A Reexamination of the Aging of Organ Leather

by
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Abstract

Based on two papers that appeared almost 30 years ago,[1,2] chrome tanning became more commonly used to tan leathers used for pipe organs because accelerated aging tests indicated that chrome tanning was more effective at retaining tensile strength. Anecdotal evidence over the last 30 years has indicated that the chrome tanned leathers have not lasted as long as hoped. Further, the atmosphere used in the accelerated testing used sulfur dioxide; and with the improvements in air quality in many parts of the world and the removal of many coal-burning ovens in American churches and their buildings, the reason for using sulfur dioxide enriched air is less justified. The work described in this paper reproduced the results of the tests done ~30 years ago, but we have also shown that using an atmosphere that is not enriched with sulfur dioxide yields very different results, namely that vegetable tanning performs superior to chrome tanning in terms of tensile strength retention.

Introduction

The origins of the pipe organ date from well before the time of Christ. Over the course of centuries, it evolved into the most complex of all musical instruments, and was considered the most complex of all machines until the Industrial Revolution. The materials used to this day to construct organs reflect the instrument's ancient history. However, technological advances in the mid-19th Century (corresponding with the Industrial Revolution) suddenly allowed for the construction of much larger and more complex instruments. These instruments were previously unthinkable because of mechanical constraints. A number of inventions allowed organbuilders to harness the power of the very air that caused the instrument to speak in order to drive pneumatic motors that assisted the functioning of the instruments. At the end of the 19th Century, the introduction of electricity further revolutionized organbuilding. No longer was the organist seated at a console that was physically attached to the instrument, but rather the console could be located at great distances from the instrument and made moveable, and enormous instruments could be constructed with few limitations. However, like with most technological advances, there is a caveat. In most instruments constructed since the late 19th Century, leather is used as a pouch membrane for pneumatic valve actions in pneumatic or electropneumatic organs. When a key is pressed, the leather pouch membrane collapses and uncovers the hole on which a pipe is seated, allowing pressurized air to enter the pipe, causing it to speak.

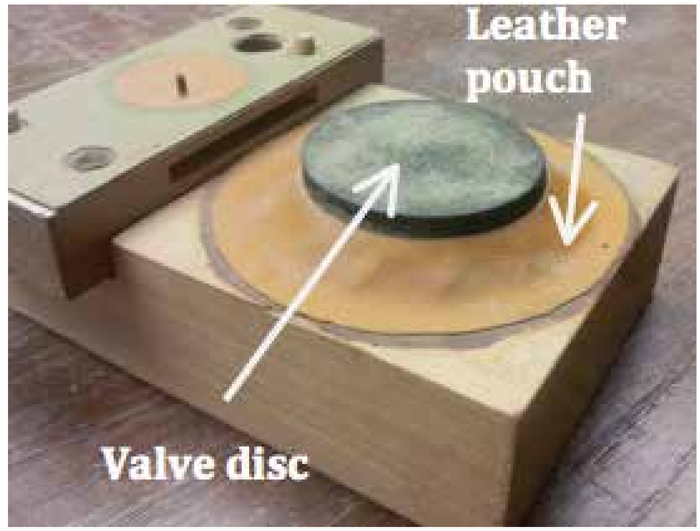

Figure 1. A picture of the pneumatic valve motor with the leather pouch and valve disc. The valve disc is what actually seals the pipe, but it is the leather pouch that collapses and allows the valve to open.

A picture of an actual pneumatic motor valve is shown in Figure 1. A medium-sized organ in a church or concert hall has several thousand of these valves; accordingly, it is not uncommon for tens of thousands of valves to be present in a single organ. When a valve fails due to decomposition, stiffening and/or cracking of the leather, the instrument falls silent, note by note until restoration and replacement of valves takes place. Although modern materials (rubber, polyurethane, vinyl) have been tried as a replacement for natural leather, leather has been found to be the best choice in terms of durability.

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For organ valves, the hides of sheep or goats are used. The issue that arises is the means by which the animal skin is treated in order to maximize longevity. Historical methods of leather treating yielded products that could last hundreds of years; however, those methods are either not fully understood, have been lost to time, or are not economically feasible to perform.[3] Leather is typically treated and tanned by first removing the hides and the skins. Once removed the skin is either rubbed with salt or put into a brine solution to prevent bacteria growth and to remove excess water. After washing with water to remove the salt, hair is removed using an alkaline solution, then treated with an enzyme solution to remove blood and non-collagen protein, and finally the skins are placed in a sulfuric-acid-salt solution. At this point, tanning begins. The two most common types of tanning are vegetable tanning and chrome tanning. For the former, leather is removed from the brine solution and placed for several days in a solution containing tannins, which are molecules that are water-soluble and isolated from tree bark. This process preserves the leather, because tannin molecules bind to the proteins in the leather and significantly increase aging stability. The only variable that the tanner can effectively change is the composition of the tannin. Chrome tanning takes place when chromium(III) sulfate (not the hexavalent chrome which is well-known to be toxic) is added to the acidified brine solution. The pH is raised after the chromium has diffused sufficiently into the leather, and with the raising of the pH, the chromium is able to react with the proteins in such a manner so as to stabilize the proteins and also help with water resistance. The chrome process is much faster than the vegetable process, taking one day (or less) instead of several days. Also, the chrome process can be more controlled than the tannin process. The level of chrome salts remaining in the leather can be quite high, on the order of 5-6%.

Seminal papers by Piltingsrud and Tancous[1,2] compared the tensile strength for differently-treated leathers in an accelerated aging test. The aging test was done by exposing the leather to a mixture of compressed air and sulfur dioxide at 67°C and 90 psig and measuring the loss in tensile strength over time with the total time being 2 weeks. Sulfur dioxide was used because of anecdotal evidence that organs where coal was burned (coal usually contains large amounts of sulfur) for fuel tended to degrade quicker. The important conclusion from this work for the purposes of this proposal was that leathers with higher chrome contents performed significantly better i.e. the percentage loss in tensile strength was less. The relevance of this test to predict aging was demonstrated by the fact that leathers that have already aged significantly (e.g. leathers made in the 19th century) performed well in this test. This paper caused most of the organbuilding industry to switch exclusively to chrome-tanned leathers. However, anecdotally, chrome-treated leathers now in use throughout the industry are not aging as well as had been expected.

The problems with this test are obvious. In today's world, particularly in the United States, the concentration of sulfur in the atmosphere is so small that it is very hard to believe that sulfur compounds can be the primary catalyst for the degradation of leather. Leather has been shown to degrade via a wet-state oxidative mechanism, e.g. caused by oxygen in the atmosphere facilitated by water in the leather and air. However, a catalyst for this oxidation mechanism is sulfur compounds.[4] To develop a test with a high concentration of sulfur does not seem justified, especially since the degradation mechanism is clearly different in the absence of sulfur. Piltingsrud and Tancous did perform the test with air; however, air alone did not cause most of the leather to age appreciably under the conditions of the test. The other clear issue is that the way in which the test was justified is not appropriate; the characteristics of ~150 year old leather (which, by the way, were vegetable tanned) are very different than today's leather. The purpose of the work described in this proposal is to develop an accelerated aging test that contains only air and water and compare the results to the test developed by Piltingsrud and Tancous.

Experimental

Materials and Apparatus

An assortment of leathers used in both trial experiments and experiments at the standard conditions were obtained from domestic and international suppliers; the Acknowledgements lists those suppliers that were generous enough to donate samples. Leather samples to be aged and tested were cut into D-1708 dogbone sized samples using a die and expulsion press from Dewes-Gumbs Die Co. Inc. Leather was cut with the grain running in the same direction. The thickness of the samples was measured using a micrometer.

A custom built stand was made using all stainless steel parts to hold the samples for aging. Two rectangles with the approximate dimensions of 5" x 4 ½" were cut from Kapton® polyimide film. A sheet using the same expanded sheet metal as the top of the stand was cut in order to act as a cover and weigh down the samples of leather and polyimide film. The samples were aged between the Kapton® sheets, which in turn were sandwiched by the metal screens. Samples were spaced evenly on top of the stand and film so that they did not overlap.

An Apache stainless steel vessel with an oval shaped opening having dimensions 5 7/8" x 4 15/16" was used to age the samples. The vessel was designed to hold sufficient pressure for these experiments. The vessel has a volume of 6.18 L with has four ¼" female NPT fittings with two of the fittings sealed using ¼" male NPT plugs from Swagelok. One of the remaining fittings was used to introduce air into the vessel while the other was connected to a pressure gauge from Swagelok; ball valves were used to isolate the vessel as appropriate. Samples were heated in an oven with digital temperature control. All tests took place at constant temperature.

A mechanical tester, from United Calibration Co., Model SSTM-2K, was used to measure mechanical properties of the samples in tension. The tensile tester has a capacity of 200 Lbf and the strain rate was 1.2 cm/min. Data from the computer, e.g. force vs. position, was analyzed using Microsoft Excel using the known dimensions of the sample. Data from four to six samples for a type of leather cut from the same hide were averaged together. Prior to testing, samples were air dried at room temperature for at least 24 hours. The result of this test is the tensile strength, which is the (force/cross-sectional area) required to break the sample and is the same measure used in the Piltingsrud and Tancous paper. A second measure, which does not appear in the Piltingsrud and Tancous paper, is the modulus, which is the force/cross sectional area required to initially stretch the sample.

Procedures

Conditions used for aging were determined experimentally. The criteria was to find a set of conditions where, over the course of a few days, the tensile strength decreased by 10-50% for most samples. Such a range was necessary so that the tests could be completed in a reasonable time frame and that differences between different samples would be evident. These experiments consisted of altering the relative humidity (referred to as humidity in this paper) and the temperature.

Trial experiments are listed below.

1. 90°C and 100% humidity. The stand was inserted into the vessel with the leather samples on it. No polyimide film or metal cover was used. Aged for two days.

2. 50°C and 100% humidity. The stand was inserted into the vessel without any polyimide film or metal cover. Aged for two days.

3. 50°C and 100% humidity. The stand was inserted into the vessel and the polyimide film was laid between the samples and the stand. A second piece of film was laid on top of the samples, and the cover was then placed on top to sandwich everything together. Aged for two days.

4. 50°C and ~5% humidity. Polyimide film and metal wire covered the samples like in trial three. The vessel was open during aging. Aged for two and five days.

5. 50°C and 15% humidity. The samples were sandwiched between the polyimide and metal sheets and heated inside the sealed vessel. Samples were aged for two and five days.

None of these conditions were appropriate. Trials 1-3 the leathers lost too much strength. Trials 4 and 5 not enough strength was lost. The sixth trial yielded appropriate conditions, which were 120°C and ~1% humidity. No extra water was used in the device and 50% relative humidity at room temperature approximately the value in our climate controlled building) corresponds to 1% humidity at 120°C. Leathers were sandwiched completely between the polyamide films and metal cover to ensure no liquid water contacted them, only vapor. The leather samples were then heated inside the completely sealed vessel and allowed to age for two and five days.

In additions, the experiments described in the paper by Piltingsrud and Tancous were replicated to ensure the viability of the experimental procedure used in this study; four vegetable tanned leathers and four chrome-tanned leathers were used. Leather cut into dogbone shapes was placed inside an airtight vessel like in the above procedure. ***All of these experiments were done in a hood with face shield and breathing mask; SO_2 is very dangerous and special permission from the supplier was necessary to order the gas.*** SO_2 was then flowed through the

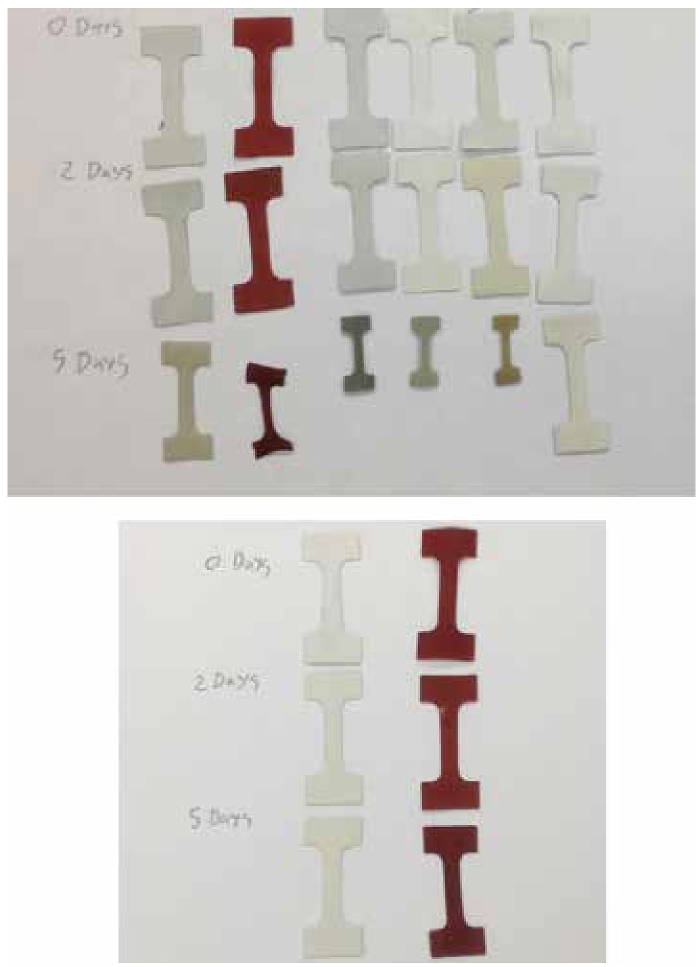
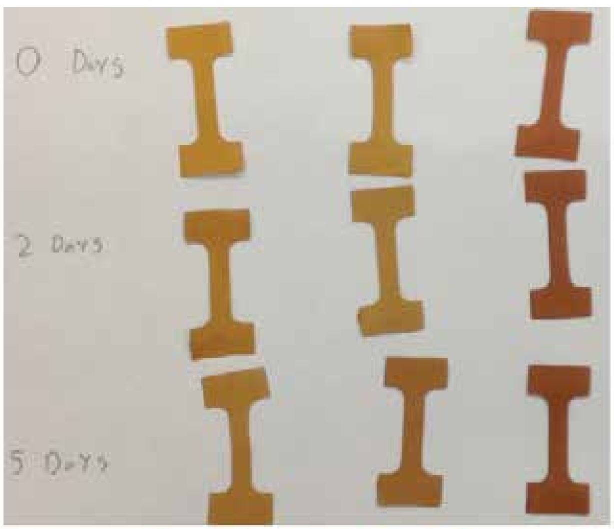


Figure 2. Pictures of the eight different chrome tanned samples after aging prior to being tested in the tensile apparatus. The 5 day samples that are boxed could not be tested.

vessel in order to purge air from the vessel. After approximately five minutes of allowing the SO_2 to flow through the vessel, the vessel was considered purged of atmospheric air and was sealed; the pressure inside was 14.7 psi (atmospheric). The vessel was then connected to compressed air and the valve was opened to allow the pressure inside the vessel to reach 90 psig. This pressure was measured using a pressure gauge attached to another valve on the vessel. Once the desired pressure had been reached, the valves were closed again and the vessel was placed in an oven at 67°C and allowed to age for two and five days; other than the pressure increase due to heating no change in pressure was noticeable during the testing. After the aging process, the vessel was depressurized and vacated of the SO_2, and the leather strips were tested for tensile strength.

Results

Figures 2-4 show the qualitative results for the different types of leathers aged at 120°C and ~1% humidity. From the pictures, the chrome leathers did not hold up as well as the other specimens.



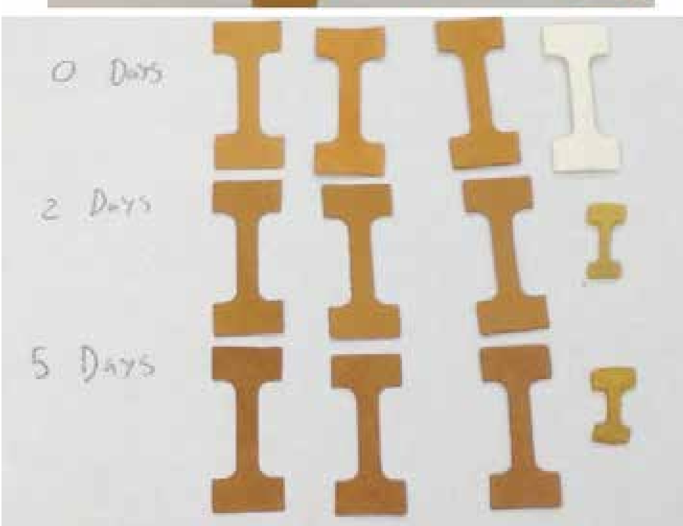


Figure 3. Pictures of the seven different vegetable tanned samples after aging prior to being tested in the tensile apparatus.

Quantitative results for tensile strength experiments are shown for the experiments in Figure 5-8. Three out of eight chrome leathers were too destroyed after five days to be tested. In Figure 5, the tensile strength was assumed to be zero for those samples that could not be tested and counted in the graphs for all samples while in Figure 6 only those samples that were not destroyed were included in the graph.

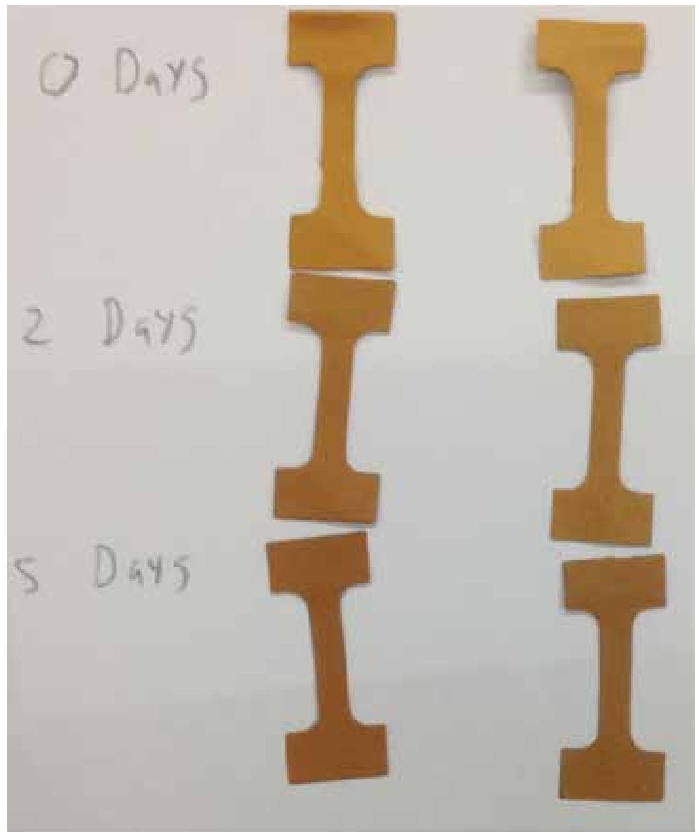


Figure 4. Pictures of the two different vegetable tanned samples after aging prior to being tested in the tensile apparatus.

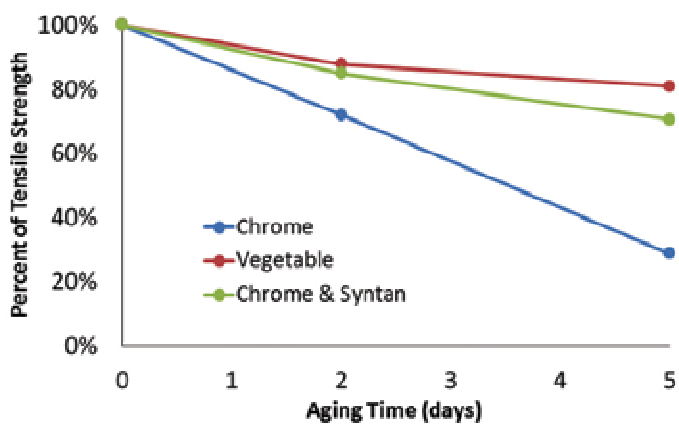


Figure 5. Averages of tensile strength retention (tensile strength after aging/tensile strength at time=0) for all samples tested at the three different times after aging started (time=0 corresponds to unaged samples). If a sample could not be tested, then the value was set to 0%.

The results from the replication of the Piltingsrud study (i.e. with SO_2) can be seen below in Figure 10.

Figures 11 and 12 show the results for the modulus, with Figure 11 the analogue of Figure 5 and Figure 12 the analogue of Figure 10. The behavior of the modulus with aging is not clear with no sulfur dioxide present, but is very clear (chrome-tanned samples are better) for the experiments mimicking the conditions of Piltingsrud and Tancous.

Discussion

Figures 5-9

The normalized tensile strength (100% is the value at time=0 which allowed for comparing all leather samples on the same basis) for chrome leathers decreased at a significantly higher rate

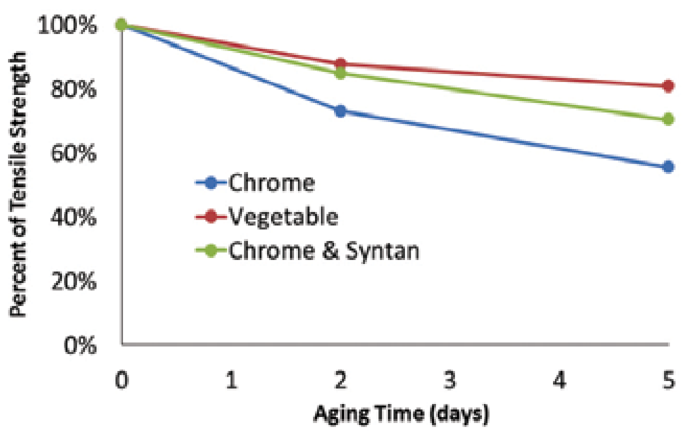


Figure 6. Averages of tensile strength retention (tensile strength after aging/tensile strength at time=0) for samples tested at the three different times after aging started (time=0 corresponds to unaged samples). If a sample could not be tested, this sample was not included in the average (which was the case for three chrome samples.

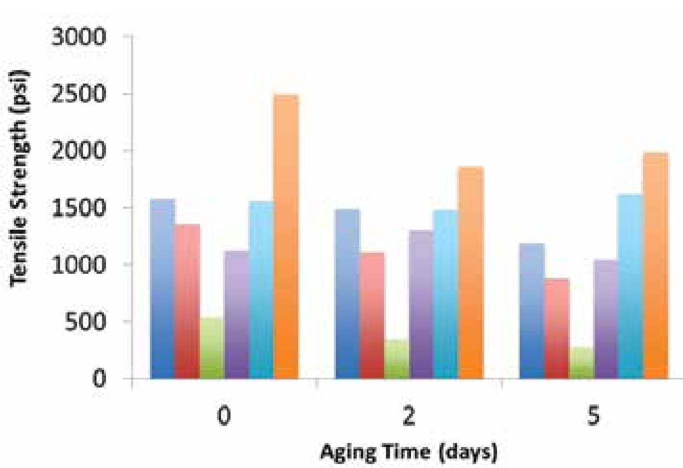


Figure 7. Tensile strengths of individual vegetable tanned leathers. The colors and order of the bars refer to the same leather. Specifically, starting from the left, all of the dark blues at 0, 2 and 5 days correspond to the same leather, while the reds correspond to the same leather etc.

than that of vegetable and chrome & syntan. Overall, the data is clear: vegetable tanning yields a leather that is able to resist aging in air better than chrome tanning.

Figure 10

One of our concerns was that there was some unknown factor that was influencing our results; for example, perhaps leathers were different 30 years ago in some key, critical aspect. The reductions at 5 days shown

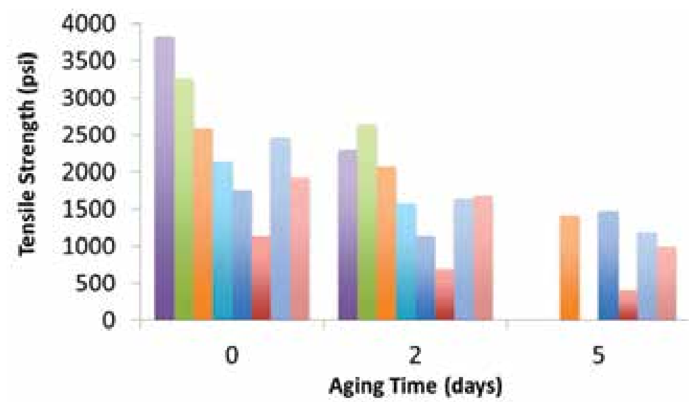


Figure 8. Tensile strengths of individual chrome tanned leathers. The colors and order of the bars refer to the same leather. Missing entries in day 5 are samples that could not be tested because the samples could not be loaded into the tensile machine without breaking.

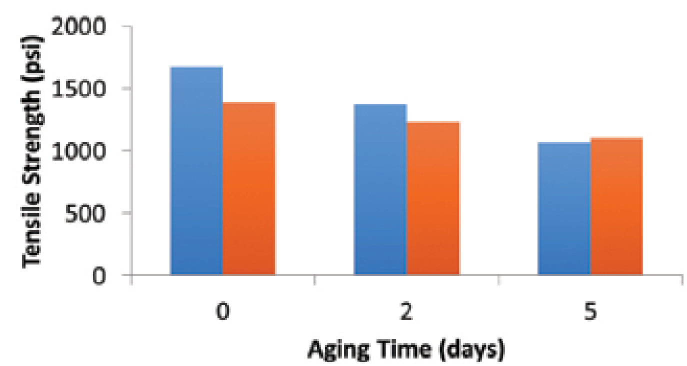


Figure 9. Tensile strengths of individual chrome tanned leathers. The colors and order of the bars refer to the same leather.

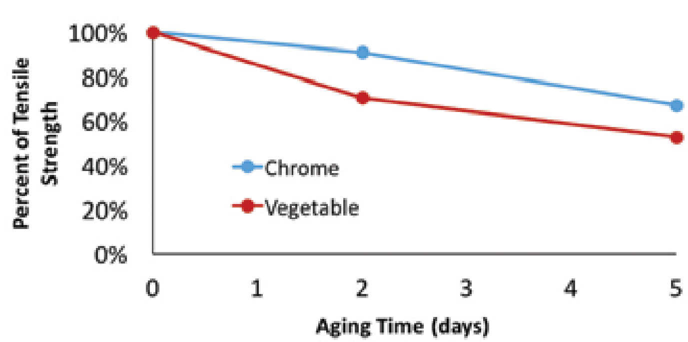


Figure 10. Averages of tensile strength retention (tensile strength after aging/tensile strength at time=0) for all samples tested in a manner that replicates Piltingsrud's experiment.[2]

in the graph essentially match those presented in the Piltingsrud and Tancous study. ***These results confirm the results determined by Piltingsrud and Tancous, namely that chrome tanned leathers lose less tensile strength when aged in an environment with significant amounts of SO_2 compared to the vegetable tanned leathers.***

Figures 11 and 12

Many materials will increase in modulus (stiffness) with aging, while others will decrease. Modulus is often termed the stiffness of the sample, and our experience certainly has been that leathers become stiffer with age. However, stiffness is usually ascertained by bending which is not at all the same as stretching (i.e. something that is harder to bend could be easier to stretch and vice-versa). Our results show that chrome samples maintain their moduli in the test done without sulfur dioxide better than vegetable tanned samples; however, we are not willing to draw any conclusions about the ability of the samples to not age given the small differences between the values. The chrome samples clearly maintain their moduli better in the case where sulfur dioxide has been added to the atmosphere. One interesting question is why didn't Piltingsrud and Tancous report modulus data as well; the data would have been available to them since measurement of tensile strength necessitates the measurement of the modulus.

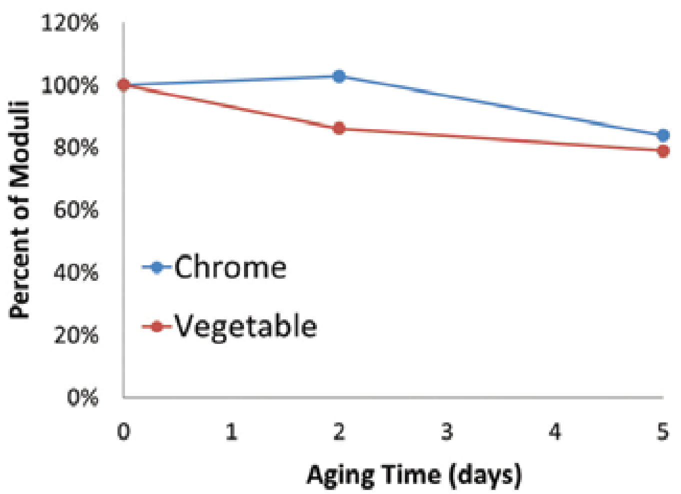


Figure 11. Averages of modulus retention (modulus after aging/ modulus at time=0) for all samples tested.

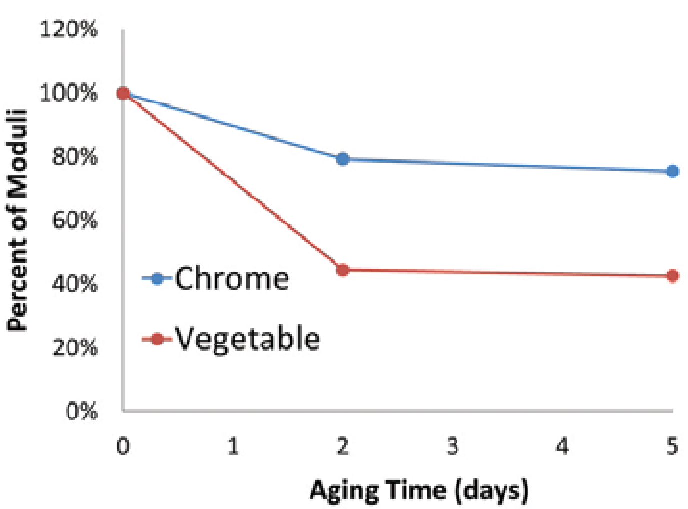


Figure 12. Averages of modulus retention (modulus after aging/modulus at time=0) for all samples tested replicating Piltingsrud's experiment.

Conclusions

Based on data displayed on charts correlating the percent of tensile strength over time, the tensile strength for chrome tanned leather decreased at a significantly higher rate than that of vegetable tanned and chrome & syntan tanned leather when samples were aged in air. At the end of the trial (five days), the tensile strength for chrome leather decreased by an overall average of 70% compared to 15% and 22% for vegetable and chrome & syntan leather respectively. Further, we replicated the testing procedure of Piltingsrud and Tancous and showed that with aging in SO_2, chrome-tanned leathers age at a lower rate vs. vegetable tanned leathers, which was the identical conclusion given by Piltingsrud and Tancous. The difference in the two results is due to the fact that SO_2 catalyzes the degradation reaction, and chromium likely captures the sulfur dioxide not allowing this gas to participate in degradation while in the case with just air, this catalysis is not occurring. Given the substantial efforts to improve air quality coupled with the removal of coal-heating in churches, these results indicate that vegetable-tanned leathers should give better performance than chrome-tanned leathers in nearly all situations.

Acknowledgements

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References

1. Piltingsrud, H. and Tancous, J.; "Aging of Organ Leather", Organ Historical Society, Richmond, VA, 1994.
2. Piltingsrud, H. and Tancous, J.; "The Development of a Standard Accelerated Aging Test for Measuring the Durability of Leathers Used in Musical Instruments", *JALCA*, **82**, 285-300, 1987.
3. Trommer, B., Schulze, A. and Hilsky G.; *JALCA*, **105**, 160-17, 2010.
4. Cheshire A.; *J. Int. Leather Trades Chem*. **30**, 134-140, 1946.