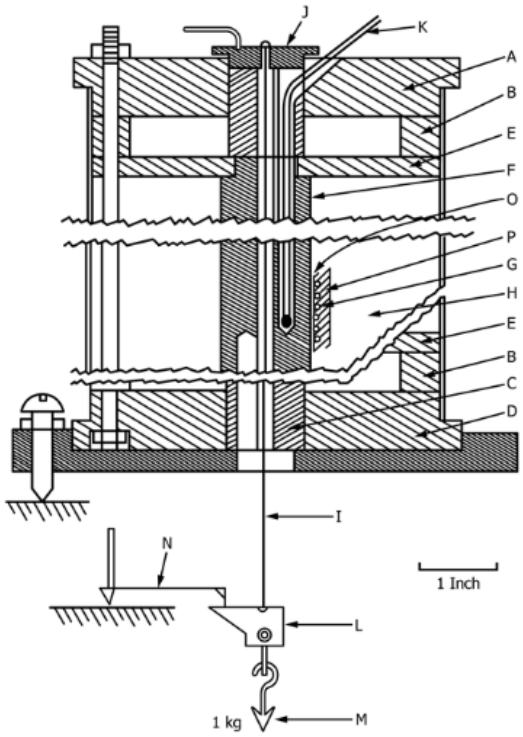
Where σ: is the value of stress in $Kpcm^{-2}$, Δ: is the optical delay in nm, e: is the thickness of glass in cm and K: is the Brewster constant with a value of 2.6 Brewster ($1\ Brewster = 1.02 \times 10^{-8} cm^2 N^{-1}$, ($Note$: $1 = \ kpcm^{-2} = 0.0981 MPa = 0.9810\ atm$)

Subsequently, all data obtained from the 32 runs performed was evaluated through an Analysis of Variance (ANOVA) aiming to identify the statistical differences of the annealing values.

2.3. Determination of the annealing range through measurements of viscosity

To determine the temperatures corresponding to the annealing and softening points using viscosity measurements, the ASTM C 336-71 [9] standard was followed. The procedure consists basically in to dilate a glass fiber supported and heated by an adequate furnace (Figure 3) aiming to measure and to record logarithmically the elongation rate as a function of the temperature in order to obtain a relation that must be straight linear, where the slope is an index of the viscosity and where it is also possible to find the temperatures of both, the annealing and the softening points. During this kind of tests, in accordance with the requirements of this method, the specimens must be 508mm of length and they must be substantially circular with an average diameter of 0.65 ± 0.10 mm. Additionally, the viscous elongation rate must be measured by a suitable extensometer while the specimen fiber is heated at a rate of 5 ± 1°C/min until to obtain an elongation rate of 0.6 mm/s, moment when the measurements must be recorded each 30s, the heating must stop and the cooling must start at a rate 4 ± 1°C/min until to obtain an elongation rate of 0.1 mm/s. On the other hand, to obtain the strain point, only it is necessary to divide the elongation rate at the annealing point

by 31.6 [9]. Finally, it is important to notice that the elongation rates at the annealing point for the majority of Soda-Lime-Silica commercial glasses are approximately 0.14 mm/min for a fiber of 0.65 mm diameter [9]



A, B, C, D—Made of asbestos-cement (Transite or equivalent)
E—Webbed asbestos-cement (Transite or equivalent) disk
F—Copper core 1⅛ in. (29 mm) outside diameter by 12 in. (305 mm) total length
G—91 turns No. 22 Nichrome V wire (or equivalent)
H—Diatomaceous earth
I—Sample fiber
J—Stainless steel support disk
K—Thermocouple
L—Lever platform
M—Load
N—Optical lever
O—Wrapping for electrical insulation (mica is suggested)
P—Refractory cement

Figure 3. *Apparatus for determination of annealing and strain points of Glass [9].*

3. RESULTS AND DISCUSSION

The values of stress into the glass obtained after performing the changes of temperature and time in the lehr are show in Figure 4. In the same way, the main factors *(A, B, C* and *D*) and the interactions of third level *(ABC, ABD, BCD* and *ACD)* are relevant as it is possible to see in the Figure 5a. It is important to notice that this relevance is high for the mentioned factors and interactions since all p-values are 0 and for this reason H0 *(Factor/Interaction is not relevant)* is rejected, which in turn means that the changes performed into the lehr are only important if the temperature of zones from 1 to 3, and the time of annealing are modified each one independently or if these variables are modified in short lists of three (Figures 5b-c), any other change into the lehr is not significant at statistical level. On the other hand, all assumptions required by the ANOVA analysis such as: normality of residuals, randomness and independence were accomplished.

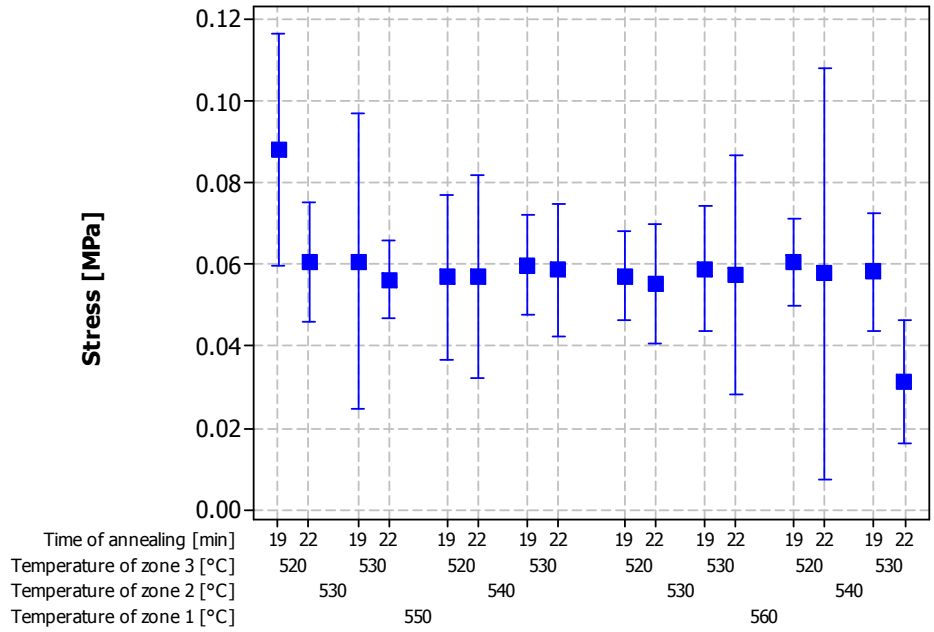
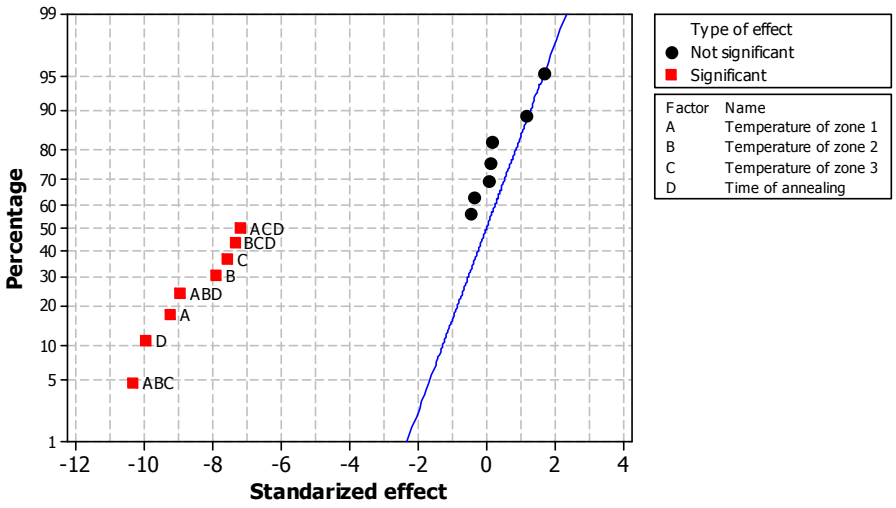
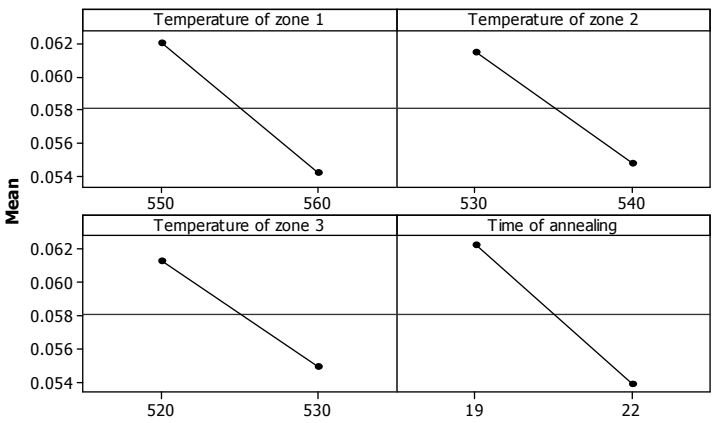


Figure 4. *Results of stress values into the glass obtained after performing the DOE.*

a)



b)



c)

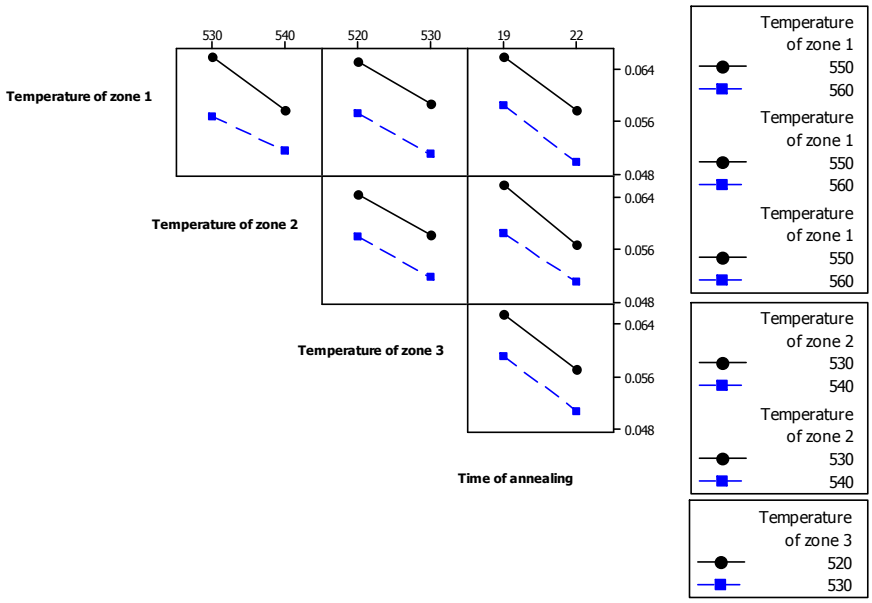


Figure 5. *Statistical analysis of the DOE. a) Normal chart of standardized effects - Stress, b) Chart of main effects – Stress and c) Chart of interactions – Stress.*

The values of stress obtained from the DOE were statistically compared with the values of stress measured in the actual process and the results are illustrated in Figure 6. In this case, both, the actual and the proposed values are equal given that the p-value from the ANOVA is > 0.05 *(p-value = 0.316)* and therefore H_0 *(H_0: the differences among means = 0)* is accepted. In this case, all assumptions required by the ANOVA analysis such as: normality of residuals, randomness and independency were also accomplished.

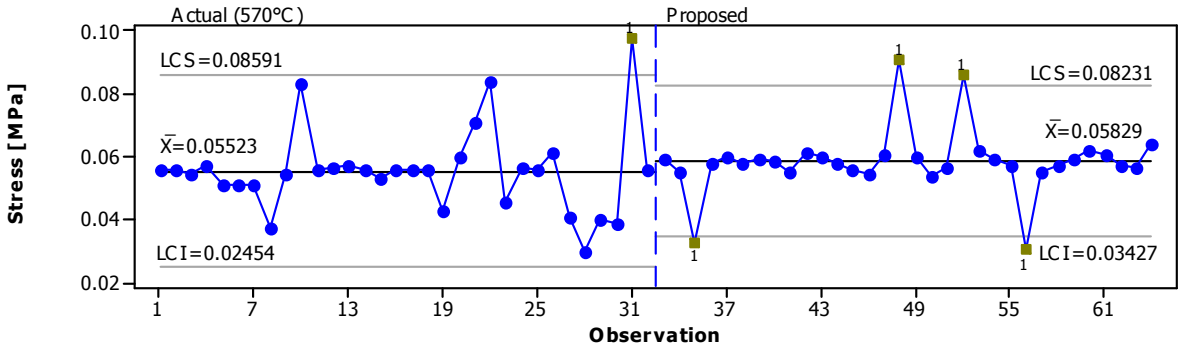


Figure 6. *Statistical comparison between the actual values of stress measured in the process and the proposed values of stress obtained after performing the DOE.*

The Figure 7 shows the statistical comparison between the values of annealing temperature obtained by viscosity measurements for both, the actual process (570°C) and the proposed processes (560 and 550°C). In this case, the actual and the proposed values of annealing temperature also are equal given that the p-value from the ANOVA is > 0.05 *(p-value = 0.988)* and therefore H_0 *(H_0: the differences among means = 0)* is accepted. Particularly, all

assumptions required by the ANOVA analysis such as: normality of residuals, randomness and independency were also accomplished.

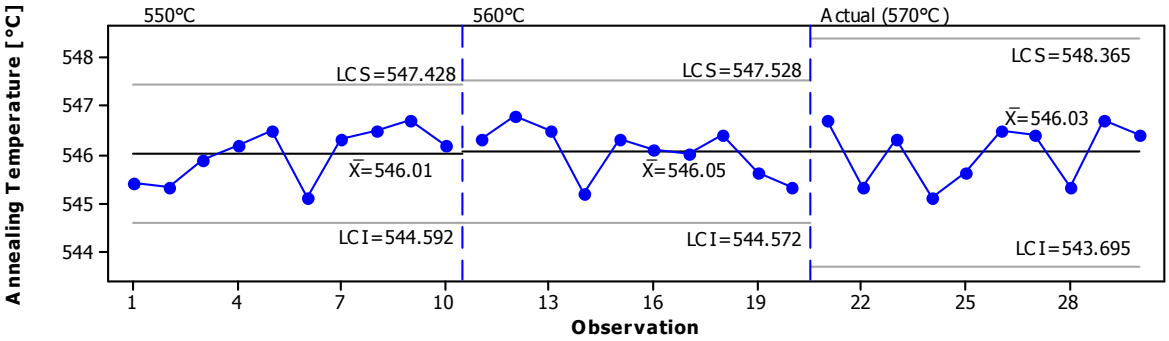


Figure 7. *Statistical comparison between the actual values of annealing temperatures obtained by viscosity measurements in the actual process (570°C), and the proposed values of annealing temperatures obtained after performing the DOE (560 and 550°C).*

From a materials science point of view, when a glass is subjected to increases of temperature, it experiments losses of rigidity since the provided energy weakens the chemical bonds of the material affecting the amorphous network. However, this process is developed in unequal and heterogenic way and for this reason the glass has neither a defined melting point, nor defined softening and annealing points [6-7], instead, these points become in wide ranges, which are necessary for the glass relaxation due to the constrains caused by the fast cooling, that can be taken in advantage for industrial proposes, aiming to decrease the energy consumptions involve. On the other hand, when the glass is subjected to temperatures close to the softening point, the cohesion of the network increases strongly and consequently the viscosity as well, affecting the annealing capacity of glass. In these case, phenomena like the high vibration of atoms losses importance and phenomena like the index of coordination become relevance due to the largest and/or the most energetic cations provide cohesion of the network and for these reasons there are increases of viscosity and therefore there are changes in the capability of annealing. In this case, the effect of changes performed into the lehrs did not affect the degree of annealing due to there are not substantial changes in viscosity as it is possible to see in Figure 7. It is important to notice that optically, the highest values of stress (0.0902 and 0.0857 MPa) and therefore the worst values of annealing degree were obtained for the runs 16 and 20 of DOE respectively, which is the reason of the color distortions shown in Figure 8, which in turn are in accordance with the lower values of temperature and time into the lehr. However, the other combinations of temperature and time allowed to obtain annealing degrees statistically equals to the annealing degrees used by the actual process saving time, energy and hence financial resources. Finally, it is important to notice that the annealing degree 3 is the maximal value acceptable for the industry and in any test performed was obtained a value smaller than 3.

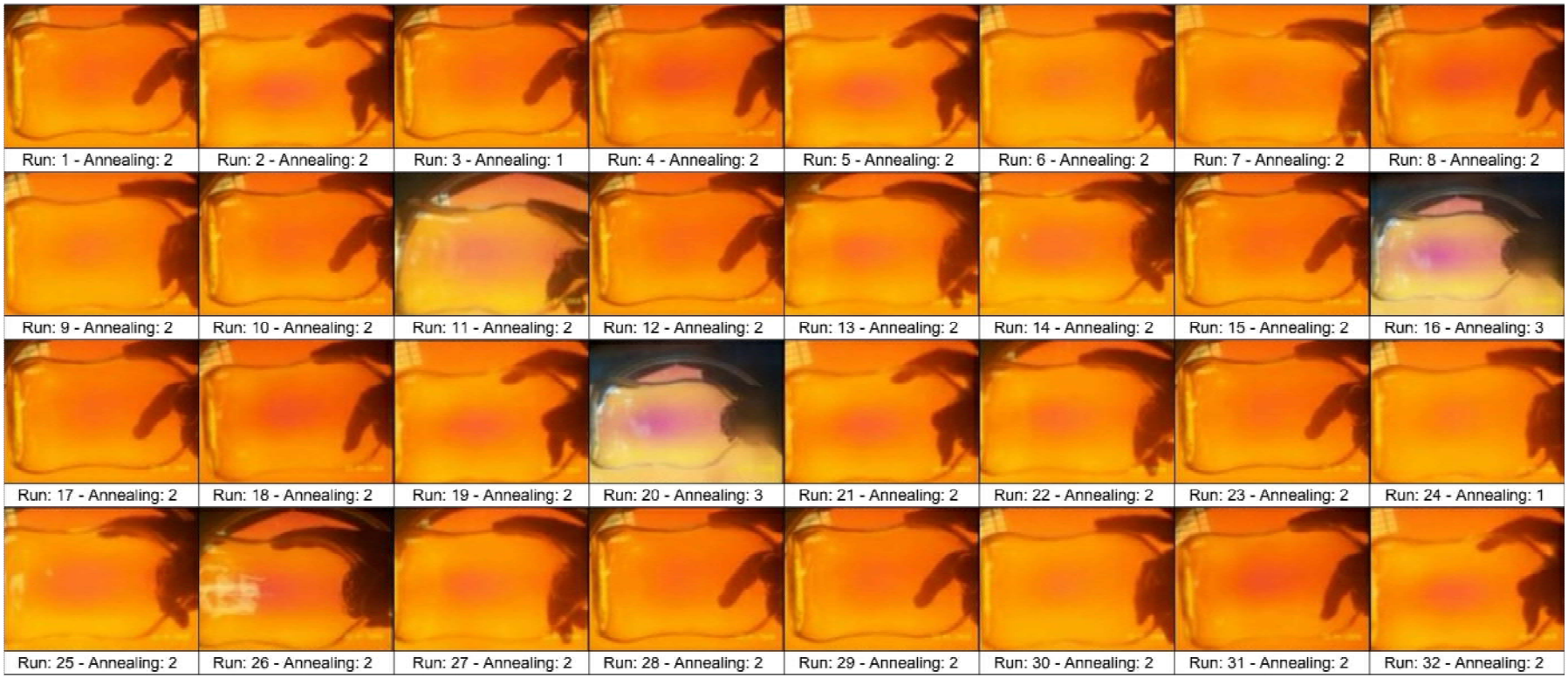


Figure 8. *Values and images of annealing degrees obtained after performing the DOE.*

4. CONCLUSIONS

The changes of temperature and time performed into the lehr did not affect the values of stress into the glass as it is possible to see in the Figure 6. This behavior was mainly due to the annealing range of glass is wide and variable, and particularly in this case, this range of annealing temperature did not change as it was confirmed by the annealing temperatures obtained through viscosity measurements shown in the Figure 7. It is important to notice that only the runs 16 and 20 of DOE obtained high values of stress that are equivalent to degree 3 of annealing, which is the maximal acceptable value for the industry.

It is possible to reduce the annealing temperature of zone 1 from 570°C (actual process) to 550°C using 22min, or to 560°C using 19 min, without compromising the glass quality as it is possible to see in Figures 4 and 6. With these conditions the annealing degree is 2 (0.058 ± 0.014 MPa), which corresponds with values that are statistically equals to the actual values used in the process (0.055 ± 0.014 MPa).

5. ACKNOWLEDGEMENTS

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