

The Accelerated Aging of Leather

1. Scope

1.1 These instructions are based on studies relating the rate of deterioration of leathers having known durabilities from long-term storage of samples, to the deterioration experienced by laboratory exposure of specimens to known contents of acid gases in air or oxygen. This is accomplished by measuring the deterioration (reduction in tensile strength) of leather specimens when they are subjected to exposure to a mixture of air, moisture and sulfur dioxide at a given temperature and pressure and for a given exposure time. The loss of tensile strength of the specimens resulting from this exposure is compared to that experienced by a variety of leathers having various tannages and having historically long and short service lifetimes. The initial tensile strength and the degree of loss of tensile strength is related to what service life can be anticipated from a given leather.

1.2 *These instructions do not purport to address all of the safety concerns, if any, associated with them. It is the responsibility of the personnel following these instructions to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.2 ASTM Standards:

D 1517 Standard Terminology Relating to Leather.

D 1610 Standard Practice for Conditioning Leather and Leather Products for Testing

D 1813 Standard Test Method for Measuring Thickness of Leather Test Specimens

D 2209 Standard Test Method for Tensile Strength of Leather

3. Terminology

3.1 For definitions of leather terms used in these instructions refer to Terminology D 1517.

4. Reagents

Sulfur Dioxide (SO₂), Anhydrous, 99.9% pure. Air: From compressor, filtered, stored at ~21°C (saturated water vapor conditions) 90 to 100 PSI delivery pressure.

5. Summary of the Practice

5.1 Specimens are prepared and placed in a pressure chamber containing known or constant quantities of air, moisture and SO₂. They are held in the chamber at a constant temperature for a given time period. After that processing, the tensile strengths of the specimens are measured along with the tensile strengths of unprocessed specimens of the same leather. The loss of tensile strength resulting from the processing relative to that of the unprocessed specimens (%) is determined and may be directly compared to that of other leathers considered for an application. Where applicable, the results may also be considered as the basis for projected service lifetimes as shown in part 11 (Interpretation of Results).

6. Significance and Use

6.1 A substantial difficulty in using leather in applications requiring very long service lives is estimating how well a particular leather will actually hold up in service. Such applications may include use in musical instruments such as pipe organs, bookbinding leathers, etc. Use of

leather in pipe organs in the past (prior to approximately 1930) demonstrated service lives frequently over 100 years, and the consequences of short service lives can result in extremely costly repairs. Many post-1930 leathers have had short service lives (as little as 15 years) due to the use of various more modern tannages and processing methods. Identifying exactly what tannage and processing was used in a particular leather and how successful this tanning and processing was can be very difficult. Failure of bookbinding and upholstery leathers formed the impetus for extensive work by leather chemists in the 1940's to identify tests that could be used to verify the durability of leather samples. Early studies by Cheshire¹ and Frey & Beebe² resulted in tests relating the rate of deterioration of leathers having known durabilities from long-term storage of samples, to the deterioration experienced by laboratory exposure of specimens to known contents of acid gases in air or oxygen. They were considered to be applicable to leathers having a wide range of tannages and processing. Later work published by Piltingsrud & Tancous³ described their modifications to those tests. Further work directed towards verifying the durability of leathers used in pipe organs resulted in the instructions described in this document. The appropriateness of its use for any given leather samples must be determined by the leather chemists utilizing the instructions. They may not be applicable for leathers having unusual tannages or treatments. Estimates of service lives made using these instructions are speculative, as it would take many decades of natural aging to verify the results (see comments in part 11).

7. Apparatus

7.1 The reaction pressure vessel (RPV) is made up of 316 Alloy Stainless Steel, Schedule 10, 3" pipe components welded together. These consist of two end caps (one end cap has a 1" hole in it), a 12" section of pipe, and a 1" NPT union (cut in 1/2). These are welded together using inert gas welding and alloy 316 stainless steel filler rod.

7.2 The RPV Valve: The valve used has 3/8" NPT threads and is made of alloy 316 stainless steel. It is a positive shutoff needle valve rated for pressures up to 1000 PSI. It is used with a 1" to 3/8" NPT 316 stainless steel reducer bushing.

7.3 RPV Pressure Gauge: The gauge used for measurements of pressure in the RPV and for filling measurements must have a range up to 125 PSI, and an accuracy of ± 2.0 PSI.

7.4 Die: Leather cutting punch type for test strip 1/4" wide by 2" long.

7.5 Oven: The RPV must be kept at a constant temperature throughout the exposure period of the test. This is best accomplished by placing the RPV in an oven having mechanical

¹ Cheshire, A., "The Aging of Leather," Journal of the International Leather Trades Chemists, June 1946, Vol. 30, No. 6, pp 134-166.

² Frey, R. W., and Beebe, C. W., "A Proposed Standard Gas Chamber for Accelerated Aging of Leather," The Journal of the American Leather Chemists Association, 1940, Vol. 35, pp 180-192.

³ Piltingsrud, H.V., and Tancous, J., "The Development of a Standard Accelerated Aging test for Measuring the Durability of Leathers Used in Musical Instruments," The Journal of the American Leather Chemists Association, 1987, 82 (9), pp 277-310.

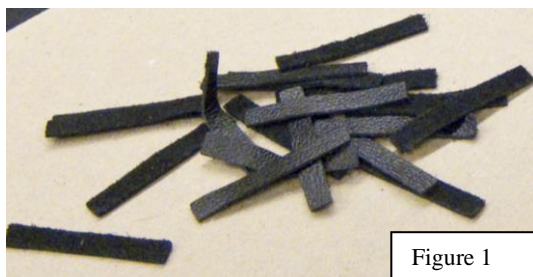
convection air circulation, and with an accurate electronic temperature control with the capability of maintaining a temperature of approximately ± 1.0 degrees C, and a uniformity of ± 4.0 degrees C. The uniformity isn't quite as important as the stability, as the thermal conductivity and thermal capacity of the RPV aids in providing thermal uniformity inside the RPV. The temperature calibration of the oven should be checked using a thermocouple thermometer. Many commercial laboratory ovens are capable of this performance.

7.6 Compressor-air storage tank system: A typical compressor-air storage tank system having a tank volume of at least 100L is quite sufficient. Make sure that there is some water in the bottom of the tank (normal for most compressor-air storage tanks that are operated frequently) so that air stored in the tank at room temperature comes to equilibrium near 100% relative humidity at laboratory room temperature. This helps to assure that the initial humidity in the RPV (Reaction Pressure Vessel) during runs is consistent run to run. **The day before the test is accomplished, the air source should be checked to assure that there is an adequate pressure to be able fill the RPV to 100 psi and that there is sufficient time before the run (at least 12 hrs) for the air in the tank to reach room temperature and humidity equilibrium.** The tank pressure is normally set to 120 PSI allowing sufficient pressure to regulate down to the desired 100 PSI in the RPV.

8. Specimens

8.1 Cut the specimens using 1/4 inch by 2 inch cutting die. Cut 15 samples for aging test if possible (see Figure 1). Cut another 15 specimens for control reference. Specimens need to be cut with the same orientation parallel or perpendicular to the backbone of the hide and in a similar location such that the specimens have similar properties. Leather should be conditioned in accordance with ASTM test method D1610.

8.2 Process only one type of leather in the RPV at a time.



9. Procedures

9.1 Assembly of the Reaction Pressure Vessel (RPV)

1. Make sure that no foreign materials are present in the interior of the RPV. If there are any residues present or you are not sure if the vessel is clean, use cleaning methods you would ordinarily use for stainless steel laboratory ware used for analytical chemistry purposes.
2. Make sure the interior of the RPV is dry by placing it in the oven (at 60 degrees C) for 15 minutes, without the valve installed. Cool the RPV to room temperature before placing specimens in it.
3. Place the specimens to be treated into the RPV.

4. Using Teflon tape sealant, prepare the valve head threads for assembly into the RPV. Make sure all old sealant is removed, using a stainless steel brush, before applying the Teflon tape. The Teflon tape is wrapped around the threads, several layers thick, depending on the thickness of the tape (see Figure 2). Methods used should result in leak free joints (see section on leak checking).

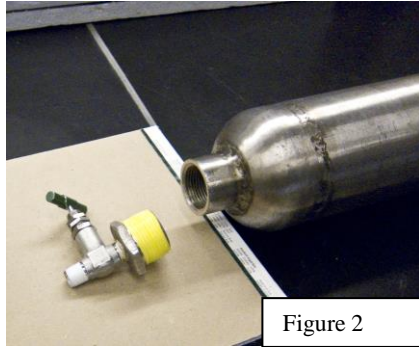


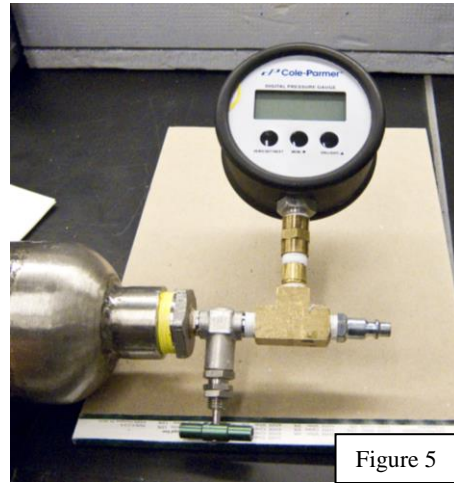
Figure 2

Insert valve head into the RPV. Threads must be tightened sufficiently so that there is no leakage when tested later by the soap bubble method. Normally tightening is accomplished by applying a locking chain clamp around the body of the RPV and a 12 inch crescent wrench on the 1 3/8 inch hex head of the valve head assembly (see Figure 3). Normally the assembly is placed on the floor and tightened as needed (as tight as an average person can tighten).



Figure 3

5. Attach the pressure gauge and the filling port (see Figure 4) to the top of the RPV valve using Teflon tape as a sealant (see Figure 5).



9.2 Filling the RPV with SO₂

1. Remove the quarter inch NPT plug from the SO₂ tank. Insert the mating connector into the threaded port on the SO₂ tank using Teflon tape as a sealant. Insert purging connector (a fitting that mates with the connector on the hose, and has a through passage allowing gas to escape) into the opposite end of the SO₂ filling hose.
2. Place the RPV, SO₂ tank and filling apparatus in a fume hood that has been determined to be suitable for working with the SO₂ used in this test. Open the SO₂ tank valve slightly allowing the SO₂ to purge the air from the interior of the SO₂ filling hose (see Figure 6).



Close the SO₂ tank valve and remove the purging connector from the SO₂ filling hose.

3. Connect the SO₂ filling hose to the filling port on the RPV, make sure the gauge reads zero before connecting to the SO₂ filling hose (see Figure 7).



4. Open the RPV valve completely (wide open) and slowly open the SO₂ tank valve so that you observe a pressure increase on the pressure gauge of approximately 1 PSI every 2 seconds. Allow the pressure in the RPV to increase to 14.7 ± 0.2 PSI. Then rapidly close the valve on the tank and the RPV.
5. Disconnect the RPV from the SO₂ filling hose.

9.3 Filling the RPV with compressed air

1. Briefly place a purging port in the compressed air tank outlet port to allow a small amount of air to bleed out of the tank. This will allow you to see where the pressure regulator is actually set in case there has been leakage through the regulator, building up pressure on the lower pressure side. Make sure that the pressure regulator is set several PSI below the 100 PSI desired setting so the pressure can then be raised up to the correct 100 PSI setting once the pressure gauge and RPV are connected.
2. Zero the pressure gauge.
3. Insert the filling port into the pressure tank outlet port and observe the pressure on the RPV pressure gauge (see Figure 8).

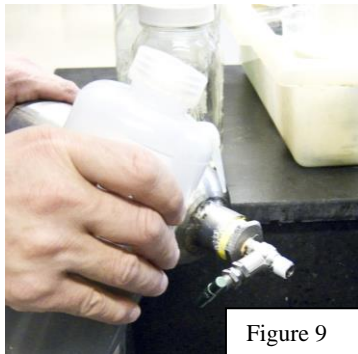


4. Slowly increase the pressure regulator pressure setting so that the pressure reading on the RPV pressure gauge is 100 PSI.
5. Open the valve to the RPV allowing the RPV to be fully filled to 100 PSI.

6. Close the valve to the RPV and remove the RPV from the outlet port of the air tank.
7. Remove the pressure gauge assembly from the RPV valve.

9.4 Leak checking

1. Use a soap water solution for leak checking. Apply soap water solution to the exposed threads of the RPV and the valve assembly (see Figure 9). Use a liquid dishwashing detergent diluted to approximately a 10% solution with water.



2. Carefully examine the bubble size for growth, which would indicate a leak.
3. With a drop of soap solution on your finger tip attempt to lace a soap water film over the exposed port of the valve. Any increase in the size of the film would indicate an internal leak of the valve. Any detected leaks should be corrected. Possible causes could be insufficient tread sealant, insufficient tightening of the joints, a defective valve, etc.
4. Apply new Teflon tape to the exposed threads on the valve and place the stainless steel cap on the valve outlet (see Figure 10).



9.5 Placing the RPV in the Oven

1. Preheat the oven to the desired operating temperature (60 degrees C) before placing the RPV in the oven. The oven can be any oven with forced air circulation that can maintain the RPV at 60 degrees \pm 1 degree C. Shown in the photos below (Figures 11 and 12) is a special purpose oven made for the task. Many laboratory ovens with forced air circulation should be sufficient.

2. Place the RPV in the oven as indicated in the photo and close the oven (see Figure 11 & 12).



9.6 Aging Process

1. The RPV is left at the desired operating temperature for 168 hrs. (one week).
2. The RPV should be rotated 180° every 24 hrs.
3. At the end of one week the RPV is removed from the oven and allowed to cool to room temperature. The stainless steel cap is removed from the assembly. Zero the pressure gauge and connect it to the valve outlet.
4. Open the valve and record the pressure reading. Pressure readings are taken before the RPV is placed in the oven and when it is removed, as a check to assure that the RPV has not leaked during the time in the oven. It is normal to see some drop in pressure due to the consumption of the reagent gasses in the RPV (oxygen and SO₂) reacting with the leather specimens in the RPV. Pressure drops up to 5% have been observed, depending on the mass of leather and the amount of chemically induced deterioration experienced by the leather.
5. Close the valve and remove the pressure gauge.
6. Vent the RPV gaseous contents into a fume hood.
7. Remove the 1 3/8 inch hex connector from the RPV.
8. While in the fume hood, purge the open RPV with compressed air to remove residual SO₂ and remove the specimens.
9. Leather specimens removed from the RPV are conditioned in the constant temperature constant humidity room (see ASTM D1610) for a minimum of 24 hours before tensile strength measurements are made.

10. Measurements of Tensile Strength

Tensile strength measurements of the specimens are performed using apparatus and procedures specified in ASTM D2209. Variation: Rectangular sample jaws with tape on sample holding surfaces were used to avoid cutting of thin leathers.

11. Interpretation of Results

Tensile strength measurements of the control specimens are averaged. Tensile strength measurements of the artificially aged (processed) specimens are also averaged. The percent loss of tensile strength for a sample is calculated by first dividing the average tensile strength of the processed specimens by the average tensile strength of the control specimens. This result is subtracted from 1, and multiplied times 100.

Often there is no historical data on a given type of leather representing its normal decrease in tensile strength with time, such as test data from long-term storage of samples of similar leathers. In such cases it may be appropriate to evaluate only the differences in the loss of tensile strength data among candidate leathers for a particular application. An example of this could be looking at only the loss of tensile strength for processed leathers seen in Figure 13, where samples Chr 1, Chr 2, and Veg 1 had losses of tensile strength resulting from accelerated aging processing of 16%, 25% and 67% respectively. If the leather samples are otherwise equal to each other in important qualities, the leathers having the lowest loss of tensile strength (Chr 1 and Chr2) would likely be the best choices for the application.

Estimates of anticipated service lifetimes of leathers for use in musical instruments have been made using data from samples analyzed using these instructions, by accepting certain assumptions. An example of this is shown in Figure 13, where tensile strength data is presented from before and after long-term natural aging of samples of leathers (24 years). Two of the samples are chrome-tanned hair sheep glove leather (leathers Chr 1 and Chr 2) typical of those presently used for pneumatic pouches in pipe organs. The third is a vegetable-tanned (Veg 1) leather commonly used for pneumatic pouches in pipe organs after approximately 1950 and pre-1990, and similar to those that typically failed after 15-25 years in service. When the samples were first tested in early 1990 they had tensile strengths as indicated in the graph at the 0 year point. Those samples were stored for approximately 24 years in a climate-controlled space similar to what might be found in the interior of a pipe organ, and were re-tested in early 2015 yielding the tensile strengths indicated at time 24 years. That gave a basis for how rapidly that leather deteriorates in natural aging (known durability). Assuming that the tensile strength loss was linear with time, a linear projection of the long-term storage data lines could be made to a value representing the minimum acceptable tensile strength for leathers used in the given application (for pipe organ small pneumatic pouch leather, 500 PSI is used) and the x-axis time at that point was read. Using that procedure, samples Chr1 and Chr 2 had anticipated service lifetimes of approximately 84 years and 110 years respectively from the time of their first tensile strength measurements in 1990 (time zero). Sample Veg 1 had a lifetime of about 25 years, consistent with experience with similar leathers. With the high starting tensile strengths of leathers Chr 1 and Chr 2 and the fairly slow loss of tensile strength observed in natural aging, these leathers are likely to have long service lifetimes similar to long-lived leathers of the past.

Specimens representing leather samples Chr 1, Chr 2, and Veg 1 were then processed using the accelerated aging test method, resulting in a further loss of tensile strengths of the leather specimens from those at the 24 year point. In order to estimate how much normal aging time the accelerated aging processing represented, the data points representing the tensile strengths after accelerated aging processing were placed along the extended graph line representing the loss of tensile strength due to normal aging. The normal aging equivalence (years) for the accelerated aging treatment was then estimated by subtracting the x axis time before the start of the accelerated aging test (24 years) from that for the x axis time position of the tensile strength data points for the processed leather at equivalent times of approximately 38 years for Chr 1 and Chr 2, and approximately 36 years for Veg 1. Subtracting 24 years from those values would result in a time equivalency for the accelerated aging processing of these

leathers of approximately 13 years. Estimated lifetimes for leathers in that class could be made using a linear projection of data lines from the accelerated aging data alone using the previously determined aging equivalency for the test. This would look much like Figure 13 if time zero years is placed where time 24 years is presently located.

Estimated lifetimes for leathers based on this treatment of the data are speculative. There is evidence that for some leathers the loss of tensile strength may have an exponential relationship with time (the rate of loss would decrease with time). If that were the case, the use of a linear relationship with time would be overly conservative.

12. Report

12.1 Average tensile strengths for control and artificially aged (processed) specimens are reported.

12.2 Indicate the orientation (parallel/perpendicular) to the backbone of the hide that the test specimens were cut.

12.3 Report average % loss of tensile strength.

Key Words

Fig. 13. Estimated Useful Life

