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Atmospheric Pollutants and the Deterioration of Leather

Abstract

Leather deterioration is a 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 exposures to test leathers and possible applications using such exposures in the testing of leathers for long-term use.

INTRODUCTION

Review of earlier deterioration of leather studies

This study was initiated to extend knowledge concerning the deterioration of leather from a variety of atmospheric chemicals. We first present a review of work done by other investigators concerning the premature deterioration of leather, as background to our recent experimental work.

In the early 20th century leather chemists in multiple countries begin to address the premature deterioration of leather and developed testing methods attempting to identify leathers that were more long-lived than others. They also developed theories as to the mechanisms of deterioration. Those investigations often centered on bookbinding and upholstery leathers due to the expectations of longevity associated with those applications. For book bindings much information was easily available by observing the condition of book bindings in libraries, with age of the bindings often available. The conditions of the storage environment were frequently evident and in some cases atmospheric pollutants were measured. Often the 'samples' were stored with numerous similar items under almost identical conditions over periods of many years. The first evidence of a deterioration pattern was seen in the early 20th century when book bindings in libraries in various locations in England were compared. It was evident that rapid deterioration occurred in situations where outside air in urban locales circulated through storage areas, and it seemed evident that the use of coal gas illumination contributed to deterioration. Both of these factors correlated well with R. F. Innes comments regarding observations much earlier by Michael Faraday in 1843 'who was consulted by the Athenaeum Club on the rotted condition of their leather upholstered armchairs. He attributed this decay to the sulfur compounds in the coal gas supplied for illumination'.[1] In the early 1930s Innes developed a wet phase testing method for bookbinding leather durability whereby leathers were wetted with hydrogen peroxide and sulfuric acid and dried. The results were in general agreement (for vegetable-tanned leathers) with deterioration experienced with aged book bindings. This eventually led to a specification by many libraries that leathers used for bookbinding must be certified to pass the 'Innes' or Printing Industry Research Association (PIRA) test.[1]

In 1934, R. W. Frey and C. W. Beebe of the United States Department of Agriculture developed a test for the durability of leather by producing accelerated aging in a gas chamber. This was accomplished by the exposure of leathers to the fumes produced by burning sulfur containing fuel. Unlike the Innes test, this was a test of leathers in a dry state. In 1940, they published a description of a standard gas exposure chamber utilising these principles.[2]

In 1946, A. Cheshire published an extensive manuscript presenting theoretical and experimental models for the deterioration of leather.[3] His research identified significant deficiencies in the tests developed by Frey, Beebe and Innes. These included a lack of knowledge as to the exact chemical species of sulfur compounds present in the exposure gas (certain short-lived species could have significant effects on the test outcome) and the actual concentrations of the sulfur compounds in the exposure gas. Regarding the Innes test, Cheshire stated that it would correctly predict leather durability only in the cases where the wet oxidation of leather was compatible with the tanning agent. Certain tanning agents, such as chrome compounds, did not stand up under wet test conditions but were excellent under dry test conditions. The metric for deterioration was loss of tensile strength (TS) or remaining TS after exposure to test conditions.

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Regarding Cheshire's chemical models for leather decay he stated 'it cannot be expected that ageing results from one cause only.' 'There are several ways in which oxygen of the air can be brought into the active state in which it becomes capable of oxidising such materials as the tannins.' He listed as possible sources: ozone, hydrogen peroxide, nitric oxide, hypochlorous acid, chlorine and its oxides, atomic (ionised) oxygen (*O) and sulfur dioxide in the presence of strong acids at high concentrations. In 1946 ozone and nitric oxide were not present in the atmosphere in significant concentrations.

Cheshire described several ways by which H_2O_2 can be present in leathers including the following: from the atmosphere (originating in combustion); by means of surface chemistry on collagen in the presence of light or with the presence of strong acids; peroxygen may 'give rise' to H_2O_2 when in the presence of H_2SO_4; some phenolic substances found in certain tannins may oxidise proteins directly or with the production of H_2O_2, and oils present in the leather may auto-oxidise accompanied by the formation of H_2O_2. He mentioned that H_2O_2 is preferentially adsorbed on the collagen surface, displacing H_2O. He said that in some cases tannins can accept oxygen, resulting in the collagen being attacked by reactive HO free radicals.

Cheshire presented a model for wet oxidation whereby acidic conditions are first created in the leather by the adsorption of atmospheric SO_2 and with surface chemistry on the collagen fibrils, the creation of SO_3 which in the presence of H_2O created H_2SO_4. He mentioned that it is possible that *O present at the collagen surface during this process could directly oxidise collagen. In the wet state hydrogen peroxide is decomposed aided by the presence of iron catalysts in the leather. He said 'the most effective general catalyst is the one usually found in both tanning materials and in pelt, namely iron in an acid-soluble form.' This decomposition oxidises the leather 'hide substance which loses its fibrous structure as a result.' He postulated a similar model for the dry state where surface chemistry with O_2 can create peroxygen reacting with SO_2 to create SO_3 and atomic oxygen, with the possible direct oxidation of collagen. In the presence of H_2O the SO^3 is converted to H_2SO_4.The decomposition of H_2O_2 most likely takes place by surface chemistry in an acidic environment, whereby *O is created, oxidising the collagen. He stated it is also possible that some solid iron compounds may also act as catalysts in the dry state.

As chemistry may vary between wet *vs.* dry conditions in the leather, some tannins may have different protective effects for the leather depending on whether the leather is wet or dry. He pointed out that certain materials present in the leather may help to protect it and that calcium oxalate present in some leathers, such as sumac-tanned leathers, appeared protective. He said that the calcium oxalate and oxalic acid present could complex the iron making it ineffective as a catalyst, and that they can also act as an antioxidant.

Cheshire showed the results of the testing of leathers having a variety of tannages. These included: leaf sumac, chestnut extract, syntan (Neosyn W. P.), myrabolam, mimosa, sulphited quebracho, gambier, and acidified mimosa. Many of these leathers were tanned in their laboratories, consequently the tannages were known and documented. He presented data from a variety of tests on leathers. These showed that the various testing methods produced different losses of TS for the different tannages, particularly between tests done wet and those done dry. The testing methods included:

(1) 72 hours at 20°C, 1ml N. H_2SO_4 & 0.6ml 30% H_2O_2 per g leather;
(2) 72 hours at 40°C over 96% H_2O_2;
(3) 17 days at 40°C over 100% H_2SO_4;
(4) 15 hours at 100°C in air after drying in air with 5% H_2SO_4;
(5) 14 days at 100°C in air;
(6) 9 days at 20°C in vacuum over H_2SO_4 after addition of 5% H_2SO_4;
(7) 17 days in air at 20°C after drying with addition of 5% H_2SO_4;
(8) 4 days at 40°C in O_2 at 100PSI after addition of 5% H_2SO_4 and drying;
(9) 17 days at 40°C over 96% H_2O_2 and 100% (fuming) H_2SO_4 (oleum);
(10) 16 weeks in gas chamber at 115°F;
(11) 4 weeks at 40°C in O_2 at 100PSI;
(12) 18 days over 20% oleum after vacuum drying.
While space limits inclusion of the data resulting from those tests and Cheshire's interpretations, readers having a special interest in this are encouraged to read Cheshire's work (reference 3).

Cheshire stated 'It has been shown that oxidation of the catechol tannins leads to increased acidity and that leathers tanned with pyrogallols such as sumac or myrobolam tend to lose acidity upon exposure to ultra-violet light or to heat and air. A similar effect is observable in the gas chamber and it is to be anticipated that much of the deterioration which occurs during that treatment is due to oxidation rather than a direct effect of sulfuric acid either as a hydrolytic agent or a dehydrant.'

Cheshire seemed inclined to favour the gas chamber test results, even though the method had its faults. In the final section of his 1946 paper 'The SO_2 and O_2 Bomb Test for Durability' Cheshire proposed a more standardised and rapid dry test method intended to supplement or replace the gas chamber method. This consisted of placing leather samples in a container with reagents of one atmosphere sulfur dioxide and six atmospheres oxygen at 40°C. The temperature was chosen to be near what could be present in normal aging, such as in the heat of the sun. The length of the exposure was one to two weeks as compared to over three months for the gas chamber method of Frey and Beebe. He stated that this 'method depends upon the theory of oxidation which requires the conversion of SO_2 to SO_3, or of H_2SO_3 to H_2SO_4 to take place upon

the surface of the leather with formation of *O as the intermediary in oxidation of the leather. Cheshire indicated that this had some consistency with Innes comment that 'the rotting of leather is caused by oxidation, and this action can only take place in the presence of sulfuric acid.' His earlier experiments with O_2 alone at 100PSI and 40°C showed little effect.

Cheshire said that 'water is more strongly adsorbed by surfaces such as charcoal, silica gel than are SO_2 or O_2 so that they will displace only a small part of the moisture bound to leather in the ordinary circumstances of aging. On the other hand, sulfuric acid is more strongly bound than water upon collagen, the heat of wetting being some 2.5 times as great... resulting in lower moisture for leathers which have picked up sulfuric acid. ...Damaged leathers usually possess lower water contents than undamaged.' Preliminary results with Cheshire's new O_2 and SO_2 test correlated well with the gas chamber tests for the leathers tested, showing sumac to have the least loss of tensile strength and with mimosa and sulfited quebracho losing the most. The same was true in the new method with sumac and full chrome tannages showing no effect. Cheshire commented that 'chrome tannage is of importance since the tannage does not admit of swelling and it is probable that few reactive groups remain on the collagen as witnessed by the abnormally high shrinkage temperature of this tannage.'

Cheshire mentioning that elastin had a greater resistance to oxidation in the wet state and likely so in dry oxidations. He said this explained why the grain layer often retained part of its strength when layers beneath suffered more degradation.

In 1948 Innes, in his chapter in 'Progress in Leather Science: 1920-1945'[1] had the following comments regarding the deterioration of leather:

1. 'The principal constituent of old leather which has rotted, as contrasted with old sound leather or with new leather, is sulphuric acid.'

2. The work has confirmed that, when untreated with protective salts, pyrogallol-tanned leathers resist decay better than catechol-tanned leathers, and he attributed that to pyrogallol leathers containing 'naturally occurring salts derived from the tanning material.'

3. Tests on vegetable-tanned leathers using the Innes test and the gas chamber test gave similar results.

4. The work has confirmed that salts added to leather greatly increase its durability, and the use of potassium citrate or lactate avoids the risk of salt spue.

5. Vegetable-tanned leathers re-tanned with alum or chromium sulphate had improved durability, with alum providing superior durability.

6. An impermeable finish, such as nitrocellulose or shellac, improves durability.

7. He stated that 'rotting must start as a hydrolysis of the protein fibre accompanied by an oxidation.'

Innes showed that leathers with a protective top coating such as nitrocellulose or shellac absorbed practically no acid. In one experiment with exposure to 'a sulphurous atmosphere,' a coated leather lost only 11% of its TS, and the uncoated leather lost 71%. He also said that 'the bulk of the evidence thus shows that grease up to the amounts usually found in practice has no preserving effect.' In an addendum to his chapter he mentioned Cheshire's tests in using SO_2 and O_2 in a pressure vessel were under test at the laboratories of the Research Association.

In 1954 R. Lollar presented a review of past work on the deterioration of leather.[4] His review include the following observations:

He referenced the work of Cheshire several times, and stated 'Cheshire has published an extensive review of previous work on the aging of leather and has extended our knowledge of the subject through some very ingenious research.'

Lollar stated that 'The fundamental form of almost all leather deterioration is a hydrolysis of the protein-tannin complex,' where water causes the rupture one or more chemical bonds. He also mentioned that 'leather is a heterogeneous system and that its resistance to deterioration is the result of many factors combined.' This was similar to Cheshire's comment that 'it cannot be expected that ageing results from one cause only.'

He also said that collagen is a relatively inert protein, but it possess many points of chemical or biological activity, such as the charged groups due to terminal amino, carboxyl or other polar groups as well as the peptide links of the protein backbone. Basic chromium salts comprise the bulk of the mineral tannages, although salts of iron, aluminum, and zirconium and certain phosphates have been shown to have tanning action.

Regarding the hydrolytic stability of leather, Lollar said:

1. Chrome tannages are completely reversible if the system is a closed one so that the acid balance is not changed irreversibly.

2. The acid uptake by the skin is an integral part of a chrome tannage system and if the acid is displaced irreversibly, the tannage will be irreversibly modified, even though actual chrome removal does not occur.

3. Many compounds or ions can exert a detanning influence upon chrome tanned leathers. Whenever chrome-tanned leather is modified so that the pH of its water extract lies outside the range of 3-5, it loses stability at an accelerated rate. Ordinary wear may bring about such conditions.

4. Vegetable tannages are perhaps less stable than chrome tannages.

Regarding shrinkage temperatures, Lollar stated that 'the shrinkage temperature of leather may be defined as that temperature at which leather, when heated in an aqueous bath, undergoes sufficient deterioration to exhibit a perceptible diminution in length and width. This shrinkage is not fully understood, but it may be observed that it is at least partially a form of hydrolytic deterioration. The shrunken leather, especially if the tannage is relatively poor, will have lost all of its leather characteristics and may have been gelatinised. Some researchers ascribe the increased shrinkage temperature due to tannage, to the stabilising cross

bridges which the tannin has formed in the collagenous main-chain network. Shrunken leather would then represent the result of hydrolytic rupture of these stabilising cross links.' Lollar also mentioned his experiments with vacuum desiccated leathers heated in the absence of water. They showed shrinkage temperatures up to 50°C higher than when done in water. They also showed that chrome tannages heated in mineral oil (a non-aqueous media) did not have their shrinkage temperature increase.

Shrinkage temperatures are often looked to as both an indication of the completeness of tanning as well as the stability of a tannage. As Lollar stated, the mechanisms are not fully understood and it is unclear as to how well it represents a leathers resistance to deterioration by means other than hydrolysis.

In 1956, a report was published by Beebe, Frey and Hannigan of the USDA Eastern Regional Research Centre comparing the results of various accelerated aging tests with long-term storage tests for book bindings.[5] Included were 24 samples tanned via vegetable-chrome, full chrome, full vegetable, and vegetable-alum processes and exposed to atmospheric pollution over time periods of 12 to 19 years. The samples were evaluated using the 'Innes' test, an oxygen bomb test (developed at the National Bureau of Standards and similar to one tried by Cheshire, which he found to be unreliable), and the Frey-Beebe 'gas chamber' test method. They concluded that the Frey-Beebe gas chamber gave the most reliable correlation to the long-term storage test, and that chrome-tanned leathers deteriorated very little. Further, the data indicated that the higher the chrome content (at least up to 4.0 percent chrome Cr_2O_3), the better the protection. Vegetable-tanned (chestnut and sulfited quebracho) leathers with alum retanning also performed very well, as did vegetable tanned samples with a chrome re-tannage (3.0 percent as Cr_2O_3). They thought that oxidation as well as hydrolysis caused the deterioration.

In 1969 R. G. H. Elliot published a review manuscript concerning past work on long-term durability tests.[6] He mentioned that the inspections of the long-term storage book bindings in the British Museum Library and the National Library of Wales made in 1950-1965 (reported by the British Leather Manufacturers Research Association) concluded that (a) the leathers tanned with chromium salts or hydrolysable (pyrogallol) tans were more durable than those tanned with condensed (catechol) tans; (b) the addition of salts increased the resistance to decay of leathers tanned with either type of vegetable tans; (c) the incidence of decay was much greater among the book bindings in London. He referenced several reports by others indicating good durability of chrome-tanned book bindings.

In 1977 B. M. Haines published a manuscript concerning the deterioration in leather bookbindings.[7] She stated that 'It must be remembered that leather technology is constantly changing and new products can be used to obtain a certain desired character in the leather but their influence as far as long-term durability is concerned is not known. There is little commercial interest in extremely long periods of durability as the market is so small.' She indicated that the long-term durability of 19th century leathers was linked to the lengthy liming of the hides, the retention of calcium salts in the skins and the buffering action of those salts. Present tanning methods remove nearly all of the calcium from skins. Regarding bookbindings, she stated 'Deterioration appears to depend on acid conditions within the leather.' At the end of the long-term storage trial the sound leathers were at a pH greater than 2.8 and the rotted leathers at a pH of 2.5 or below. Consequently, it is essential that a binding leather should at the outset have a pH above 3.5.' The inclusion of buffer salts will serve to maintain this pH level. She concluded that for bookbindings, the principal path of deterioration was oxidation of collagen. She added that the addition of buffer salts should not occur without considering their reaction with the tanning agents present and that they could un-tan chromium tanning agents. She said 'The generally better performance of untanned and chrome tanned material indicates that some vegetable tans play a definite and positive role in the degradation process.' She said that by 1970 after 35 years of storage, the long-term storage test of bookbinding leathers concluded 'the P.I.R.A. test has shown to be an unreliable guide as to long-term durability.' She mentioned that in addition to SO_2, atmospheric ozone and oxides of nitrogen are possibly involved in the deterioration of leather.

In the 1980s Piltingsrud and Tancous reviewed Cheshire's work with his SO_2 and O_2 test for durability and decided that its routine application as a test required some changes.[8] Cheshire's use of six atmospheres of pure oxygen with combustible materials appeared to be too dangerous for routine laboratory use, even though Cheshire did include an aluminum rupture disk in his design in case an explosion occurred. They chose to reduce the oxygen concentration to the 21% present in ambient air and to raise the reaction temperature to 67°C to achieve the desired reactivity. A modification of that test method was later included as part of an ASTM Standard Practice.[9] Significant changes incorporated in the ASTM Standard Practice were to reduce the exposure temperature to 60°C and to use of an exposure time of 72 hours.

Leather chemistry in the latter part of the 20th century and to date in the 21st century has advanced in its understanding of the structure of leather collagen and its interaction with tanning processes and tannins. Vegetable tanning is believed to result largely from hydrogen bonding of tannin phenolic OH groups with peptide C=O and NH polar side chains.[10] Recent research suggests that tanning with chromium sulphate is more complex than earlier thought.[11] A. Covington *et al.* have proposed that chromium (III) is covalently bound at carboxyl sidechains of collagen microfibrils and that the sulphate ion is not directly bound to the chromium. Instead, the triple-helix microfibrils are surrounded by 'a supramolecular water sheath

nucleated at the hydroxyproline sidechains' and that the chromium (III) and the sulphate ion' create a matrix with that structure. Covington mentioned that a high shrinkage temperature can be achieved only by tanning with at least two conventional components, with the primary tanning agent locked in place by a secondary tanning agent. It suggests that he considered the sulphate ion as a secondary tanning agent in chrome tanning. This model also seems to correlate well with previous experiences with certain combination tannages and their resistance to artificial aging. These recent models of tanning may also result in new, more stable tannages.

A 21st century view of atmospheric pollutant gases

In the early 20th century SO_2 played a large part in leather deterioration in urban centres. In British libraries at that time SO_2 levels varied considerably, depending on the location of the library and the isolation of the library rooms in a building. Innes, in his 1948 report, mentioned that SO_2 in London air never exceeded 1ppm. In one library in the heart of London, pollution was very low. The library had no windows and very little ventilation. Books stored there had little deterioration with age. Books in libraries with 'freely opened windows' had bookbinding decay in 'a comparatively short time.' In the present time pollutant concentrations can be quite local, even down to neighborhoods in large cities. Higher concentrations are often associated with proximity to heavy vehicle traffic, a factory, fossil fuel heating plants or large areas downwind of power plants. Consequently, average concentrations over a large area for a particular pollutant may not correlate to the deterioration of leathers used in a particular location in that area. In many applications it would appear prudent to choose leathers having an established resistance to deterioration, as it is unknown what pollutant concentrations they will be exposed to. While present large area SO_2 levels are much lower than in the 20th century, SO_2 levels in a particular location where leather is used and requiring long-term durability, such as in a pipe organ, may have SO_2 levels that contribute significantly to shortening its lifetime.

NO_2 and the deterioration of leather

Cheshire[3] and Haines[7] mentioned that atmospheric ozone and NO were possible pollutants that could cause deterioration of leather. At the time of Cheshire's publication in the 1940s he stated that nearly all ozone present was created in the stratosphere and brought to ground level through 'air currents' whereby it could decompose in sunlight freeing *O. He said that it was suggested by others that ozone might prove a useful reagent for testing the resistance of leathers to oxidation but that unless the ozone is produced at the leather (collagen) surface, no reaction would occur likely to degrade leather. Due to the extreme reactivity of ozone it is likely that most of it would react with materials at the surface of the leather, with little remaining to diffuse through the leather matrix and react with collagen within the leather. He said NO was present in the atmosphere in small amounts resulting principally from thunderstorms. When Haines mentioned ozone and oxides of nitrogen in 1977, those had become significant pollutants.

USDHEW data for the Los Angeles area show SO_2 concentrations in the 1960s of up to 100ppb, and with some areas in the US of up to 790ppb. Rapid reductions in SO_2 followed the implementation of the 1970 Clean Air Act[12] and further reductions came after amendments to the Clean Air Act in 1990. This resulted in US national average concentrations (based on daily max. 1 hour average over many sites) down to 165ppb in the early 1980s and present day values of less than 10ppb.[13] Up until the 1990s SO_2 was a major contributor to acid rain. As SO_2 levels decreased NO_2 became a major contributor. Natural production of NO_x from decaying vegetation, lightning, volcanos and the oceans as well as its production in high temperature combustion in transportation, power production and heating produces significant quantities of NO and NO_2 in the atmosphere.[14] The US national average concentration in 1980 was approximately 115ppb and in 2020 40ppb.[15] While US SO_2 levels dropped considerably since 1980 (approximately 94%), NO_2 levels dropped by approximately 64% and unlike SO_2 have leveled out since 2010.[16] While US and western European levels of SO_2 and NO_2 have been lowering, progress has not been as good in East Asian countries. Between 2005 and 2014 China had increases of 20-50% in NO_2 concentrations, however some urban areas had reductions.[17] Considering that NO_2 levels have been plateauing in the US at significant levels, we considered it useful to explore the effects of NO_x on leather.

EXPERIMENTAL PROCEDURES

In order to explore the effects of NO_2 on leather, it was desired that leathers having a variety of tannages be tested with exposures to NO_2, and also tested with some previously established methods. Tests included initial TS measurements following ASTM D2209-00,[18] TS losses after exposure to SO_2 with compressed air (SO_2 test),[8,9] and TS losses after exposures to NO_2 in air for 24 and 72 hours. The SO_2 test was included to compare results from a test presently used as an indicator of leather longevity with results from the NO_2 exposures. TS measurements were based on the use of approximately 10 specimens of a given leather, and the reported TS values were the mean values of the applicable groups of specimens. TS measurements typically had standard deviations of approximately 10% of the mean of the measured values and with a standard error of the mean of 3%. The specimens were die-cut parallel to and at least 25mm from the backbone of the leather side. Specimens were 9.5mm x 63mm or 6.4mm x 50.8mm. Sample acidity and difference figures (developed by R. F. Innes to detect strong *versus* weak acids[1]) were measured for each of the test leathers before and after each of the test treatments,

following ISO 4045:2018 (E).[19] Sample shrinkage temperatures were measured for each of the test leathers before and after each of the test treatments following ASTM D6076-08.[20]

It proved nearly impossible to obtain certain vegetable-tanned leathers having well documented tannages and with the variety of tannages desired. Consequently, we produced some vegetable-tanned leathers in a laboratory. Those leathers started with hair sheepskins (HS) from the same lot of skins, tanned with tara, valonia, mimosa, and bisulfited quebracho tannins. Other leathers tested included commercially-produced mimosa-tanned HS, chestnut-tanned goatskin, full-chrome-tanned goatskin, and a chrome-containing bovine embossed leather for auto applications. All of these leathers, except for the embossed leather, had no surface treatments. It should be noted that tannages attributed to the commercially-produced leathers were not completely verifiable. The commercial full-chrome-tanned goatskin was fairly well documented.

The laboratory-tanned leathers (LAB) used the following materials and procedures:

The skins to be tanned were small de-limed HS. They were first pickled, as follows:

Water equal to 40% of the mass of the wet skins was added to a small rotating drum.

Sodium chloride equal to 8% of the mass of the wet skins was added.

Formic acid equal to 1.5% of the mass of the wet skins was added.

That mixture was run for 30 minutes.

Sulfuric acid equal to 0.4% of the mass of the wet skins was added.

The pH of the liquid was verified to be between 2.2 and 2.4.

That mixture was run for 30 minutes.

The liquid was drained from the skins, completing the pickling process.

Tanning took place in four 2L tumbler cylinders having approximately equal wet masses of skins in each and a different tannin in each.

Water equal to 300% of the mass of the wet skins was added to the cylinders.

Tannin equal to 10% of the mass of the wet skins was added.

The mixture was run for 2 hours at 10-12rpm.

Tannin equal to 20% of mass of the wet skins plus 250ml of water was added, increasing the concentration of tannin.

The mixture was run for 10 hours at 2-3rpm.

Tannin equal to 10% of mass of wet skins was added, increasing the concentration of tannin.

Mixture was run for 1 hour at 2-3rpm.

250ml of water was added.

The mixture was run for 4 hours at 2-3rpm.

Tannin equal to 10% of mass of wet skins was added, increasing the concentration of tannin.

Mixture was run for 12 hours at 2-3rpm.

The skins were removed from the cylinders and washed with water in the rotating drum.

A light fatliquoring of the tanned skins was accomplished by adding a commercial fatliquor to the drum equal to 1% of the mass of the wet skins.

It was run for 1 hour at 50°C.

The tanned skins were drained of liquid and horsed up (placed on a board allowing time for all chemical reactions to be completed).

The tanned skins were stapled to wooden boards and allowed to dry.

The tanned skins were staked and trimmed.

The flesh sides were sanded to remove loose material and produce a more even thickness.

Initial investigations of the effects of NO_2 on leather started with laboratory preparation of NO_2. Laboratory preparation was undertaken to avoid the very high costs for transporting high concentrations of NO_2 as hazardous material. We used a common reaction for laboratory preparation of NO_2 using concentrated nitric acid and metallic copper as follows:[21]

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

The mixture of concentrated HNO_3 and copper metal in a glass flask was placed in a water bath to control the reaction rate. The NO_2 gas generated was then condensed in a flask having ¼" glass beads at a temperature close to 0°C. The glass beads gave a large surface area for the gas to condense on forming a small pool of liquid NO_2 at the bottom of the flask. The condensation flask was then put in a water bath at 30°C to evaporate the condensed NO_2 and transfer it to a 1.4L 316 stainless steel reaction pressure vessel (RPV). The NO_2 was allowed to flow into the bottom of the RPV for several minutes, purging most air from the RPV. The RPV was then closed off and allowed to condition for 24 hours at 40°C allowing small amounts of NO and N_2O_4 produced and trapped to convert to NO_2. Excess pressure after the conditioning was vented to atmospheric pressure. Various concentrations of NO_2 in the RPV were produced by sequential additions of compressed air to the RPV followed by venting of the diluted contents to atmospheric pressure until the desired concentrations were achieved. At that point leather specimens were placed in the RPV with the air/NO_2 mixture. Concentrations of NO_2 that were less than 1000ppm in air were verified using a California Analytical Model 600 CLD NO_x analyser. That analyser was self-calibrating using a certified standard NO_2 and air mixture calibration gas. The calibration gas had an analytical uncertainty of ± 2%, and the stability of the analyser was less than 1% of full scale in 24 hours.

The first experiment was carried out using approximately 1g of leather in the RPV having a concentration of 13% NO_2 in air. After 24 hours of exposure the specimens were examined. The specimens had all liquefied, with the liquid having a pH of approximately 0.17. The second experiment had approximately 1g of leather made up of two leather types, one a commercial chestnut vegetable-tanned goatskin and another a commercial full chrome-tanned goatskin with thicknesses of approximately 0.75mm. Mean TSs of specimen groups before exposures were

measured. After 72 hours of exposure at 60°C and a calculated concentration of approximately 0.21% NO_2, the specimens were tested and the mean TS losses were determined. The chrome-tanned leather had a 30% loss of TS and the vegetable-tanned leather had a 74% loss of TS. The measured NO_2 concentration in the air in the RPV after the test run was negligible. While the experiments with SO_2 and air in the RPV for leather longevity testing resulted in relatively minor loss of SO_2 and air during a test, typically 1-2%, average concentrations with these NO_2 exposures was unknown and it is likely that it was much lower than the initial calculated 0.21%. This made it difficult to correlate the results of such exposures with how the leather might react under normal exposures at low and fairly constant concentrations of NO_2. After considering the results of the first two NO_2 experiments, it was decided that the exposure of the leathers in the RPV was not a suitable way to measure leather deterioration by exposure to NO_2.

In order to achieve more realistic results of leather deterioration (loss of TS) from NO_2 exposures, we decided to establish continuous flow conditions around the leather samples with air having a known concentration of NO_2. This was done using a 1L glass exposure flask with various gas flow tubes and a thermocouple temperature probe entering the flask through a silicone rubber stopper. We estimated from the two previous experiments that we did not need very high concentrations of NO_2 and could instead conduct continuous flow experiments using commercial NO_2 in air supplied from a compressed gas cylinder containing 5000ppm of NO_2 in air (Fig. 1).

The temperature was maintained in the exposure flask with a magnetic stirrer/hot plate under the flask. A magnetic stirrer bar in the bottom of the flask kept the gas in the flask well mixed. The temperature in the reaction flask was measured with a thermocouple temperature probe in the flask. Leather specimens were placed on a stainless steel screen placed about mid-level in the flask.

Initial test exposures using specimens of commercial chestnut-tanned goat leather were made at 22°C and 60°C. For 24 hours exposures at concentrations of 600ppm NO_2 in air, the mean loss of TS for the exposed specimens was 35% at 22°C and 66% at 60°C. The temperature we chose for exposure of leather specimens was somewhat arbitrary. Control of the temperature required it be over the approximately 22°C laboratory room temperature but not so hot as to have a deleterious thermal effect on the leather. A temperature of 60°C was chosen (same temperature as used in the SO_2 test).

Exposure concentrations were determined by measuring the NO_2 concentration in ppm exiting the flask at the start of the exposure and at the end of the exposure, taking the average of those two measurements. Concentration measurements of NO_2 in the air exiting the flask were made by inflating a Tedlar film sample bag with the exhaust air exiting the flask through the vent tube. The gas in the sample bag was then analysed using a California Analytical NO_x analyser.

Atmospheric pressure fluctuates while experiments take place. These fluctuations tend to correspond to a few percent in air density and were not corrected for. However, consulting air density *vs.* temperature charts,[22] the density of air at 60°C in the exposure flask was approximately 11% lower than that at 22°C. This correction resulted in a lower mass concentration of NO_2 the samples were exposed to, since the concentration of NO_2 was measured in ppm in air after the effluent from the exposure flask had cooled back to 22°C.

Subsequent runs were made at a NO_2 concentration of approximately 620ppm (corrected for air density at 60°C), exposure times of 24 hours and a temperature of 60°C. The loss of TS using these conditions

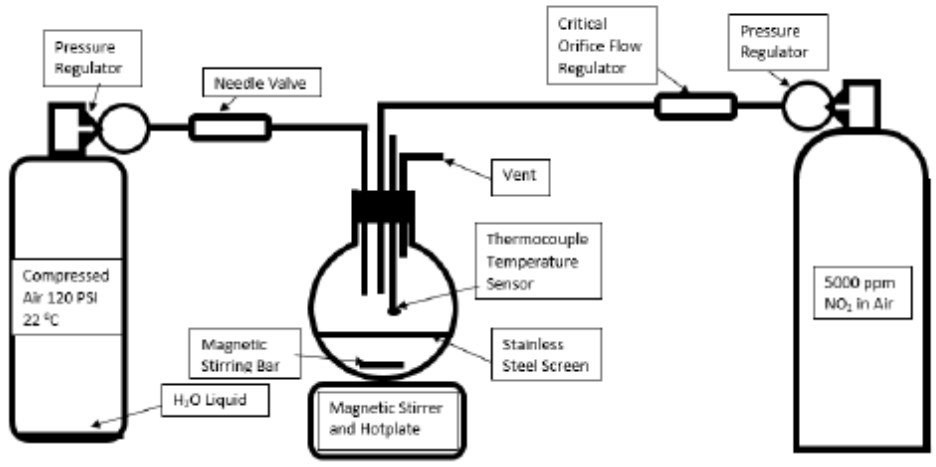


Figure 1. Apparatus for exposure of leather specimens to known concentrations of NO_2.

produced significant deterioration in test specimens while still giving an easily measurable range of mean loss of TS, with acceptable accuracy.

The flow rate through the exposure flask was chosen as a compromise of keeping the concentration fairly constant throughout an exposure while not exhausting the NO_2 gas supply too soon. Consumption of NO_2 during an exposure by reaction with the specimens would cause some reduction in the NO_2 concentration throughout the exposure period. It was found that a total flow rate into the exposure flask of 3L/h kept the NO_2 concentration of the gas exiting the vent tube (at approximately 22°C) typically within about 10% of that entering the flask. The largest NO_2 concentration loss in the flask was experienced in the first few hours after starting the exposure and tapering off to a small difference from the initial gas mixture after the first 5 hours. Producing that total flow rate with an NO_2 concentration of 700ppm (620ppm at 60°C in the exposure flask), a flow of 0.42L/h of 5000ppm NO_2 gas was required. The gas from the cylinder passed through a pressure regulator and a critical orifice to produce that flow rate. This was mixed with a flow of compressed air of 2.58L/h into the reaction flask.

The supplied air was stored in a tank at 120PSI (approximately 105 PSI gauge) with liquid water present. The relative humidity of that air at atmospheric pressure was measured to be approximately 13 % at 22°C. Mixed with the dry air of the NO_2 gas supply, the relative humidity entering the reaction flask was calculated to be approximately 11%. Flow measurements were made using a bubble film flowmeter with a manufacturer-estimated accuracy of ±2%.

Equipment and supplies

Thermocouple Thermometer: Traceable Products Model 4135CC.

Tensile Strength Measurement Apparatus: Stable Micro Systems (SMS), Model XT2i.

NO_2/air test gas: Praxair Certified Standard grade, 5000ppm NO_2, ± 2%.

NO_2/air calibration gas: Praxair Certified Standard grade, 300ppm NO_2, ± 2%.

NO_x Meter: California Analytical, Model 600 CLD C ETL.

Shrink Temperature Apparatus was as described in ASTM D6076-08.

Relative Humidity Meter: Traceable Products.

Bubble Film Flowmeter: SKC Laboratory Film Flowmeter 311-1000.

pH Meter: Fisher Accumet Model 15.

Pressure gauge: Ashcroft DG25 Digital Pressure Gauge, 0-150PSI.

Standards for pH: Ricca Chemical Co., Buffer References for pH3, Cat. # 1495-16; for pH9, Cat. # 1590-16.

RESULTS AND DISCUSSION

The loss of mean TS for the exposed leather specimens using the SO_2 test can be seen in Table I. The LAB valonia, LAB mimosa and LAB quebracho leathers had the least TS loss, ranging from 14-20%. The commercial mimosa and chestnut-tanned leathers had the highest TS losses, ranging from 63-75%. The chrome-containing leathers ranged from 34-46%. It could be that the LAB valonia, mimosa and quebracho leathers had some tanning-induced chemical protection to collagen oxidation occurring with the SO_2 test. The commercial chestnut and mimosa leathers had the highest TS loss using the SO_2 test whereas the LAB mimosa leather had one of the lowest TS losses. One may have expected the two mimosa-tanned leathers to have similar results, showing the difficulty in predicting the durability of any leather without 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 their durability.

The 24 hour NO_2 exposures showed the four LAB vegetable-tanned leathers to have moderate TS loss, the two commercial vegetable-tanned leather had high TS loss and the two chrome-containing leathers had the lowest TS loss. The low TS losses for the LAB valonia, mimosa and quebracho leathers experienced with the SO_2 test were not observed with the 24 hour NO_2 test. Any protective agents in the LAB valonia, LAB mimosa and LAB quebracho leathers against SO_2 exposures seemed less effective against NO_2 exposures. The two commercial vegetable-tanned leathers again had the highest losses of TS ranging from 62-66%. The two chrome-containing leathers had the lowest TS loss, ranging from 16-32%.

For the 72 hour NO_2 exposures, all of the vegetable-tanned leathers had a high loss of TS, ranging from 73-88%. The two chrome-containing leathers had much lower losses, ranging from 36-50%. We speculated that the lower loss of TS of the commercial auto chrome-containing leather vs the commercial chrome-containing goat leather may be due to the surface treatment (finish) of the auto leather and/or an unknown retannage of that leather. This difference decreased with the longer exposure time and became similar to the results with the 72 hour SO_2 test. It is possible that diffusion of NO_2 through the flesh side to the grain layer was more significant with the longer exposure time.

The initial shrink temperatures (Table II) for the vegetable-tanned leathers had similar values, ranging from 71-80°C. Initial values for the two chrome-tanned leathers were much higher, ranging from 95-108°C with the higher chrome content leather having the higher shrink temperature. These values were consistent with what would be expected for the two groups of leathers if they were properly tanned. 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

TABLE I
Loss of tensile strength for leathers of various tannages

Tannage	Initial tensile strength (PSI)	SO_2 Test, 168h Loss of tensile strength (%)	NO_2 24h Exp. Loss of tensile strength (%)	NO_2 72h Exp. 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 quebracho	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

TABLE II
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) (°C)	Shrink temperature after NO_2 72h aging (°C)
LAB tara	71	40	45	48
LAB valonia	76	39	55	55
LAB mimosa	79	39	52	50
LAB quebracho	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

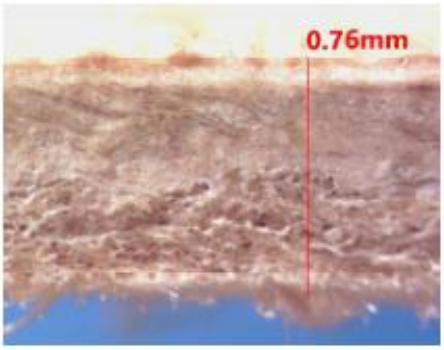
TABLE III
Acidity and difference figures for leathers of various tannages before and after test exposures

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 quebracho	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

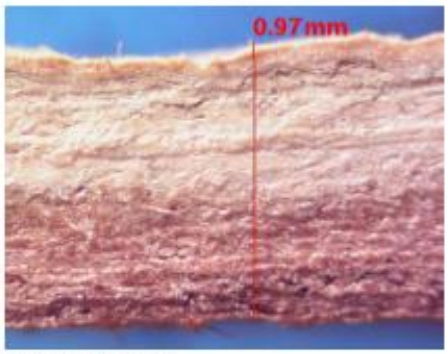
substantially reduced from pre-exposure values but higher than for the vegetable-tanned leathers.

All of the leathers with the exception of the commercial mimosa had moderate initial acidities ranging from 3.43-3.63pH and difference figures indicating organic acids as the likely sources of acidity (Table III). The ISO standard for measuring acidity and difference figures states that difference figures of 0.7 to 1.0 are associated with strong acids.[18] The commercial mimosa had an initial pH of 2.80 and with a difference figure of 1.08, indicating a mineral acid as the likely source of acidity. It is likely that acidity was created in the tanning process as it was recently tanned. All of the exposed leathers had lower pHs resulting from the test exposures and their difference figures indicated mineral acid content. The acidity increase for the LAB valonia, mimosa and quebracho leathers exposed to SO_2 was less than that for LAB tara. That may have been related to the lower loss of TS for those leathers and possibly indicating some buffering properties of the tanning. That acidity difference among those leathers was not as evident in the exposures to NO_2.

NO_2 is recognised as a powerful oxidising agent, with weak bonding of oxygen (ON–O = 305kJ/mol).[23] As such, its interaction with the collagen in leather as an oxidiser may be much more direct than the routes described earlier for SO_2 exposures whereby the acidification of leather and surface chemistry reactions on the collagen are typically required to produce *O or



1. LAB tara HS Control



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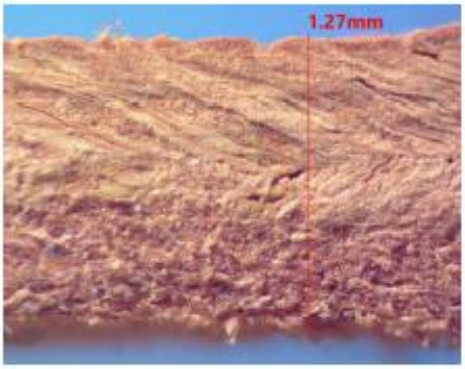
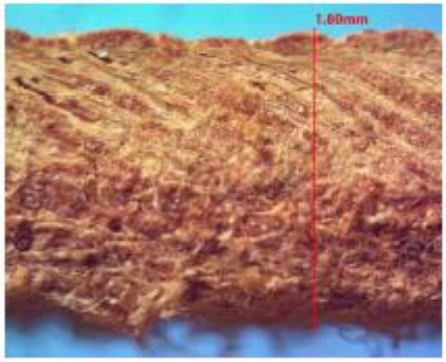
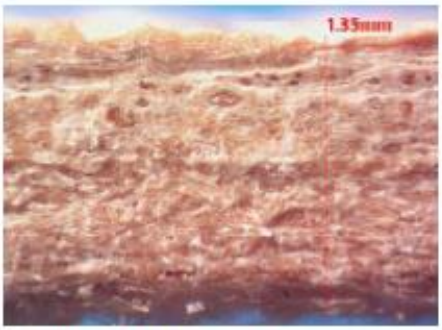


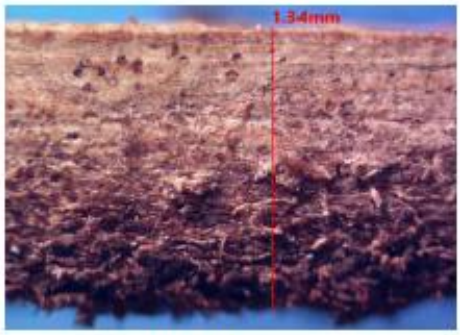
3. LAB tara HS 24 h NO_2



4. LAB tara HS 72 h NO_2



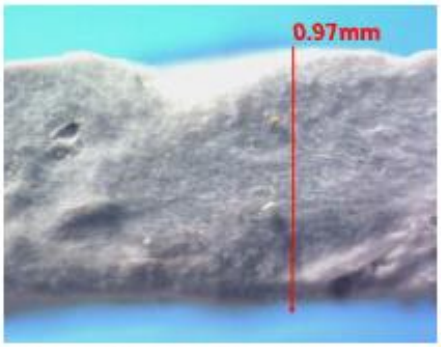
5. Commercial mimosa HS Control



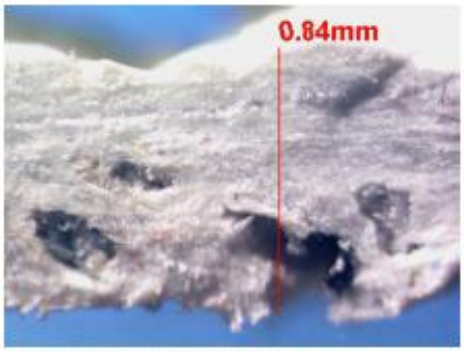
6. Commercial mimosa HS SO_2

7. Commercial mimosa HS 24h NO_2

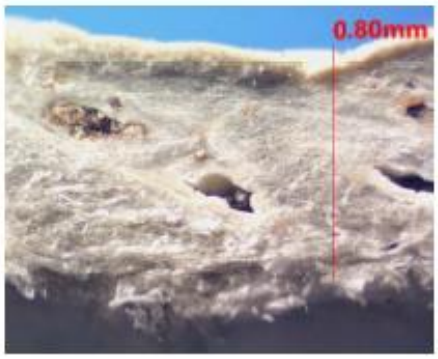
8. Commercial mimosa HS 72h NO_2



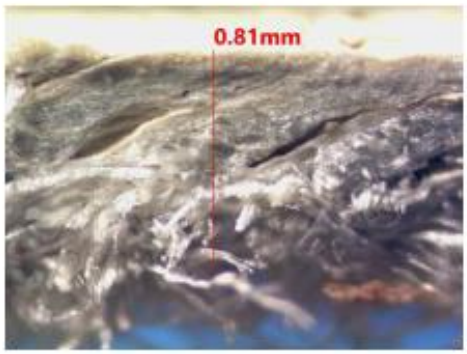
9. Commercial chrome HS Control



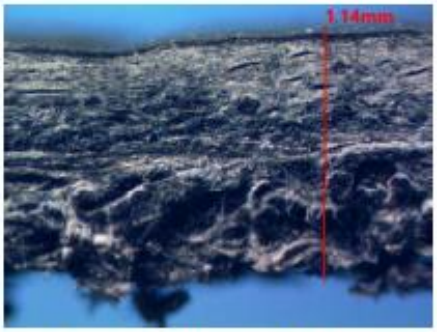
10. Commercial chrome HS SO_2



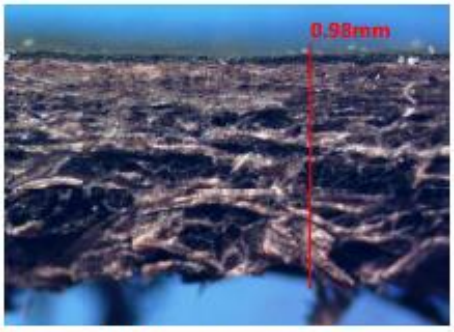
11. Commercial chrome HS 24h NO_2



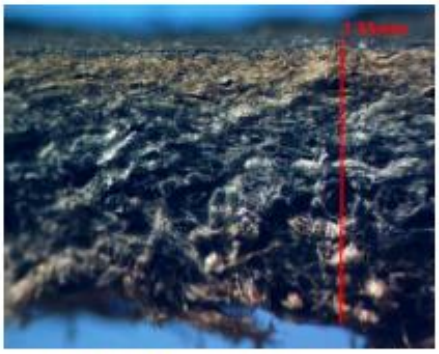
12. Commercial chrome HS 72h NO_2



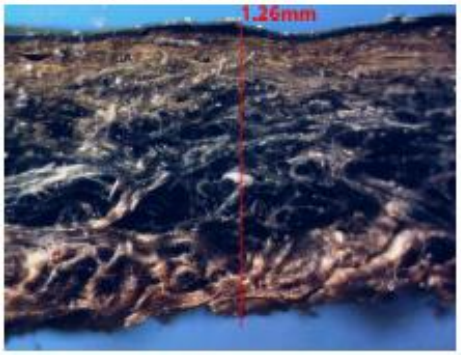
13. Commercial auto bovine control



14. Commercial auto bovine SO_2



15. Commercial auto bovine 24h NO_2



16. Commercial auto bovine 72h NO_2

OH ions that oxidise the collagen. While the specific reactions need to be better defined, it seems possible that the decomposition of NO_2 to NO and *O at the collagen surface directly oxidises collagen. Likewise, it may also oxidise other leather components. The data also show substantial increases of leather acidity with both SO_2 and NO_2 exposures and with difference figures indicating mineral acids such as H_2SO_4 and HNO_3. Depending on the tannage of the leather it is possible that oxidation of tannins could precede the oxidation of the collagen to which they are bound.

Photomicrographs

Photomicrographs 1-16 show examples of the visual colour changes in test specimens having different tannages and their exposures to SO_2 and 24 hours and 72 hours of NO_2. The photos are of cross sections of the leather with the grain layer at top and the flesh at the bottom. Comparison should be made of the colour appearance of the control specimens *vs.* the new shades of brown in specimens exposed to air containing SO_2 or NO_2. These suggest that the results of the exposures were not just at the boundaries (top and bottom) of the leather but instead fairly even throughout the leather. Since these leathers were approximately 1mm thick, that could differ with thicker leathers or leathers with penetration-resistant surface treatments or stuffing of the leathers. The commercial chrome-tanned goat leather showed little colour changes compared to the vegetable-tanned leathers. The colour changes seen in the vegetable-tanned leathers may be due to the oxidation of the tannins or to changes in pH. The commercial embossed auto leather was dyed black, changing its appearance. Its appearance after the exposures was different than the commercial chrome-containing HS leather, instead having colour changes similar to vegetable-tanned leathers. Whether this was due to oxidation of the dye or tannins is not known. It is possible that this leather had a combination tannage and that may also have contributed to its lower loss of TS. Its relatively lower Cr_2O_3 content could also be due to a higher tannage effectiveness, but its lower shrinkage temperature could argue against that.

Photomicrographs of samples with either the SO_2 or NO_2 exposures may provide a visual distribution of vegetable tannins. While this is not quantitative, it could prove to be useful.

The lower loss of TS for chrome-containing leather for both SO_2 and NO_2 exposures may be related to the bond strengths of chrome *vs.* vegetable tannins and collagen and the protection of what portion of the active sites on collagen is achieved. In looking at the shrink temperatures for the two chrome-containing leathers there is a significant drop after each of the three test exposures, but they do not drop as low as the vegetable-tanned leathers for the SO_2 and 24 hour NO_2 exposures. While the commercial chrome-containing goat leather has a higher shrink temperature than the commercial auto leather, it appears to be less resistant to loss of TS than the commercial auto leather. It is interesting to consider how the complex matrix proposed by Covington for the chrome (III)-sulphate counterion tannage would apply to combination tannages with chrome.

Longevity projections

It is interesting to consider the implications of NO_2 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 NO_2 concentrations. A rough calculation of this was made using data from room temperature (22°C) testing of commercial chestnut-tanned goat leather using 24 hour (0.00213yrs) exposures at concentrations of 600ppm (600,000 ppb) NO_2 in air (= 1667ppb-yrs). This resulted in a mean loss of TS for the exposed specimens of 35%. If one assumes that the same TS loss could be obtained by a much longer exposure at a much lower concentration, such as the 2020 NO_2 average national concentration in the US (40ppb), dividing 40ppb into 1667 = 42yrs. exposure time that would be required. The data in Table I. showed that this same leather had the highest loss of TS for 24 hour exposure to NO_2 at 60°C of any of the leathers tested. Many leathers, particularly those chrome tanned, would require much longer exposure times or higher concentrations of NO_2 to achieve an equivalent loss of TS. If one compares the loss of TS for 24 hour exposures to NO_2 at 60°C for the commercial chestnut-tanned leather (66%) to the commercial chrome-containing goat leather (32%), the chrome-containing leather has approximately 49% less TS loss. If one assumes that the changes in TS loss change in equal proportions for both of the leathers with a change in exposure temperature from 22°C to 60°C, the chrome-containing leather would lose approximately 35% of its initial TS in 82 years. It is unknown whether a protracted exposure at a much lower NO_2 concentrations would increase or decrease the relative loss of TS in exposed leathers. While years of projected lifetime using any long-term durability test is speculative, comparisons of results from various leather samples could be useful.

It should be noted that the 40ppb NO_2 is an average concentration over the US. It is possible that local (down to individual neighbourhoods) average concentrations could be much higher where a particular leather application spends its lifetime. SO_2 concentrations may also vary considerably, depending on location, and it could also contribute significantly to the deterioration of leather. NO_2 contribution to the acidification of leather may contribute to further deterioration through alternate chemical pathways than the direct oxidation of collagen.

CONCLUSIONS

The historical studies of leather deterioration and the present studies using NO_2 have further supported the comments of earlier researchers in leather deterioration studies, that there is likely to be no single mechanism explaining the deterioration of leather. It seems likely that the mechanisms of leather deterioration dominant

in the earlier 20th century, using the models of Innes, Cheshire and Frey and Beebe, do not fully apply to the deterioration resulting from an aggressive oxidiser such as NO_2, that may directly oxidise collagen, tannins and other leather components. Atmospheric NO_2 presents a long-term exposure to leather that may produce significant deterioration of leather. Unlike ozone, NO_2 appears to be stable enough to at least partially diffuse through the collagen structure of leather, possibly resulting in oxidation of the collagen throughout the leather as well as acidifying the leather.

The SO_2 test results differed somewhat from those of the 24 hour NO_2 exposure results. Some vegetable-tanned leathers were much less affected than others by the SO_2 test. That was much less the case for the corresponding 24 hour NO_2 results. Also, the chrome-containing leathers appeared less affected by the NO_2 exposures than the SO_2 tests. It seems likely that differences in the chemistry of the interactions of SO_2 *vs.* NO_2 with leathers affects various leathers differently. The results for the commercial mimosa leather may be an example of where the initial TS and shrink temperature did not reveal the likely shorter lifetime of that leather that the SO_2 test and NO_2 exposure results suggested. While SO_2 may not presently represent the most prominent path for atmospheric pollution-caused deterioration of leather, it is still present and may be significant in some localities where the burning of coal is prominent. The SO_2 test is probably an easier test to administer in a laboratory, consequently, it could be an appropriate choice for ranking leathers containing chrome but with unknown tannages, as to their likely durability. Overall, the NO_2 test may be a more rigorous and/or pertinent test for leather durability considering present atmospheric concentrations.

Laboratory exposure of leathers to NO_2 may provide another useful tool in evaluating the long-term durability of the leathers. Further work may be appropriate for establishing a standard testing method using NO_2. For a comprehensive evaluation of the long-term durability of a leather, the use of both the established SO_2 test and a future NO_2 test, as well as acidity and shrink tests, could be prudent.

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Authors' Biographical Notes

Harley Piltingsrud, M.S., retired from the National Institute for Occupational Safety and Health (NIOSH) (CDC) as a Senior Research Physicist. Preceding that, he worked in research positions at The National Reactor Testing Station (Atomic Energy Commission), The US Air Force Radiological Health Laboratory, and The US Food and Drug Administration Nuclear Medicine Research Laboratory. He is the author of over 40 scientific publications, and holds seven U.S. Patents. His work spanned many fields including radiation protection, nuclear medicine and analytical instrument development for field measurements of chemical pollutants. He worked for many years on American National Standards Institute (ANSI) standards and chaired a major ANSI accredited committee for six years. He has been involved in the restoration of pipe organs since the 1980s. At that time he and leather chemist, Jean Tancous, studied the problem of the rapid deterioration of leathers used in pipe organs. That resulted in the publication of 'The Development of a Standard Accelerated Aging Test for Measuring the Durability of Leather Used in Musical Instruments' (*J. Amer. Leather Chem. Ass.*,1987, **82**, 277.), followed by an expanded article published by the International Society of Organbuilders, ISO Yearbook 1992, 'Aging of Organ Leather.'

Kadir Donmez, M.S., retired recently from the Leather Research Laboratory at the University of Cincinnati as Associate Director of the laboratory. He received a Masters in Leather Science from the University of Cincinnati and was involved in the leather Industry for over 36 years, with 30 years of work experience in leather testing. He worked at various leather tanneries over the years and published a number of articles in the *Journal of American Leather Chemists Association* (*JALCA*) and others. He was a member of the ASTM D31 committee for many years, and chairman for the D31.01 Vegetable Leather, D31.05 Upholstery subcommittees. He served as the Secretary/Treasurer of the American Leather Chemists Association (ALCA) for 10 years. He received the ALSOP Award from the ALCA in 2014. He has served on the editorial board of the *JALCA* from 2015 to 2021.

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