Original Article

Determination Of The Best Treatment For The Tannery Industry Using Sodium Silicate (Na_2SiO_3) With Sulfuric Acid (H_2SO_4)

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Abstract

The present work aims to synthesize silica sol from the acidification of sulfuric acid plus sodium silicate. Three solutions of sodium silicate were prepared at different concentrations; these were mixed with a 17% diluted sulfuric acid solution until a whitish colloidal suspension was obtained. The pH of the final solutions obtained was determined. The colloidal suspensions obtained and the gel formed were analyzed in an infrared spectrophotometer to compare the functional groups they present with those of conventional chromium salt. Finally, tanning tests were carried out with the silica sol obtained plus an aldehyde, where the typical quality parameters of leather were analyzed: dry rubbing abrasion, elongation percentage, temperature shrinkage and tensile strength. These results were compared with the data of leather tanned with chromium salts. For the comparison, statistical tests such as multiple ranges, anova, and determination of means were carried out. It is obtained as a result that the process should be carried out at room temperature up to a pH of 2.5; the infrared spectrum reveals that the functional groups of sodium silicate are similar to the chromium salts used for the tanning process. The statistical analysis shows that the silica sol obtained from a 1/5 solution of sodium silicate presents quality parameters statistically similar to those obtained from conventional chrome salt tanning.

Keywords: Silica Sol, Tanning, Leather quality, Infrared spectrum, Temperature, Concentrations.

Resumen

El presente trabajo tiene como objetivo sintetizar la sol de sílice a partir de la acidificación de ácido sulfúrico más silicato de sodio. Para lograr esto se preparó tres soluciones de silicato de sodio a diferentes concentraciones, estos se mezclaron con una solución de ácido sulfúrico diluida al 17%, hasta obtener una suspensión coloidal blanquecina. Se determinó el pH, de las soluciones finales obtenidas. Posteriormente se realizaron pruebas a diferentes temperaturas para encontrar la influencia de esta sobre el proceso, las suspensiones coloidales obtenidas, así como el gel formado fueron analizados en un espectrofotómetro infrarrojo, para comparar los grupos funcionales que presentan frente a los grupos funcionales que presenta una sal de cromo convencional. Finalmente se realizaron pruebas de curtición con la sol de sílice obtenida más un aldehído donde se analizaron los parámetros de calidad típico de un cuero que son: abrasión al frote en seco, porcentaje de elongación, contracción a la temperatura y resistencia a la tensión, estos resultados fueron comparados con los datos de un cuero curtido con las sales de cromo. Para la comparación se realizaron pruebas estadísticas como la de los rangos múltiples, anova, y determinación de medias. Se obtiene como resultado que el proceso se debe realizar a temperatura ambiente llegando hasta un pH de 2,5, el espectro infrarrojo revela que los grupos funcionales del silicato de sodio son similares a las sales de cromo utilizadas para el proceso de curtición. El análisis estadístico muestra que la sol de sílice obtenida a partir de una solución de 1/5 de silicato de sodio presenta los parámetros de calidad estadísticamente similares a los que se obtienen de una curtición de sales de cromo convencional.

Palabras clave: Sol de Sílice, Curticion, Calidad del cuero, Espectro infrarrojo, Temperatura, Concentraciones.

I. INTRODUCTION

Leather is a durable and flexible product that is in great demand today. This product is obtained using many chemical products (1,2). Among all the chemicals used, the tanning agent is the most important since it defines the properties of the leather obtained, and it is the one that converts the raw hide into leather by stabilizing the collagen in the hide. (3,4). Although there are several types of tanning agents, about 90% of leather products are currently obtained using commercial chromium salts, especially chromium sulfate, due to their excellent properties (5,6). (5,6). Commercial chromium sulfate contains 23% chromium (III) in the form of chromium oxide; Cr^{3+} is the one that reacts with the carboxylic groups of collagen to form a complex. This reaction provides the leather with stability against heat and enzymatic attack. (2,7)This process occurs through the different layers of the leather; the Cr3+ must penetrate through all of them to obtain the leather. To ensure that the chromium has reached all the layers of the raw hide, chromium salt is usually added in excess to the process (8). The latter results in only 60% of the chromium initially added joining with the hide to form leather, while the rest is waste in the process wastewater (9,10). (9,10).

Trivalent chromium present in wastewater constitutes a severe threat to human health. Excess chromium ion in the body has been associated with carcinogenic effects, and once it interacts with the cell, it can accumulate on the cell surface, causing morphological alterations (11,12). On the other hand, Cr(III) present in the effluent can easily oxidize to Cr(VI) due to contact with oxidizing agents and pH variations, Cr(VI) is a great threat to both terrestrial and marine ecosystems due to its high toxicity (13). It also has carcinogenic and mutagenic characteristics and causes allergies in humans.

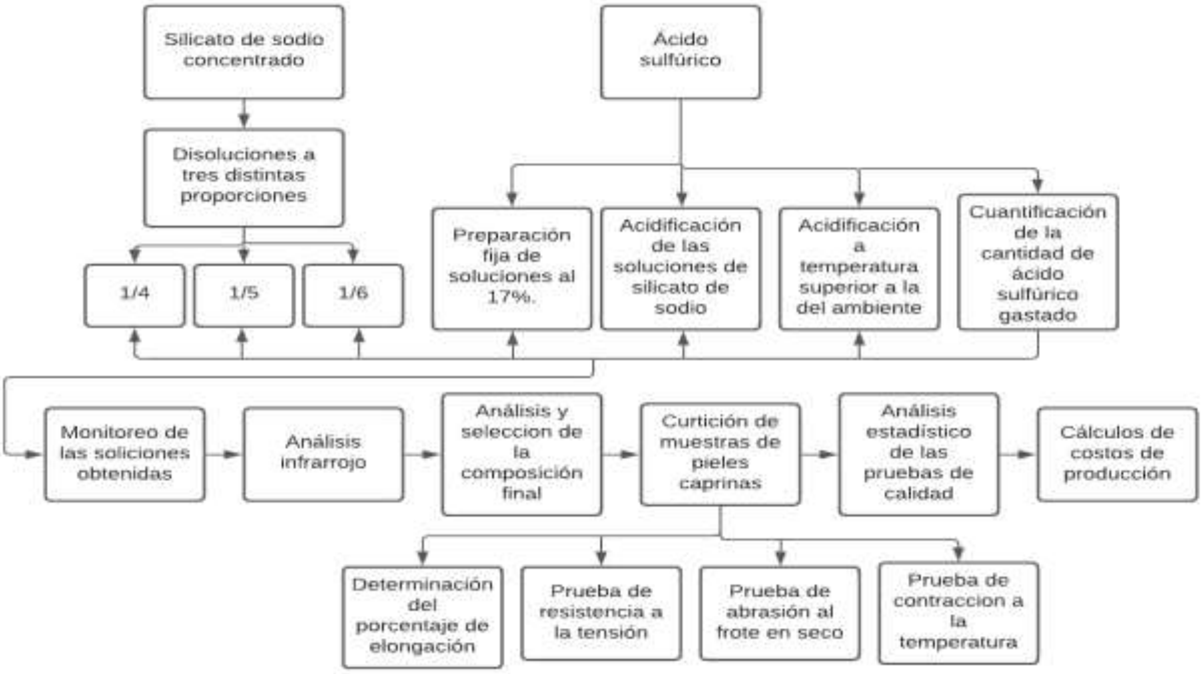
Despite the drawbacks above, the leather industry represents an important economic sector in several world regions (14). Because of the latter, research is needed to enable the production of leather goods without causing damage to the environment. In order to improve the chromium-based production systems, as a first step, it has been decided to develop systems for recycling the excess chromium that ends up in the effluent. Recycling can be done directly, which is the cheapest option if the liquor resulting from the tanning process is wholly recirculated to the tanning process (15,16), or indirectly if the chromium is recovered from the effluent by the addition of a precipitating agent such as magnesium oxide or sodium hydroxide (17-19). The recovered chromium is mixed with chromium sulfate at a ratio of 30/70% (18,19).

Another alternative proposed is based on improving the efficiency of the chromium absorption process within the leather, using agents that improve chromium depletion during the tanning process. Usually, these agents have high carboxylic groups which react with the collagen of the leather, making it interact more easily with Cr(III), which increases the amount of chromium retained in the leather (20). Compounds that aid in the further depletion of chromium can be used in conjunction with chromium sulfate in the liquor or as a solvent in place of water (14).

The elimination of chromium within the industry through alternative tanning agents has been proposed to solve the environmental problem related to the use of chromium in leather production. These are vegetable tanning agents and other less toxic metallic agents made from iron, zinc, titanium and zirconium (21). These agents require an auxiliary agent, usually an aldehyde, to transform the hide into the leather (2,7).

Silicon tanning is a good alternative to chromium sulfate for leather production, specifically in its silicic acid form with the aid of an aldehyde. The leather obtained by using this tanning agent has good mechanical characteristics (22). Dissolved silicic acid is presented as a colloidal suspension of high molecular hydration of silica particles dispersed in water, which can be obtained from sodium silicate with the acidification of sulfuric acid by ion exchange. Once the silica has been activated, it is used in treating wastewater, municipal water, fabric finishing, reinforcement of synthetic polymers and mainly in tanning different types of leather (23). Depending on the conditions of concentration, pH, humidity and temperature, silica sol can polymerize and form a gel by eliminating the solvent (23). The silica sol suspension is very sensitive to the described conditions and tends to polymerize rapidly, and once it reaches its polymerized form, it cannot be used in the tanning process. Thus, the present work aims to identify the conditions under which a stable colloidal suspension of silica sol can be obtained and used to produce chrome-free leather (8).

Figure 1. Research design.



II. MATERIALS AND METHODS

The general scheme of work to be followed in this research is summarized in Figure 1.

Materials:

- Water
- Sodium silicate
- Sulfuric acid

Instruments

- Stirring rod
- Beaker
- pH meter
- Spectrophotometer
- Reverbero
- Thermometer

Methods:

- ✓ **Identification of variables**

Dependent Variables:

- Physical condition
- Production costs
- Sulfuric acid consumed
- Elongation percentage
- Tensile strength
- Dry rubbing abrasion

Independent Variables:

- pH
- Silicate concentration
- Operating temperature

✓ **Sample size**

Aqueous solutions of 25 ml of sodium silicate will be studied as a sample from which dilutions are prepared by adding water to the different established proportions of 1/4, 1/5 and 1/6, which will be acidified with sulfuric acid until the formation of a colloidal suspension is observed.

✓ **Sample selection**

A commercial sodium silicate solution of density 1.41 was selected to prepare the three different dilutions to be used, and commercial sulfuric acid of density 1.82 was also selected.

For the tanning tests, convenience sampling was conducted, where the skins were selected based on their characteristics. The skins selected must not present scratches or stains and must be fresh. They will be the size of a sheet of Din A4 paper.

✓ **Preparation of silica sol**

The three sodium silicate solutions were acidified to study the influence of pH by adding a dilute solution of sulfuric acid. The sulfuric acid was added slowly and varying 5ml of this one, maintaining constant agitation. In each variation, the mixture was left to stand for 15 minutes and the pH reading was taken for each variation; additionally, the changes were observed.

Physical tests are produced to verify at which points a whitish gel is formed and at which point a colloidal suspension is reached in each sample studied.

Once the colloidal suspension was obtained, an aliquot was taken and examined in an infrared spectrophotometer, where the identification of functional groups was carried out to corroborate the formation of silicic acid.

Three different sodium silicate solutions were prepared to study the effect of the operating temperature; these were taken directly to the pH, where the formation of the colloidal suspension was identified. Agitation was kept constant, and the samples were evaluated at a temperature of 20 and 30 ºC, which was kept constant during the whole operation.

Finally, once the influence of pH and temperature had been analyzed, the gel formed during the tests was collected and analyzed in the infrared spectrophotometer to determine the functional groups present.

✓ **Quality tests carried out on tanned leather**

To carry out the tests, the hides were grouped in three blocks, two of which were tanned with a colloidal suspension of silica sol at different concentrations and the other with a colloidal suspension of silica sol at different concentrations.

The latter was provided by the ALCE company, leather that was tanned with a conventional chrome salt. Subsequently, quality tests were applied to all the blocks to compare the values between them.

a) Resistencia a la tensión

The tensile strength test requires the leather to be cut as a sample specimen. Since the test shows the strength of the leather by breaking, it is mandatory. According to the IUP-6 standard, the leather must have a minimum strength of 150 kg/cm2.

The test is performed at room temperature and proceeds as follows:

- With the help of a caliper, the thickness measurements of the specimen were taken at three different points. The average of the measurements will be the thickness used for the calculations.
- With the help of the caliper, the width of the leather is measured and the initial length of the leather is determined.
- The leather specimen is placed in the test equipment. It is clamped with the help of the clamping jaws, taking care that there is no slipping or folds in the tested specimen.
- Once the sample specimen has been placed, the leather is subjected to different magnitudes of load through the mobile clamp. This produces an increase in the dimensions of the specimen in only one direction.

Due to the characteristics of the test, the machine intended for the evaluation must be capable of:

- Stretch the leather in one direction only at a constant speed.
- Measure and record the magnitude of the load applied to the leather and the increase in its dimensions.
- Produce sufficient load to produce rupture or permanent deformation of the tested specimen.

Once the load data has been recorded, the tensile strength is calculated using the formula:

$$R = \frac{C}{\varepsilon * A}$$

Where:

R= voltage resistance

C= breaking load

ε= average leather thickness

A= width of leather

This test is applied to all tanned leather samples following the same procedure.

This test measures the leather's ability to deform (degree of stretching) before rupture or permanent deformation under multidirectional forces. In this way, it emulates the stresses to which the leather would be subjected in a real situation.

This test is directly related to the tensile strength test because if a low value is presented in this test, the same will occur in the tensile strength test. According to the IUP-6 leather quality standard, leather must have a minimum elongation percentage of 40%.

In order to carry out this test, the following must be done:

- A leather test tube is cut
- The initial length of the leather is measured
- The specimen is placed in the jaws of the equipment.
- The value of the initial meter is recorded
- The equipment is started up, at which time the ends of the specimen are separated at a constant speed until they break.
- The test is stopped and the value of the final meter is noted.

- The percentage of elongation is determined with the formula:

$$\%E = \frac{mf - mi}{Lo} * 100$$

Where:

%E= Percentage of elongation

mf= final meter value

mi= initial meter value

Lo= initial length of the specimen

This test is applied to all tanned hides by repeating the same procedure.

b) 2.12.3.3 Porcentaje de contracción

The shrinkage temperature is an indication that the tanning process is complete. This test determines the percentage by which the leather shrinks when subjected to a specific temperature. The temperature at which leather shrinks varies according to the tanning agent used, with chromium salts producing the highest shrinkage temperature (22). This temperature is lowered when other tanning agents are used and according to the standard, the minimum temperature at which the test must be carried out is 70 ºC, and the shrinkage percentage must not be higher than 10% (24). (24).

The procedure for this test consists of:

- A circular piece of leather is cut out and its dimensions are determined.
- Water is prepared at 90 ºC
- The leather is immersed for 5 seconds and the temperature is kept constant.
- The piece of leather is removed
- The final length of the leather is measured
- The shrinkage percentage is calculated as follows:

$$\%C = \frac{Lo - Lf}{Lo} * 100$$

Where:

%C= percentage shrinkage

Lo= Initial leather length

Lf= Final length of leather

c) 2.12.3.4 Dry rubbing abrasion

The dry rubbing abrasion indicates that the agent directly attacks the leather finishes, especially to know how fixed the color is in the leather, thus defining its resistance.

The process of this test is described below:

- Cut out a circular piece of leather and felt, preferably white.
- The samples are placed in the abrasimeter, the felt goes on the upper part and the leather on the lower part, producing a back-and-forth rubbing movement against the stretched leather.
- Evaluate the degree of damage or change experienced in the finish coat, felt pad staining and color change of the test sample.
- A new pad is used for each determination and remains as a record of the test.
- The number of rubs, the force and the amplitude with which they are performed are fixed, which makes it possible to quantify the staining produced.
- It is measured by cycles according to the scale shown in Table 1.

RANGE	RATING
0 - 50	Malo
50 - 100	Good
100- 150	Very good
>200	Excellent

Table 1: Rating Scale for Abrasion Resistance

III. RESULTS

Influence of pH

The influence of pH on the physical state of the mixture is shown in Table 2. In the first moments of the addition of acid to the silicate, there is no visible change in the density of the sample; this may be because there is no significant concentration of silicic acid formed. The average pH at which gel formation begins in the three samples is 11.557, and this gel gains density as the pH decreases. These observations coincide with those reported by Zapater Bes et al. and Claramunt et al. (25, 26), where it is pointed out that at alkaline pH the acidified sodium silicate tends to polymerize and form gels.

The gel begins to lose density at an average pH of 9.323; this value is within the range shown by Lepore (27), who points out that in the range of 8-10, unstable sols are formed that tend to gel over time.

Finally, it is observed that in the three samples, there is a colloidal suspension at an average pH of about 2.52, which coincides with the range described by (26), and it is also an advantageous condition since it has been demonstrated that this pH is optimal for tanning with silica sol.

	Aqueous solution	Gel solution	Colloidal solution
[] 1/4	12,37-11,9	11.73-3,03	2.67-2.52
[] 1/5	12.4-11.6	11.4-2.71	2.64-2.48
[] 1/6	12.9-11.77	11.54-2.97	2.58

Table 2. Influence of pH.

Influence of temperature

The results are shown in Table 3, where it is observed that when the operating temperature is raised, the final solution becomes unstable and polymerizes, forming a gel. The latter is related to the elimination of solute caused by the increase in temperature, which allows a higher concentration of silicon atoms to interact to form the silica gel (28).

Sample	**Temperature (ºC)**	**Gel formation**
1/4	20	Does not form gel
1/5		Does not form gel
1/6		Does not form gel
1/4	30	Gel form after 30 minutes
1/5		Gel form after 2 hours

1/6		Gel form at 4 hours

Table 3: Effect of operating temperature

Infrared Spectrum

Figure 2 shows the infrared spectra of each sample's silica sol colloidal suspensions, all of which show the same transmittance peaks. In the spectra, a broad and intense band can be seen at 3344.93 that would correspond to an O-H stretching of the acid, a medium intense peak can also be seen at 1641.13 cm-1 that is related to the Si=O stretching, a weak intensity peak can also be found at 1097.3 cm-1 related to a simple Si-O bond. In the same figures, in blue color, the spectrum of the commercial chromium salt used for tanning, chromic sulfate, shows a broad band at 3348.78 belonging to the stretching of the O-H bonds. The band at 1119.48 is associated with the presence of sulfate groups in the sample. (29). As can be seen, both spectra are practically identical; it is noteworthy that both possess the -OH functional group. This group allows the tanning agent to form complexes between the structure of the metal atom and the collagen of the skin (30), which allows the leather to be tanned.

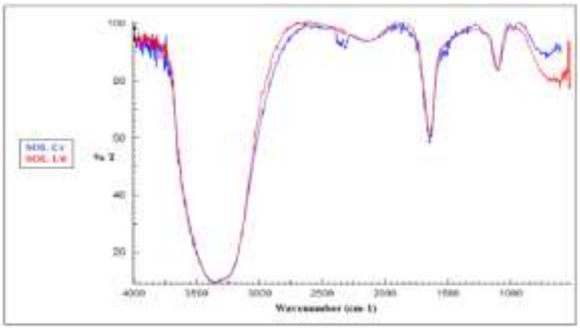


Figure 2. Infrared spectrum of the sol obtained from the ¼ sample and chromium salt.

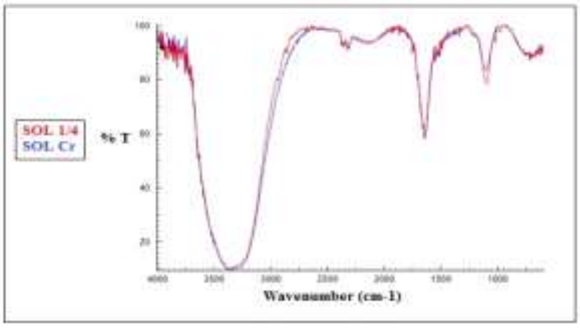


Figure 3. Infrared spectrum of the sun obtained from the 1/5 sample and chromium salt.

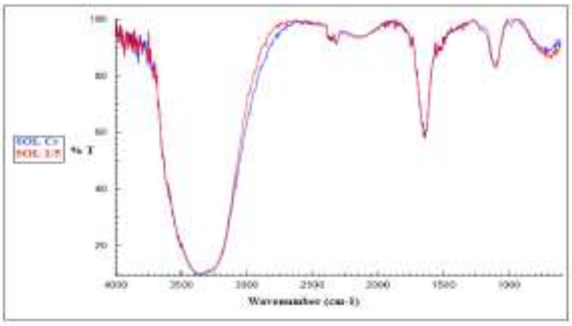


Figure 4. Infrared spectrum of the sol obtained from the 1/6 sample and chromium salt.

Tensile strength

Treatment	Repetitions	Tensile strength (N/Cm^2)
T1 (SILICA SOL 15 % - 1/4)	1	2857.14
	2	2946.43
	3	4047.62
	4	4238.10
T2 (SILICA SOL 15 % - 1/5)	1	2011.58
	2	3531.43
	3	4017.86
	4	2295.71
T3 (CHROME TANNING %)	1	2105.84
	2	2200.00
	3	2379.22
	4	1943.41

Table 4: Tensile strength results.

The anova analysis performed to compare treatments T1-T3 yields the results shown in Table 5.

Source	Sum of Squares	Gl	Medium Square	F-Ratio	P-Value
Between groups	3.72757E6	1	3.72757E6	13.46	0.0105
Within the groups	1.66186E6	6	2,77E5		
Total (Corr.)	5.38943E6	7			

Table 5: ANOVA test results for comparison T1-T3

The anova analysis performed to compare treatments T2-T3 yields the results shown in Table 6.

Source	Sum of Squares	Gl	Medium Square	F-Ratio	P-Value
Between groups	1.30259E6	1	1.30259E6	2.71	0.1509
Within the groups	2.88578E6	6	4,81E5		
Total (Corr.)	4.18837E6	7			

Table 6: ANOVA test results for T2-T3 comparison.

Elongation Percentage

Treatment	Repetitions	Elongation percentage

T1 (SILICA SOL 15 % - 1/4)	1	57.50
	2	90.00
	3	57.50
	4	65.00
T2 (SILICA SOL 15 % - 1/5)	1	147.50
	2	82.50
	3	62.50
	4	62.50
T3 (CHROME TANNING %)	1	57.50
	2	67.50
	3	60.00
	4	55.00

Table 7: Results for the elongation percentage test.

Comparing treatments T1 and T3 through ANOVA analysis, the results shown in Table 8 are obtained, while for the comparison of samples T2 and T3, the results are shown in Table 9.

Source	**Sum of Squares**	**Gl**	**Medium Square**	**F-Ratio**	**P-Value**
Between groups	112.5	1	112.5	0.84	0.3938
Within the groups	800.0	6	133.333		
Total (Corr.)	912.5	7			

Table 8: ANOVA table comparing T1-T3 elongation percentage**.**

Source	**Sum of Squares**	**Gl**	**Medium Square**	**F-Ratio**	**P-Value**
Between groups	1653.13	1	1653.13	2.00	0.2069
Within the groups	4956.25	6	826.042		
Total (Corr.)	6609.38	7			

Table 9: ANOVA table comparing T2-T3 elongation percentage**.**

Percentage shrinkage

Percentage shrinkage tests were carried out at 90 **ºC.**

Treatment	Repetitions	Percentage shrinkage
T1 (SILICA SOL 15 % - 1/4)	1	15,63
	2	16,67
	3	9,68
	4	16,67
T2 (SILICA SOL 15 % - 1/5)	1	12,77
	2	28,13
	3	15,63
	4	15,63
T3 (CHROME TANNING %)	1	3,23
	2	6,25
	3	3,13
	4	3,13

Table 10: Results for the elongation percentage test.

Since the results for the shrinkage percentage of treatments T1 and T2, which correspond to the tanning done with silica sol at different proportions, exceed the 10% established in the methodology, they do not comply with this quality parameter and therefore, it is not necessary to perform an ANOVA analysis in this test.

Dry rub abrasion test

Treatment	Repetitions	Result Obtained
T1 (SILICON SUN 15 % - 1/4)	1	100
	2	150
	3	100
	4	100
T2 (SILICON SUN 15 % - 1/5)	1	150
	2	150
	3	150
	4	100
T3 (CHROME TANNING %)	1	100
	2	150
	3	150
	4	100

Table 11: Results for dry rubbing abrasion test.

This test is qualitative, so it is advisable to perform a Kruskal-Wallis test to compare the different treatments, the results of which are shown in Table 12.

	Sample Size	Average Range	Statistician	P-Value
G 1/4	4	5.0	1.83333	0.39985
G 1/5	4	8.0		
Chrome	4	6.5		

Table 12: Kruskal-Wallis test for dry rubbing abrasion.

IV. DISCUSSION

As shown in the previous section the study of the influence of pH on the obtaining of the silica suspension is remarkable since, at basic pH values, this tends to form silica polymers in gel form, while the more the sample is acidified, the more the polymer tends to break and form the colloidal suspension. For the three cases studied, the suspension is formed in a pH range of 2.5 to 2.7; in addition, during the acidification process, it was observed that this should be carried out slowly and with diluted sulfuric acid, since when working with a concentrated one, the silicate sample gelled abruptly.

As expected, the increased operating temperature is counterproductive since it contributes to the elimination of water, so the silicate particles are closer to each other and tend to polymerize.

As can be seen in tables 4 to 12, the leathers obtained from the silica sol tanning process comply with the IUP-6 quality standard except for the shrinkage percentage; this shows that these products have good mechanical properties and, according to the ANOVA analysis, statistically they have quality values that do not differ significantly from the values obtained from the leathers tanned with a commercial chrome salt, being the sol 1/5 sample the one that most resembles the properties of the latter. On the other hand, the fact that both samples did not pass the shrinkage test indicates that their hydrothermal properties are inferior to those of the leathers obtained from chromium salt. This is to be expected since, as China et al. (14) state, tanning agents that do not use chromium tend to withstand lower temperatures before undergoing mechanical deformation; however, this parameter can be corrected by using silicon in combination with another tanning agent such as aluminum (31,32).

V. CONCLUSIONS

Silica sol was successfully obtained from commercial sodium silicate in combination with sulfuric acid, and it was found that it is necessary to perform this process at room temperature and to bring the pH to a value of 2.5- 2.7.

With the help of infrared spectrophotometry, the silica sol presents functional groups similar to those found in the commercial chromium sulfate solution used in traditional leather tanning.

Quality tests show that silica sol tanning produces hides with mechanical properties similar to those produced by the traditional chrome sulfate process; however, their thermal stability is inferior to that exhibited by-products obtained from chrome sulfate.

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