**STUDIES ON THE INFLUENCE OF CLIMATIC CHANGES IN CRUST AND FINISHED LEATHERS**

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**ABSTRACT**

Leather and leather products are constantly exposed to outdoor environment therefore it faces various climatic changes with geographical location and time. Exposure of leather and leather products to different climatic condition causes fading of color, reduction in tensile strength, stiffening and cracking over period of time. This is due to light intensity, humidity, temperature etc. This could be seen in the shoe, glove and garment leathers. Among the various factors UV exposure is the most influential factor responsible for color fading. Compounds which are capable of absorbing UV rays (i.e. UV absorbers) and radical scavengers are used with a view to improve light fastness and to avoid other undesirable effect of changes in climatic conditions. In the present project, the compatibility of UV absorbers and radical scavengers will be evaluated along with leather finishing. Furthermore, possibility of incorporation of UV absorbers during post tanning process will be optimized. The leather which is treated with those compounds are exposed to various climatic conditions and studied for the impacts.

Keywords: climatic changes, UV absorbers, finished leather.

**INTRODUCTION**

Most colored materials owe their color due to presence of substances that absorb light of wavelength within visible portion of spectrum (380-780nm). The absorption of light by colored compounds is due to electronic transition between different orbitals within molecule and wavelengths absorbed are determined by energy difference between orbitals. Every dye or pigment therefore exhibits a pattern of absorption arising from its chemical structure. When dye molecules absorb photons from UV wavelength (200-320nm) the electrons from double bonds are excited to higher energy state, which in presence of atmospheric oxygen forms singlet oxygen radical forming dye radical which reacts with other molecule around. Thus the ability of dye molecule to absorb light is affected due to cleavage of double bonds (photo bleaching). Exposure to UVR for longer period of time results in reduction of strength properties. The amount of UV radiation in a location changes with following factors. 1. Geographical position: If a part of earth is closer to the equator, the UV radiation will be more in comparison of other part. Australia has higher level of solar UVR in comparison with Europe and North America mainly due to its geographical position. 2. Sun Height: When the sun remains high in the sky, the UV radiation found shorter distance to travel through so less UVR is absorbed by the atmosphere and more passes to earth.3. Ozone: Ozone is a form of oxygen that occurs naturally in the upper atmosphere and has the ability to absorb UV radiation. Ozone levels rise and fall naturally from day to day and seasonally. Atmospheric absorption prevents most of UV radiation to reach to the ground level.Other factors are clouds,smog and pollutants. Damage caused by exposure to UV can be reduced by application of UV absorbers and radical scavengers for finished leather by using them in intermediate coats in finishing. Blend of UV absorbers and HALS were added along with finishing chemicals (.i.e. binders, pigments, wax emulsions etc.) and it is spray coated then plated. Incorporation of performance and specialty chemicals during finishing obtaining UV and climatic resistance. This might be a way forward for the protection of non-finished leathers like suedes, nubucks etc. By incorporating UV resistance in leather, it also improve light fastness and retain the strength characteristics for a long period of time.

**MATERIALS AND METHODS**

**UV absorbers and HALS (hindered amine light stabilizers)**

UV absorbers are organic or inorganic colorless compounds with very strong absorption in the UV range of 290 – 360 nm. UV absorbers incorporated in to the material convert electronic excitation energy in to thermal energy. They function as radical scavengers and oxygen scavengers. The high-energy short wave UVR excites the UV absorber to a high energy absorbed may then be dissipated as longer wave radiation.

UV Absorbers soak up detrimental UV rays from sunlight, converting them into heat, which is then dissipated through the surface of the coating - Hindered Amine Light Stabilizers (HALS) do not absorb radiation; instead they protect the coating resin from the harmful effect of photochemically-produced ‘free radicals’ by neutralizing them, hindering chemical degradation. HALS regenerate themselves during the neutralization process, so go on providing protection throughout the lifetime of the coating.

**Finishing Formulation**

Finishing season is prepared for adding UV absorbers and HALS to the intermediate coat .The season is combination of soft and medium soft resin binder, medium polyurethane, isopropyl alcohol, wax emulsions, pigment, dye solution. Then blend of UV absorber and HALS was added to the season (1% of total formulation).

Then the dyed crust which is chrome tanned is spray coated with the above prepared season, dried and then plated.

**Climatic Chamber-Leather Ageing**

The finished leather sample A (conventional resin finished leather) and sample B(resin finished leather with UV absorbers and HALS) were placed inside the climatic chamber (Environmental test chamber CTC/TTC) and subjected to ageing for two days. Climatic chamber has arrangements for adjusting temperature (4-80 ℃) and relative humidity (25 -90%) Temperature and relative humidity were adjusted to 27℃ and 60% respectively.

**Tensile, Tear strength and grain crack index**

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.Specimens were conditioned at 80±4oF and 65±2% R.H. over a period of 48 h. Physical properties such as tensile strength, % elongation at break and tear strength were examined as per the standard procedures.

**Fastness to dry and wet rubbing**

Samples of appropriate size (5 x 14 cm) were cut from the official sampling position and after conditioning they were tested according to standard test method using SATRA Crockmeter. Leather samples were subjected to rubbing with felt (dry-150 rubs, wet- 50 rubs).

**RESULTS AND DISCUSSION**

**Ageing (climatic chamber) -** The sample which has UV absorber and HALS (**sampleB)** is compared with conventional finished leather (**sample A)**. The leathers are exposed to the three main environmental parameters, i.e., temperature, relative humidity and UV radiation. A climatic chamber is used in order to identify the most important variables. The leathers are exposed to UV radiation at varied intensities. Then following tests are performed.

**Physical Testing**-**Strength and Fastness Properties**

**Measurement of Distension and Strength of Grain by Ball Burst Test: SATRA TM 24, ISO 3379**

**Sample A-Conventional Chrome Tanned Resin Finished Leather**

**Sample B-Conventional Chrome Tanned Resin Finished Leather**

**Fastness Properties to Dry and Wet Rubbing-SATRA TM 173**

**EXPOSING SAMPLE A (CONTROL) WITHOUT UV ABSORBER AND SAMPLE B (EXPERIMENT) WITH UV ABSORBERS TO ARTIFICIAL UV RADIATION AND SUNLIGHT**

Two leather samples A (Control) and B(experiment) were prepared by using two halfs of a single goat skin which is chrome tanned ,retanned with acrylic ,melamine based and replacement syntans ,fatliquored with synthetic , semi synthetic fatliquors and brown dyed.

Sample A is conventionally resin finished with soft, medium soft resin binders, pigments, wax emulsion and dye solution. The finishing season is coated on leather with spraygun and is dryed and plated.

In sample B benzophenone is applied after intermediate coats by preparing solution of benzophenone in isopropyl alcohol (1:10 ratio) to required quantity to spray across entire sample in two coats. Then it is top coated with laquer, dried and plated.

From sample A four square pieces of leather were cut two for exposing in sunlight and artificial UV radiation and two samples were used to analyse the colour change during the process of exposing. Four square pieces from sample B were also cut for same purpose as sample A (control).

They were designated as follows

C-1 > sample A which is not to be exposed to UV radiation in order to compare with sample C-2.

C-2 > sample A which is to be exposed to UV radiation to analyze the photobleaching caused by UV rays.

C-3>sample A which is not to be exposed to sunlight in order to compare with sample C-4.

C-4> sample A which is to be exposed to UV radiation to analyze the photobleaching caused by UV rays from sunlight.

C-5 > sample which is not to be exposed to UV radiation in order to compare with sample C-6.

C-6 > sample B which is to be exposed to UV radiation to analyze the photobleaching caused by UV rays.

C-7>sample which is not to be exposed to sunlight in order to compare with sample C-8.

C-8> sample which is to be exposed to UV radiation to analyze the photobleaching caused by UV rays from sunlight.

**IRRADIATION IN ARTIFICIAL UV CHAMBER**

This UV chamber has xenon arc lamp to supply UV radiation to the samples. The wavelength can be adjusted between 280-340 nm and so the intensity. The wavength is set at 310 nm and sample C-2 and C-6 were placed inside the chamber. The irradiation continues for 24 hours in 6 sessions with 4 hour exposure time. Then the change in color (photobleaching) is analysed using spectrophotometer in terms of l\*a\*b values.

**IRRADIATION IN SUNLIGHT**

The samples C-4 and C-8 were placed on a flat place where direct sunlight falls. The conditions of climate were 29℃, 65% relative humidity and uv index 6-8.The irradiation is continued for 24 hours in 6 sessions with four hours exposure time. . Then the change in color (photobleaching) is analysed using spectrophotometer in terms of l\*a\*b values.

**IDENTIFICATION OF COLOUR CHANGE USING \*L, \*A, \*B VALUES AFTER EXPOSING THE SAMPLES TO ARTIFICIAL UV RADIATION AND SUNLIGHT.**

**LAB COLOR SPACE**

Even if two colors look the same to one person, slight differences may be found when evaluated with a color measurement instrument. Color difference can be defined as the numerical comparison of a sample's color to the standard. It indicates the differences in absolute color coordinates and is referred to as Delta (Δ). This formula can be used to calculate the difference between two colors to identify the color difference between two samples which cannot be detected by human eye.

To begin, the sample color and the standard color should be measured and the values for each measurement saved. The color differences between the sample and standard are calculated using the resulting colorimetric values

Defined by the Commission Internationale de l'Eclairage (CIE), the L\*a\*b\* color space was modeled after a color-opponent theory stating that two colors cannot be red and green at the same time or yellow and blue at the same time. As shown below, L\* indicates lightness, a\* is the red/green coordinate, and b\* is the yellow/blue coordinate. Deltas for L\* (ΔL\*), a\* (Δa\*) and b\* (Δb\*) may be positive (+) or negative ( -). The total difference, Delta E (ΔE\*), however, is always positive.

ΔL\* (L\* sample minus L\* standard) = difference in lightness and darkness (+ = lighter, - = darker)  
Δa\* (a\* sample minus a\* standard) = difference in red and green (+ = redder, - = greener)  
Δb\* (b\* sample minus b\* standard) = difference in yellow and blue (+ = yellower, - = bluer)

ΔE\* = total color difference

To determine the total color difference between all three coordinates, the following formula is used:   
ΔE\* = [ΔL\*2 + Δa\*2 + Δb\*2]1/2

**Evaluation of color change in sample without UV absorbers (sample A) and with UV absorbers (Sample B) after exposing them to artificial UV radiation and sunlight.**

**SAMPLE A (WITHOUT UV ABSORBERS)**

To identify the color change in sample A, two square pieces of sample A were cut from nearby portions i.e. in the butt region of the sample). Since we expose each sample to two conditions (i.e. artificial UV light and sunlight) four square pieces of sample A were cut. They were carefully designated as follows

C-1 > sample which is not exposed to UV radiation in order to compare with sample C-2.

C-2 > sample which is exposed to UV radiation to analyze the photobleaching caused by UV rays.

C-3>sample which is not exposed to sunlight in order to compare with sample C-4.

C-4> sample which is exposed to UV radiation to analyze the photobleaching caused by UV rays from sunlight.

**SAMPLE B (WITH UV ABSORBERS)**

To identify the color change in sample B, two square pieces of sample B were cut from nearby portions (i.e. in the butt region of the sample). Since we expose each sample to two conditions (i.e. artificial uv light and sunlight) four square pieces of sample were cut. They were carefully designated as follows

C-5 > sample which is not exposed to UV radiation in order to compare with sample C-6.

C-6 > sample which is exposed to UV radiation to analyze the photobleaching caused by UV rays.

C-7>sample which is not exposed to sunlight in order to compare with sample C-4.

C-8> sample which is exposed to UV radiation to analyze the photobleaching caused by UV rays from sunlight.

**Color difference between sample C-5 and C-6**

THE ABOVE READINGS SHOWS THAT SAMPLE B HAS BETTER RESISTANCE THAN SAMPLE A TO COLOUR CHANGE WHEN EXPOSED TO ARTIFICIAL UV RADIATION AND SUNLIGHT

**Conclusion**

The above results shows that leather with UV absorbers (Sample B) showed higher strength properties than conventional leather (Sample A).UV absorbers have significantly improved physical and fastness properties of the sample by incorporating resistance to climatic changes .

**Acknowledgement**

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Table.1.

|  |  |
| --- | --- |
| **Component** | **Parts** |
| SOFT RESIN BINDER | 80 |
| MEDIUM SOFT RESIN BINDER | 60 |
| SOFT PROTEIN BINDER | 60 |
| MEDIUM POLYURETHANE | 40 |
| BENZOPHENONE SOLN(10% SOLN IN ISOPROPYL ALCOHOL) | 1 |
| SEASON WAX | 20 |
| PIGMENT | 50 |
| DYE SOLUTION | 20 |
| WATER | 630 |

Table II

|  |  |  |  |
| --- | --- | --- | --- |
| **SAMPLE** | **l (lightness or darkness)** | **a(redness or greenness)** | **b(yellowness or blueness)** |
| **C-1** | **27.934** | **4.355** | **3.559** |
| **C-2** | **28.535** | **4.505** | **3.794** |

Table III

Table 3.21 Tests for physical properties of leather

|  |  |
| --- | --- |
| IUP 8 | Measurement of tear strength |
| IUP 6 | Measurement of tensile strength |
| SATRA TM 24 | Measurement of distension and strength of grain by ball burst test |
| SATRA TM 173 | Fastness to dry and wet rubbing |

Table IV: Measurement of tear strength

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Tear strength(max)  [N] | Tear strength  [N/mm] | Thickness[mm] | Direction | Type of failure |
| 1 | 54.27 | 60.98 | 0.89 | Along | N |
| 2 | 63.98 | 75.27 | 0.85 | Along | N |
| 3 | 60.14 | 75.18 | 0.80 | Across | N |
| 4 | 49.91 | 66.55 | 0.75 | Across | N |

|  |  |  |
| --- | --- | --- |
| **Rub fastness** | **Material** | **Felt** |
| **Dry 150 rubs**  **Wet 50 rubs** | Grey scale rate | Grey scale rate |
| 4/3  1/2 | 4/3  1 |

**Sample A-Conventional Chrome Tanned Resin Finished Leather**

Table 3.28 Measurement of rub fastness

**Sample B-Conventional Chrome Tanned Resin Finished Leather**

|  |  |  |
| --- | --- | --- |
| **Rub fastness** | **Material** | **Felt** |
| **Dry 150 rubs**  **Wet 50 rubs** | Grey scale rate | Grey scale rate |
| 4/3  2 | 4/3  1 |

Table 3.29 Measurement of rub fastnes**s**

Table V: Measurement of tear strength

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Tear strength(max)  [N] | Tear strength  [N/mm] | Thickness[mm] | Direction | Type of failure |
| 1 | 87.01 | 87.01 | 1.00 | along | N |
| 2 | 87.23 | 85.52 | 1.02 | along | N |
| 3 | 87.94 | 97.71 | 0.90 | across | N |
| 4 | 83.86 | 94.23 | 0.89 | across | N |

Table V: Measurement of tensile strength

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Maximum  Load [N] | Tensile strength [N/mm^2] | Elongation at break  [%] | Extension at maximum load [mm] | Thickness  [mm] | Direction |
| 1 | 153.03 | 32.56 | 56.01 | 28.00 | 0.47 | Along |
| 2 | 201.90 | 26.92 | 58.01 | 29.00 | 0.75 | Along |
| 3 | 109.00 | 17.58 | 56.34 | 28.17 | 0.62 | Across |
| 4 | 111.85 | 17.21 | 55.67 | 27.84 | 0.65 | Across |

Table VII: Measurement of tensile strength

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Maximum  Load [N] | Tensile  Strength  [N/mm^2] | Elongation  at break  [%] | Extension at  Maximum load [mm] | Thickness  [mm] | Direction |
| 5 | 396.19 | 38.47 | 56.01 | 28.00 | 1.03 | Along |
| 6 | 274.72 | 25.92 | 48.67 | 24.34 | 1.06 | Along |
| 7 | 213.48 | 20.53 | 58.34 | 29.17 | 1.04 | Across |
| 8 | 257.87 | 25.04 | 66.01 | 33.00 | 1.03 | Across |

Table 3.26 Measurement of grain crack index

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Load at grain crack, kg | 22 | 18 | 22 | Mean: 20.67 |
| Distension at grain crack, mm | 11.33 | 10.14 | 10.99 | Mean: 10.82 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Load at grain crack, kg | 44 | 42 | 40 | Mean: 42 |
| Distension at grain crack, mm | 12.68 | 12.68 | 19.77 | Mean: 12.04 |

Table 3.27 Measurement of grain crack index

**Color difference between sample C-1 and C-2**

Δl = l (sample C-2) -l (sample C-1)

= 28.535-27.934

= 0.399

Δa = a (sample C-2)-a(sample C-1)

= 4.505-4.355

=0.150

Δb = b (sample C-2)-b (sample C-1)

= 3.794-3.559

=0.235

ΔE = [Δl\*2 + Δa\*2 + Δb\*2]1/2

= 0.784

**Color difference between sample C-3 and C-4**

|  |  |  |  |
| --- | --- | --- | --- |
| **SAMPLE** | **l(lightness or darkness)** | **a(redness or greenness)** | **b(yellowness or blueness)** |
| **C-3** | **28.438** | **4.533** | **3.403** |
| **C-4** | **28.938** | **4.603** | **3.636** |

Δl = l (sample C-4) -l (sample C-3)

= 28.938-28.438

= 0.500

Δa = a (sample C-4)-a(sample C-3)

= 4.603-4.533

=0.70

Δb = b (sample C-4)-b (sample C-3)

= 3.636-3.403

= 0.233

ΔE = [Δl\*2 + Δa\*2 + Δb\*2]1/2

= 1.433

|  |  |  |  |
| --- | --- | --- | --- |
| **SAMPLE** | **l (lightness or darkness)** | **a(redness or greenness)** | **b(yellowness or blueness)** |
| **C-5** | **28.535** | **4.342** | **3.317** |
| **C-6** | **28.562** | **4.353** | **3.302** |

Δl = l (sample C-6) -l (sample C-5)

= 28.562-28.535

= 0.027

Δa = a (sample C-6)-a(sample C-5)

= 4.353-4.342

=0.011

Δb = b (sample C-6)-b (sample C-5)

= 3.302-3.317

=0.016

ΔE = [Δl\*2 + Δa\*2 + Δb\*2]1/2

= 0.108

**Color difference between sample C-7 and C-8**

|  |  |  |  |
| --- | --- | --- | --- |
| **SAMPLE** | **l (lightness or darkness)** | **a(redness or greenness)** | **b(yellowness or blueness)** |
| **C-7** | **28.334** | **4.489** | **3.508** |
| **C-8** | **28.398** | **4.543** | **3.558** |

Δl = l (sample C-8) -l (sample C-7)

= 28.398-28.334

= 0.064

Δa = a (sample C-8)-a(sample C-7)

= 4.543-4.489

=0.054

Δb = b (sample C-8)-b (sample C-7)

= 3.558-3.508

=0.050

ΔE = [Δl\*2 + Δa\*2 + Δb\*2]1/2

= 0.168

|  |  |
| --- | --- |
|  |  |
|  |  |
| **3.2.1 SATRA TM 162 tear strength of leather/ISO 3377:2002/IUP 8 double edge tear / IUP 40**    **CONDITIONS:** temperature 20℃,relative humidity: 65%  **Sample A-conventional chrome tanned resin finished leather** |  |
|  |  |
| **Mean tear strength** : **69.5 N/mm** |  |
| **Sample B-chrome tanned resin finished leather with UV absorber and HALS**  **Mean tear strength: 91.12 N/mm** |  |
| **3.2.2Tensile Strength of Leather- ISO 3376:2002/IUP 6/SATRA TM 43**  **Conditions:** Temperature 20℃, Relative Humidity: 65%  **Sample A-Conventional Chrome Tanned Resin Finished Leather**  **Mean Tensile Strength: 23.56N/mm2**  **Sample B-Chrome Tanned Resin Finished Leather With UV Absorbers & HALS**    **Mean Tensile Strength: 27.49N/mm2** |  |