# Leather for Pipe Organs

## Summary of "Atmospheric Pollutants and the Deterioration of Leather"

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Leather deterioration is at topic of interest to leather scientists, producers and users. Test methods associated with leather longevity are valuable for any leathers where long-term durability is important. The "introduction" of this paper presents an historical review of research concerning the mechanisms involved in leather deterioration, with an emphasis on deterioration connected to atmospheric pollutants. Also presented are the results of experiments evaluating the effects of nitrogen dioxide (an atmospheric pollutant) exposures to test leathers and possible applications using such exposures in the testing of leathers for long-term use.

**Only with proper testing can leathers being offered to the industry be depended on. Since only chrome-tanned leathers are recommended, the following testing should be done:**

- **A tensile strength measurement**
- **A chrome content analysis (as chromium oxide)**
- **A shrink temperature test**
- **An acidity and difference figure test**
- **It would be advantageous to also have either the sulfur dioxide test or testing with exposures to nitrogen dioxide, however very few laboratories are set up to conduct those tests.**
- **The results of the tests along with an indication of acceptable ranges for each test should be made available to organ builders.**

### Introduction

Review of earlier deterioration of leather studies:

The review of past studies related to early failure of leather covered a time period from the mid-19$^{th}$ century to the end of the 20$^{th}$ century. As presented in the review of past research, much of leather deterioration in the past could be associated with sulfur dioxide (a pollutant gas) in the atmosphere. Past studies included many of the references in "The Aging of Organ Leather," but in many cases are examined in more detail than in that publication.

Included are some existing methods for testing various properties of leather that can give useful information about the results of leather tanning and the potential longevity of leather specimens. These include a description by R. M. Lollar of the "shrink temperature" test applied to leather and its meaning and importance. Shrink temperatures of leather samples are an indication of the quality of the tanning process for the given leather. Another test, the R. F. Innes "sample acidity and difference figures test" is used to determine the acidity of leather and the kind of acid (strong vs. week) present. This indicates whether unusually large amounts of acid are present and if these are of the "strong acid" types likely introduced during tanning. Significant amounts of strong acids could affect the longevity of the leather. These tests together with others can help form a picture of the leathers probable longevity.

### Nitrogen Dioxide and the deterioration of leather

The investigations by A. Cheshire and B. Haines mentioned the possibility of atmospheric nitrogen dioxide contributing to leather deterioration. During the first half of the 20$^{th}$ century

most nitrogen dioxide came from natural decay of organic matter and lightning. That changed as combustion of fuels for the production of locomotion and electricity increased, and usually involved higher temperature combustion which typically produced more nitrogen dioxide as a byproduct. The US Department of Health Education and Welfare (DHEW), the US Environmental Protection Agency (EPA) and other research records showed that sulfur dioxide in the atmosphere had been dramatically reduced in the time period from 1970 to 1990 due to the requirements of the US Clean Air Act. While oxides of nitrogen (primarily nitrogen dioxide) levels had dropped much less in that time period, they had plateaued after 2010 at levels of concern for leather longevity. In some parts of the world nitrogen dioxide levels are increasing. These facts supported the need for research concerning the potential effects of nitrogen dioxide on the longevity of leathers.

**Experimental Procedures**

We first decided what kinds of leather we needed to test and what kind of tests were needed. We decided that we should include some leathers with tanning methods that had proven very durable in historic pipe organs. Many organ builders in the early part of the 20$^{th}$ century used vegetable-tanned leather, leather tanning that used components of plants that had chemical contents that could stabilize hides, making leather. Many of those proved durable for well over 50 years. Very few tanners now supply vegetable-tanned leather. In obtaining test leathers, it proved nearly impossible for us to obtain vegetable-tanned leathers having well-documented tannages and with the variety of tanning desired. Consequently, we decided to make certain vegetable-tanned leathers in the laboratory. Those leathers started with hair sheep (a variety of sheep) hides from a single lot of hides. We tanned these with tara, valonia, mimosa, and bisulfited quebracho vegetable tanning agents. Those leathers were labeled LAB tara, LAB valonia, LAB mimosa and LAB quebracho. Other leathers tested included two commercially-produced vegtetable-tanned leathers, mimosa-tanned hairsheep, and chestnut-tanned goatskin. They were labeled Com. mimosa and Com. chestnut. We also included a chrome- tanned goatskin and a chrome-containing bovine (cow) embossed leather for auto applications. They were labeled Com chrome and Com. auto chrome. All of these leathers, except for the embossed leather, had no surface treatments such as glossiness or printed patterns. Nearly all leather now used in pipe organs are chrome-tanned. It should be noted that tanning methods attributed to the commercially-produced leathers were not completely verifiable. The commercial full chrome-tanned goatskin was fairly well documented.

We decided that the leather samples should be tested first using a method presently considered the most common longevity indicating test, the sulfur dioxide and compressed air test (sulfur dioxide test). The procedures followed an existing test practice, ASTM D8137-18, published by a leading standards organization, ASTM International. A description of that test practice is presented in a separate paper “Accelerated Aging of Leather.” A group of like samples were also exposed to known concentrations of nitrogen dioxide, and its effects were measured. That gave a comparison of results using the sulfur dioxide test to the nitrogen dioxide exposure results.

The experimental apparatus used produced a continuous flow of air with a known concentration of nitrogen dioxide and water vapor, at a fixed temperature. The deterioration of the leather samples (the loss of tensile strength) was quantified by measuring the tensile strength of the leather samples before and after test exposures. Tensile strength is the force, in pounds, required to tear a sample into two pieces. It is normally measured in pounds per square inch to compensate for the different thickness and widths of the leather samples. Dividing the after exposure tensile strength by the before tensile strength X 100 gives the percent deterioration. The

details of the construction of the apparatus and the method of calculating the results can be seen in the journal publication "Atmospheric Pollution and the Deterioration of Leather."

**Results and Discussion**

Below are the Data tables from that paper. $NO_2$ is nitrogen dioxide and $SO_2$ is sulfur dioxide.

Table I. Loss of Tensile Strength for Leathers of Various Tannages.

| Tannage | Initial Tensile Strength (PSI) | $SO_2$ 168h Aging Loss of Tensile Strength (%) | $NO_2$ 24h Aging Loss of Tensile Strength (%) | $NO_2$ 72h Aging Loss of Tensile Strength (%) | Chrome Content ($Cr_2O_3$ %) |
|---|---|---|---|---|---|
| LAB tara | 2474 | 47 | 47 | 74 | |
| LAB valonia | 3144 | 14 | 41 | 81 | |
| LAB mimosa | 3053 | 15 | 37 | 77 | |
| LAB quabracho | 2236 | 20 | 42 | 81 | |
| Com. mimosa | 4079 | 63 | 62 | 88 | |
| Com. chestnut | 1650 | 76 | 66 | 73 | |
| Com. chrome | 3584 | 46 | 32 | 50 | 3.8 |
| Com. auto chrome | 2863 | 34 | 16 | 36 | 2.5 |

TableII. Shrink Temperatures for Leathers of Various Tannages.

| Tannage | Initial Shrink Temperature (°C) | Shrink Temperature after $SO_2$ Aging (°C) | Shrink Temperature after $NO_2$ 24h Aging (°C) | Shrink Temperature after $NO_2$ 72h Aging (°C) |
|---|---|---|---|---|
| LRL Tara | 71 | 40 | 45 | 48 |
| LRL Valonia | 76 | 39 | 55 | 55 |
| LRL Mimosa | 79 | 39 | 52 | 50 |
| LRL Quabracho | 80 | 46 | 48 | 49 |
| Com. Mimosa | 77 | Sample Torn | Sample Torn | Sample Torn |
| Com. Chestnut | 77 | 54 | 47 | 46 |
| Com. Chrome | 108 | 63 | 64 | 56 |
| Com. Auto Chrome | 95 | 55 | 67 | 56 |

Table III. Acidity and Difference Figures for Leathers of Various Tannages Before and After Test Exposures.

| Tannage | Initial Acidity (pH) | Difference Figure | Acidity after $SO_2$ Aging (pH) | Difference Figure | Acidity after $NO_2$ 24h Aging (pH) | Difference Figure | Acidity after $NO_2$ 72h Aging (pH) | Difference Figure |
|---|---|---|---|---|---|---|---|---|
| LAB tara | 3.47 | 0.32 | 2.10 | 0.93 | 2.20 | 0.90 | 2.10 | 0.91 |
| LAB valonia | 3.50 | 0.54 | 2.31 | 0.85 | 2.12 | 0.99 | 2.11 | 0.91 |
| LAB mimosa | 3.50 | 0.47 | 2.40 | 0.83 | 2.19 | 0.84 | 2.21 | 0.82 |
| LAB quabracho | 3.43 | 0.54 | 2.38 | 0.88 | 2.23 | 0.95 | 2.17 | 0.91 |
| Com. mimosa | 2.80 | 1.08 | 2.12 | 0.84 | 2.21 | 0.94 | 2.20 | 0.91 |
| Com. chestnut | 3.62 | 0.61 | 2.26 | 0.95 | 2.33 | 0.96 | 2.15 | 1.19 |
| Com. chrome | 3.40 | 0.44 | 2.24 | 0.92 | 2.23 | 1.04 | 2.12 | 1.06 |
| Com. auto chrome | 3.63 | 0.25 | 2.15 | 1.02 | 2.29 | 1.07 | 2.21 | 1.13 |

You can see in Table 1, that the sulfur dioxide test indicated that some of the laboratory produced vegetable-tanned leathers were more resistant to deterioration than others. It could be that the LAB valonia, mimosa and quabracho leathers had some special chemical protection against sulfur dioxide exposure as a result of its tanning. The tara-tanned leather lost more strength than the others. Also the two commercial vegetable-tanned leathers, the mimosa and chestnut tanned leathers, had the least resistance to deterioration of all the leathers tested. The chrome-containing leathers had moderate tensile strength loss.

One might have expected the two mimosa-tanned leathers to have similar results since they both started with similar hair sheep hides and tanning agents. However, the commercial mimosa-tanned leather had over 4 times the tensile strength loss than the laboratory-tanned mimosa leather. **This shows how difficult it is to predict the durability of any specific leather without appropriate testing. Commercially tanned leathers can have a variety of unknown chemical and physical treatments that can be difficult to identify after-the-fact and that may affect the durability of the leather.**

There were two different exposure times for the nitrogen dioxide exposures to the samples, 24 and 72 hours. This was done because we weren't sure what the range of deterioration would be on the various samples. It can be seen that all of the vegetable-tanned leathers deteriorated significantly from the nitrogen dioxide exposures. The laboratory tanned mimosa had a little more resistance than the others. The low TS losses for the LRL valonia, mimosa and quabracho leathers with the sulfur dioxide test was not seen in the nitrogen dioxide exposures. Any protective agents in those leathers against sulfur dioxide exposures seemed ineffective against nitrogen dioxide exposures. The two commercial vegetable-tanned leathers again had the highest

losses of TS. For nitrogen dioxide exposures, the two leathers with chrome tanning had significantly lower deterioration.

We have speculated that the lower loss of TS of the commercial auto chrome-containing leather compared to the commercial chrome-containing goat leather may be due to the plastic-like surface treatment of the auto leather and/or an unknown components in the tanning of that leather. This difference decreased with the longer exposure time and became similar to the results with the 72 h sulfur dioxide test. It is possible that diffusion of nitrogen dioxide through the flesh side to the grain layer was more significant with the longer exposure time.

The shrink test is often used to give an idea of how well tanned a particular leather is. If the shrink temperature for a given leather falls within a certain range expected for a particular kind of tanning, it is considered to likely be properly tanned. **The initial shrink temperatures for the vegetable-tanned leathers had similar values, ranging from 71-80 $^0$C. Initial values for the two chrome-tanned leathers were much higher, ranging from 95- 108 $^0$C with the higher chrome content leather having the higher shrink temperature. These values were consistent with what would be expected for vegetable vs. chrome-containing leathers if they were properly tanned.** Such measurements may be useful as one of several tests for leather samples after tanning. It should be noted that the measurement of chrome content in a leather does not alone indicate that the tanning chemistry required to make the leather durable has happened.

Shrink temperatures for leathers after aging exposures were similar for the vegetable-tanned leathers, and substantially reduced from pre-exposure values, with the exception of the commercially-tanned mimosa leather. That leather was so weak that it tore apart with the slight tension on it in the testing apparatus. Shrink temperatures for the exposed chrome-containing leathers were similar and substantially reduced from pre-exposure values but higher than for the vegetable-tanned leathers except for the 72h nitrogen dioxide exposures. It is not clear how to relate the shrink temperature results for the exposed samples to potential longevity, as the leather has been chemically altered by the nitrogen dioxide exposure.

**All of the leathers with the exception of the commercial mimosa had moderate initial acid content, and the difference figures that indicated that the acids were organic acids. The values found for organic acids could be considered normal for properly processed leathers.** The commercial mimosa had higher acidity and its difference figure indicated a mineral acid as the predominant source of acidity. It is likely that acidity was produced in the tanning process. That initial acidity of that leather as well as its very poor shrink temperature suggest a tanning process leading to a shorter service life.

The data also shows substantial increases of leather acidity resulting from both sulfur dioxide and nitrogen dioxide exposures and with difference figures that indicated mineral acids, such as sulfuric acid and nitric acid. That would be an expected result from the sulfur dioxide and nitrogen dioxide exposures.

The acidity increase for the LAB valonia, mimosa and quabracho leathers exposed to sulfur dioxide was less than that for LAB tara. That may have been connected to the lower loss of TS

for those leathers and possibly indicated some special protective properties of the tanning. The acidity difference among those leathers was not as evident when exposed to nitrogen dioxide.

**Longevity Projections**

We performed calculations considering the nitrogen dioxide concentrations and exposure times for the test leathers in this study and what corresponding exposure times would be required for the same effect using present atmospheric nitrogen dioxide concentrations. We used data from **room temperature testing** of commercial chestnut-tanned goat leather using 24 h exposures at concentrations of 600 parts per million nitrogen dioxide in air. That resulted in a loss of TS's in the exposed specimens of 35%. **Comparing this to present nitrogen dioxide concentrations in the US (35 to 70 parts per billion in air), 47.6 and 23.8 years respectively of exposure would be implied for the same deterioration.** The data in Table I. showed that this same leather had the highest loss of TS for 24 h exposure to nitrogen dioxide at 60 $^{0}$C of any of the leathers tested. Many leathers, particularly those chrome-tanned, would require much longer exposure times or higher concentrations of nitrogen dioxide to achieve an equivalent deterioration. **The two chrome-containing leathers would lose approximately 35% of their initial TS in 95 and 48 years.**

**Conclusions**

The above history and studies using nitrogen dioxide have further supported the comments of earlier researchers in leather deterioration studies, that there is likely no single mechanism explaining the deterioration of leather. The mechanisms of leather deterioration dominant in the earlier 20$^{th}$ century from sulfur dioxide appears to be different from that from nitrogen dioxide. Nitrogen dioxide is a much more aggressive oxidizer than sulfur dioxide and it likely directly attacks the collagen in the leather. **Long-term exposure of leather to present concentrations of nitrogen dioxide in the atmosphere may produce significant deterioration of leather.** Nitrogen dioxide appears to be stable enough to diffuse through the collagen structure of leather, enabling oxidation of the collagen.

**In the present time pollutant concentrations can be quite local, even down to neighborhoods in large cities. The proximity to heavy vehicle traffic, or larger areas downwind of a power plant, a factory, or fossil fuel heating equipment could result in long-term exposures to leathers in pipe organs much above average concentrations in the region. While present sulfur dioxide levels are much lower than in the 20$^{th}$ century, deterioration of leather from atmospheric sulfur dioxide is only one route to that result. It appears that nitrogen dioxide exposure is the present problem. Present atmospheric concentrations of nitrogen dioxide likely have a significant deteriorating effect on leather. In the time frame for use in pipe organs (up to 100y) its effect is likely important. In pipe organ applications it would be prudent to choose leathers having an established resistance to deterioration from acid gases such as sulfur dioxide and nitrogen dioxide, as it is unknown what pollutant concentrations they will be exposed to.**

Some vegetable-tanned leathers had significant resistance to deterioration from sulfur dioxide. However, that could be seen in our study only for the laboratory tanned leathers. The importance

of that for the pipe organ industry is minimal, since their commercial availability is minimal. Chrome tanned leathers also resisted deterioration from sulfur dioxide, and are commercially widely available. When examining resistance to nitrogen dioxide, the vegetable-tanned leathers had lower resistance to deterioration than chrome containing leathers. **It appears that full chrome-tanned leathers that are properly tanned are the best choice for use in pipe organs based on their resistance to deterioration and their commercial availability.**

The nitrogen dioxide test might be a more rigorous and/or pertinent test for leather durability considering the present atmospheric pollutant concentrations. While sulfur dioxide may not represent the most prominent path to the deterioration of leather in the present, it may be considered to be a useful means for testing leather durability where the indirect route to oxidation of collagen is being evaluated. The sulfur dioxide test is probably an easier test to administer in a laboratory. Consequently, it could be a good choice for ranking leathers as to their likely durability when they contain chrome but have unknown tanning.

**The results of the tests performed indicated that commercial leathers cannot be relied on to have the long-term durability that pipe organs demand without adequate testing.**

**Only with proper testing can leathers being offered to the pipe organ industry be depended on. Since only chrome-tanned leathers are recommended, the following tests should be done:**

- **A chrome content analysis (as percent chromium oxide, $Cr_2O_3$)**
- **A shrink temperature test**
- **An acidity and difference figure test**
- **It would be advantageous to also have either the sulfur dioxide test or testing with exposures to nitrogen dioxide, however very few laboratories are set up to conduct those tests.**