ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

IMPROVEMENT OF COLOUR UNIFORMITY DURING DYEING OPERATION: THE CASE OF DRESS GLOVING LEATHER

BY

WONDWOSSEN MAMUYE

ADVISORS

Dr. BERHANU ASSEFA

Dr. R. ARAVINDHAN

Mrs. MALATHY JAWAHAR

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This is to certify that the Thesis prepared by Wondwossen Mamuye, entitled: ***Improvement of colour uniformity during dyeing operation: the case of dress gloving leather*** and submitted in partial fulfilment of the requirements for Degree of Master of Science in Chemical Engineering (Leather Technology) complies with the regulations of the University and meets the accepted standards with respect originality and quality.

<u>Approved by Examining Board</u>

Dr. Berhanu Assefa ____________________ ____________________
Dean, School of Chemical Signature Date
and Bio Engineering,

Dr. R. Aravindhan ____________________ ____________________
Advisor Signature Date

Dr. Shegaw Ahmed ____________________ ____________________
Internal Examiner Signature Date

Dr. J. Kanagaraj ____________________ ____________________
External Examiner Signature Date

____

School Dean/Graduate programs Coordinator

ABSTRACT

In leather industry, the tanner produces a production lot with large number of leather samples to match a colour provided by a client. However, even when the leathers are dyed with the same colorants under well monitored conditions may show some colour non-uniformity. This is highly challenging today for leather manufacturers, especially glove producers to sort colour of leathers consistently. The present study is focused on identifying the factors of colour variation during dyeing operation and reducing colour non-uniformity by managing the factors with well-designed dyeing recipe.

Dyeing properties of the dyestuffs was investigated, by choosing two commercially available dye stuffs. Factors of colour non-uniformity are identified by conducting dye trials on possible causes of colour non-uniformity with four different well-designed dyeing recipes. When concentration of dyestuff, substance of skin or length of dyeing float are varied individually keeping others factors the same, a perceivable total colour difference ($\Delta E^* \geq 0.5$) is observed.

Controlling and monitoring of colour non-uniformity is analyzed by conducting dye trials using four different well-designed dyeing recipes viz. reverse dyeing recipe, regular dyeing recipe, the multiple stage dyeing recipe and regular dyeing recipe with dye levelling agent. The total colour difference (ΔE^*) values obtained using multiple stage dyeing recipe was smallest as compared to the other three recipes by varying all possible factors of colour non-uniformity individually. From these observations, multiple stage dyeing recipe was the best alternative way to manage colour non-uniformity.

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LIST OF ACRONYMS

CIE	Commission Internationale d'Eclairage
CLRI	Central Leather Research Institute
CSIR	Center for Scientific Industrial Research
DG	Director General
ΔE	Energy difference
ΔE*	Total Colour difference
Eg	Energy at ground state
Es	Energy at exited state
Eq	Equation
LIDI	Leather Industry Development Institute
mg	milligram
OD	Optical Density
ppm	parts per million
UV	Ultra Violet radiation

CHAPTER 1

INTRODUCTION

1.1 Background

Dyeing is one of the most important steps in tanning industry. It is a unit operation used for colouring the leather in the drum. Colour is usually the first property of leather to be assessed by consumer or customer. Every customer will make judgments in a glance: colour, depth of shade, uniformity and seriously checks the colour matching of the dyed dress glove leather with its original ordered colour weather it is in agreed tolerance limit or not. Therefore, dyeing is critical that the science and hence the technology of colouration is well understood [1].

Leather is a difficult substrate to dye; it has structural differences as well as other imperfections. To achieve the target of a level and uniform dyeing the leather dyer needs to be experienced and to have a thorough understanding of the dyeing properties of the dyes. Uniformly tanned leather, a suitable selection of dyes and well-designed dyeing recipe are essential for an even shade.

All dyes work on the same principle. The colour is generated by creation of delocalized electrons, made possible by chemically synthesizing molecules that contain a system of conjugated double bonds (i.e. alternate double and single bonds). The groups with the delocalized electrons are called ‘chromophores’, because they are the primary sources of colour. Often the chromophores are linked by the azo group, N=N, which can contribute to the delocalization of electrons over the chromophore system [2].

Leather colouration is relatively straight forward when dealing with pigments, but when the dyestuff confers transparent colour to the leather, the outcome is dependent on the following parameters [1].

- Dyestuff chemistry and mechanism of fixation.
- Relative affinities of the dyestuff and substrate.
- Nature of substrate, including its colour.
- Illumination of the colour, the perceived colour depends on the light source, an effect called ``metamerism´´.

Leather manufacturers often need to produce production lots consisting of large number of leathers to match a colour provided by the customer. The colour variation may be due to inconsistencies in raw material selection, pre and post dyeing processes, dye diffusion rate and uptake characteristics, dyeing float length, temperature, fixation pH etc. After skins are processed and finished with all the necessary sensory and functional properties needed for an end use, the finished leather may be rejected if the colour is not matched to the buyer's sample/swatch [2].

Therefore, this study focuses on identifying the significant factors of colour variations, setting controlling, and monitoring mechanisms for drum dyeing operation of dress gloving leather through process optimization to minimize the colour non-uniformity among different batches of production.

1.2 Statement of the problem

Dress gloving leathers are not generally pigment finished because commonly used are too hard binders for the purpose and considerably reduce the run of the leathers. The colour non-uniformity of dyed dress glove leather cannot be corrected with finishing. Therefore, drum dyeing for dress glove leather is pivotal unit operation to be conducted accordingly to colour matching of the customer ordered colour.

There are different process factors for variation of colour of dyed dress glove leather from the customer's order colour during conducting dyeing operation. This study focuses on identifying the factors of colour variations, setting controlling and monitoring mechanisms for drum dyeing operation of dress gloving leathers to minimize the colour mismatch between different batches of production.

1.3 Research Questions

Which dye properties affect the colour of the dyed leather during dyeing operation?

What are the factors (causes) for colour non-uniformity during dyeing operation of dress gloving leather?

How the colour non-uniformity will be controlled and monitored to improve the existing situation of colour uniformity observed in our country's tanneries?

1.4 Objectives

1.4.1 General objective

The main objective of this work is to reduce colour non-uniformity during drum dyeing operation for dress gloving leather by identifying, controlling and monitoring the factors of colour variations.

1.4.2 Specific objectives

- to identify the effect of various factors such as the type of dye used, order of addition of dyes, thickness of the raw material, float length and temperature on the drum dyeing of dress glove leather
- to optimize the dyeing recipe
- to employ the optimized process to improve the existing colour non-uniformity of the sheep dress glove leather in tanneries

1.5 Significance of study

This research work helps to produce consistent colour of dress gloving leather for different batches of production in agreed tolerance limit. It minimizes the rework/redyeing to correct the colour variation from one batch to other batch of production. Ultimately, it reduces colour mismatching complaints by customers especially for export market of dress gloving leathers in Ethiopia.

1.6 Scope of the study

The scope of this research work will cover pre-dyeing, dyeing and post-dyeing operations that affects the end colour of sheep dress glove leather at laboratory scale (using testing drums).

CHAPTER 2

LITERATURE REVIEW

2.1 Leather

Leather is a natural protein polymer treated with tanning agents to make it resistant to enzymatic attack and putrefaction and to improve its several physical properties. It is made from hides and skins, which are by-products of slaughterhouses. It is made by subjecting the proteins of animal skin to a process known as tannage, whereby the skin becomes more durable and capable of being used for a wide range of purposes [3].

Leather is a difficult substrate to dye; it has structural differences as well as other imperfections [4]. To achieve the target of a level and uniform dyeing the leather dyer needs to be experienced and to have a thorough understanding of the dyeing properties of the dyes. Uniformly tanned leather and a suitable selection of dyes are essential for an even shade.

The application of water soluble organic dyestuffs to leather results in colored leather which can be used as it is to produce an 'aniline leather' without pigmented finishing, providing the grain quality is appropriate. One of the best representatives of aniline leather is gloving leather. Suede leathers also fit in this category as no further coloration beyond dyeing is done to these leathers. Natural looking leather needs a constant and uniform shade consistent with the sample color provided by the customer.

Leather dyeing will be discussed in this literature review to provide an understanding of the application of soluble organic dyestuffs in aqueous floats to wet leather. This leads to fixation of the dye molecules not only on the surface of the tanned fiber network but inside as well. This type of coloration of leather is completely different from the finish operations performed on crust leather manufacture where insoluble dyestuffs and/or pigments are applied together with polymeric binder substances on the surface of the dry leather [5].

An introduction into leather dyeing has to start with the statement that the shade of any leather is influenced to a certain degree by the starting color of the chrome-tanned leather. The starting material for leather dyeing begins green-blue in color rather than white like cotton and other textiles. As a result, the potential shades of dyed chrome leather are not very brilliant.

2.2 Dyeing

As stated above the color is one property desired by the customer and this can be realized using colorants where dyes are main colorant being used at this stage. Dyes are complex, natural or synthetic, inorganic or organic solvent soluble colored compounds having the properties of imparting their permanent color to other substrates collagen, wool & cotton, etc. fibres [6]. Dyeing is mainly to improve aesthetic appeal or appearance and make the leather adaptable to fashion style. Dyes can be categorized as acid, direct (substantive), mordant, and reactive according to the dyeing behavior towards natural or synthetic fibers. All are either cationic or anionic in nature and acid dyes are the main dyestuffs being utilized by tanning industry. The kind of re-tanning materials being used have impact on the penetration and depth of shade. Thus, right combination of re-tanning materials and dyes should be taken into account. The more phenolic type syntans are being used in re-tanning, the lighter the color shade will be. Dyes can be installed the form of powder, paste or solution. The study on chemical and physical interactions involving leather dyeing revealed that the exact mechanism may involve the interaction of the dye molecules with the reactive functional groups collagen or collagen tanning agent complex or both [7].

2.3 Light and Colour

Light is a form of energy that travels through space like a wave and is characterized by its wavelength. It is made up of seven bands of varying wavelengths viz. Red, Orange, Yellow, Green, Blue, Indigo and Violet. White light is actually composed of all colors in equal amounts. It can only be broken up by prisms or by colorants such as pigments and dyes. The surface has no colorant so the light is reflected. It can be fully absorbed by the surface. A transparent surface may let the entire light pass through or a colored surface may absorb part [8].

Color is the human eye’s perception of reflected radiation in the visible region of the electromagnetic spectrum (400–700 nm). It originates from electromagnetic energy changes in electron orbitals, caused by the absorption of photons. Objects appear colored when they absorb a particular color of light, thereby "subtracting" that color from white light. All other colors are reflected. The energy gap between two orbitals determines the wavelength of light absorbed by a material and thus the color [9]. A molecule with an energy-level gap that corresponds to visible light appears colored (It might be a dyestuff or a pigment). When a molecule interact with radiant energy, the molecule is said to be excited, because the outer valence electrons undergo transition from original energy level ground state (Eg) to an excited state (Es) [10].

The transition energy is given by the following equation:

$$\boxed{\Delta E = Es - E\,g = h\,\upsilon} \qquad \ldots\ldots\ldots \text{ Eq (2.1)}$$

where ΔE is transition energy;
Es is energy at excited state
Eg is energy at ground state
h is Planck's constant
υ is frequency of the light
Colour has three dimensions or qualities viz; hue, value and Intensity.
Hue: - the name given to a color. Example: Red, Orange, Violet etc
Value: - the lightness or darkness of a color
Intensity: - the brightness or dullness of a color

2.4 Dyestuff

Dyes are aromatic compounds & their structure includes aryl rings which have delocalized electron systems. Delocalized electrons are electrons in a molecule, ion or solid metal that are not associated with atom or one covalent bond. Delocalized electrons are contained within an orbital that extends over several adjacent atoms. Dyes are aromatic organic compounds, and as such are based fundamentally on the structure of benzene. Benzene aryl rings are responsible for the absorption of electromagnetic radiation of varying wavelengths, depending on the energy of the electron clouds. To us, benzene appears to be a colourless fluid. In fact, it absorbs electromagnetic radiation just as dyes do, but it does so at about 200 nm so that we do not see it [7].

Chromophore from the Greek "Chroma"=colour and the verb "Phore"=to bear, carry. Thus a group which is responsible for the colour of a compound is called a chromophore (colour-bearing group). Chromophores function by altering the energy in the delocalized electron cloud of the dye, and this alteration results in the compound absorbing radiation from within the visible range instead of outside it [2].

Colour in dyes is a consequence of the presence of a Chromophore. Dyes are aromatic compounds their structure includes aryl rings which have delocalized electron systems. These are responsible for the absorption of electromagnetic radiation of varying wavelengths, depending on the energy of the electron clouds. Chromophores are atomic configurations which can alter the energy in delocalized systems. They are composed of atoms joined in a sequence composed of alternating single and double bonds. Chromophore configurations often exist as multiple units, having conjugated double bonds. This is due to the interaction between the double bonds, which causes partial delocalization of the electrons involved in the bonds. Auxochromes are groups which attach to non-ionizing compounds yet retain their ability to ionize. The addition of ionizing groups resulted in a deepening and intensifying of the colour of compounds [7].

The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state. In the conjugated chromophores, the electrons jump between energy levels that are extended pi orbitals, created by a series of alternating single and double bonds, often in aromatic systems.

Coloured organic compounds

- Often contain unsaturated groups, -C=O, -C=C, -N=N-
- Usually part of extended delocalized electron system called the chromophore.
- Electrons in double bonds more spread out - require less energy to excite than those in single bonds particularly in conjugated system.
- Absorption of radiation in visible region.
- OH, $-NH^2$, or NR_2 attached to chromophores to enhance or modify the colours.
- Lone pair electrons become involved in the delocalized system.
- Small changes change the energy of light absorbed and therefore the colour.

Auxochromes are saturated groups possess unshared electrons and does not absorb in near UV or visible radiations e.g. OH, NH_2. But when attached to chromophoric molecule, increase both its wave length and intensity of absorption maximum. Auxochromes regulate the intensity of color. They are chemical groups that make dyes water soluble. They also provide chemical groups that form bonds between the dye and fiber. A dye bath must contain both chromophores and auxochromes, either from the dyestuff alone or a mixture of dye and other added chemicals. Because auxochrome enters into resonance interaction with the chromophore, thus increase the extent of conjugation; shift the absorption maximum to longer wave length [2].

Unlike most organic compounds, dyes possess colour because they

- Absorb light in the visible spectrum (400–700 nm),
- Have at least one chromophore (colour-bearing group),
- Have a conjugated system, i.e. a structure with alternating double and single bonds, and
- Exhibit resonance of electrons, which is a stabilizing force in organic compounds.

When any one of these features is lacking from the molecular structure the colour is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colorant and they are most often used to influence dye solubility [4].

Dyestuffs are generally synthesized organic chemical molecules of an aromatic or sometimes heterocyclic nature. The synthetic dyes used to colour leather in the wet-end are traditionally the anionic, water-soluble, acid dyes. Other dye types such as direct, soluble sulfur and reactive are used but to a much lesser extent and mainly to achieve special colors or fastness properties.

2.5 Dyeing operation

Dyeing is one of the most important steps in tanning industry. Leathers are dyed to impart colour as demanded by the fashion. Colour is usually the first property of leather to be assessed by consumer or customer. Every customer will make judgments in a glance: colour, depth of shade, uniformity and seriously checks the colour matching of the dyed dress glove leather with its original ordered colour weather it is in agreed tolerance limit or not. Therefore, dyeing is critical that the science and hence the technology of colouration is well understood.

Colour matching prediction is relatively straight forward when dealing with pigments, but when the dyestuff confers transparent colour to the leather, the outcome is dependent on the following parameters.

- Dyestuff chemistry and mechanism of fixation.
- Relative affinities of the dyestuff and substrate.
- Nature of substrate, including its colour.
- Illumination of the colour, the perceived colour depends on the light source, an effect called ``metamerism´´.

2.6 Dyeing quality problems

For a tannery the key elements required from wet-end dyes are: [1]

- Consistence for reproducible production batches;
- Quality to meet the required colour specification;
- Flexibility to apply to various types of leather;
- Economical cost of dyes.

However, the above-mentioned elements are not easy tasks to maintain for tanners. The major reason for the different dyeing behavior of dyes in leather is their varying affinity for the leather substrate and the variations between the dyes themselves. The behavior of leather dyes is primarily determined by the charge of both the dye and the leather to be dyed. Differences in exhaustion rate or bath exhaustion and in build-up of the dye on specific leathers are the chief problems. The affinity of a dye to leather depends mutually on the structure and state of both the dye and the substrate (leather). For the leather, it depends on the type of tannage, the presence of chemical active substances in the float, surface active agents on the fiber surface, salt content of the float etc. For the dye, it depends on the structure of the dyestuff or mixtures thereof, their sensitivity to any of the dyeing conditions such as temperature, acidity, float length and so on.

The reaction of the dye with the leather is a chemical reaction and is ruled by the laws of chemical reactivity. This reaction is a heterogeneous one between a soluble compound and an insoluble substrate. The desired result is a surface fiber reaction that is uniform in colour regardless of whether the colour is deeply tinted or very faint. And this is necessary in spite of the fact that the substrate is quite often very uneven in structure [6].

2.7 Colour measurement instrument

2.7.1 Reflectance Spectrophotometer

One of the most objective ways to measure color is to use diffuse-reflected spectrophotometry. Light reflected from the material is collected in an integration sphere, normalized to the source light of the reflectance, and calibrated with the measurement of a pure white standard (100% reflection) and a black box (zero reflection) over the entire wavelength spectrum of visible light.

The spectrophotometer is a physical tool which is eminently suited to measure the most important variable of all, the shade and strength of the dyestuffs themselves, whether they may be in solution or on the fiber. Spectrophotometer used by dyeing factory and colorant manufacturers all over the world. Normally lab manager analyses the color of swatch with the help of spectrophotometer.

Reflectance Spectrophotometer interfaced with computer is largely used to quantify colour numerically. CIE colorimeteric mathematical model are used by these spectrophotometers to relate human perception of colour to instrumental responses. From this mathematical model colorimetric scales such as CIE L*a*b* can be derived and used to communicate as well as quantify colour and its appearance. The colour values obtained from this system describe the magnitude of difference in colour between the standard and sample in a way which is understandable to the human observer [11]. Thus, when instruments are used to shade sort materials, they do not only provide an objective numerical colour difference but also more accurate, repeatable and can distinguish even small colour difference when compared to a human expert. When buyer and seller are at different locations they can measure samples at their respective locations and can correlate the reported colour values thus minimizing the inter-instrument variation which leads to a better objective system comparing visual assessment by two different human observers.

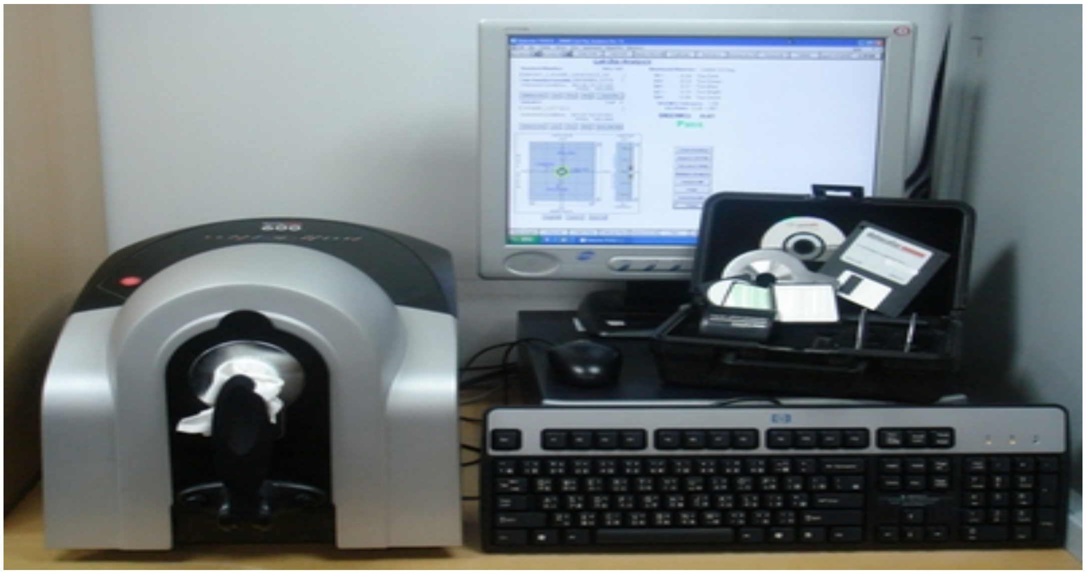

Fig 2.1. Reflectance spectrophotometer

Functions of reflectance spectrophotometer are:

- Color difference
- Metamerism
- Pass/fail operation
- Fastness rating
- Shade library
- Cost comparison
- Color match production
- Reflectance curve

2.7.2 The CIE Lab-System

The CIE Lab-System is a colour space, which was specified by the International Commission on Illumination CIE (Commission Internationale d'Eclairage) in the year 1976. It was further derived from the CIE colour system and is based on the CIE “master” space which was introduced in the year 1931. CIELab system is today the most common colour system. On the basis of this equipment independent 3D-colour model, colour differences can be identified numerically. The model is impartial and complies nearly the human perceptiveness, by adapting the geometrical distance between two colours in the colour space with the human perception [12].

The CIELAB color scale is an approximately uniform color scale. In a uniform color scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted. The CIELAB color space is organized in a cube form. The L* axis runs from top to bottom. The maximum for L* is 100, which represents a perfect reflecting diffuser. The minimum for L* is zero, which represents black. The a* and b* axes have no specific numerical limits. Positive a* is red. Negative a* is green. Positive b* is yellow. Negative b* is blue [13].

Below is a diagram representing the CIELAB color space.

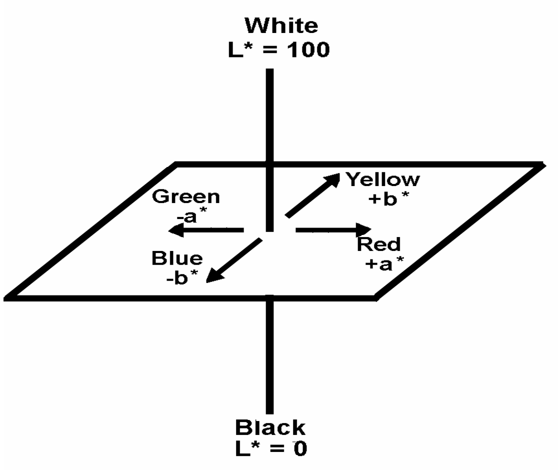

Fig. 2.2 A diagram for CIELAB color space

The measured spectral curves will be reducing on three coordinates. The axes of the coordinates are positioned rectangular on each other [14].

- L*, the light intensity, from 0 = absolute black to 100 = absolute white.
- a*, describes the red - green axis. Negative values are green, the positives are red.
- b*, describes the yellow - blue axis. Negative values are blue, the positives are yellow.

There are delta values associated with this color scale. ΔL*, Δa*, and Δb* indicate how much a standard and sample differ from one another in L*, a*, and b*. These delta values are often used for quality control or formula adjustment. Tolerances may be set for the delta values. Delta values that are out of the tolerances indicate that there is too much difference between the standard and the sample. The type of correction needed may be determined by which delta value is out of tolerance. For example, if Δa* is out of tolerance, the redness/greenness needs to be adjusted. Whether the sample is redder or greener than the standard, it is indicated by the sign of the delta value. For example, if Δa* is positive, the sample is redder than the standard [15].

The total color difference, ΔE*, may also be calculated. The ΔE* is a single value which takes into account the differences between the L*, a*, and b* of the sample and standard. It does not indicate which parameter(s) (L*, a*, and/or b*) are out of tolerances if ΔE* is out of tolerance. It may also be misleading in some cases where ΔL*, Δa*, or Δb* is out of tolerance, but ΔE* is still within tolerance [16]

$\Delta L^* = L^*_{sample} - L^*_{standard}$ + ΔL* means sample is lighter than standard

- ΔL* means sample is darker than standard

$\Delta a^* = a^*_{sample} - a^*_{standard}$ + Δa* means sample is redder than standard

- Δa* means sample is greener than standard

$\Delta b^* = b^*_{sample} - b^*_{standard}$ +Δb* means sample is yellower than standard

-Δb* means sample is bluer than standard

Deltas for L* (ΔL*), a* (Δa*) and b* (Δb*) may be positive (+) or negative (-).

The total difference, Delta E (ΔE*), however, is always positive.

To determine the total color difference between all three coordinates, the following formula is used [11]:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

…………..Eq (2.2)

Therewith the colour can be accurately described in the colour space. The calculation is effected under consideration of a standard light and an ordinary observer, that is, the colour values are calculated under defined physical conditions. ΔE - (*Delta E, dE*): The measure of change in visual perception of two given colors. Delta E is a metric for understanding how the human eye perceives color difference. The term *delta* comes from mathematics, meaning change in a variable or function. The suffix *E* references the German word *Empfindung*, which broadly means sensation [17]. On a typical scale, the Delta E value will range from 0 to 100.

Table 2.1 The delta E values and their meaning to human perception

the Delta E value	**Meaning**
Less than 0.5	no color difference
0.5-1.0	difference only perceivable for experienced observers
1.0-2.0	Medium difference, also obvious to an untrained eye
2.0-4.0	perceivable color difference
4.0-5.0	significant color difference
Larger than 5	different color

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Raw materials and chemicals

- Thirty pieces of good quality (grade I-III) wet blue sheep skins having average size of 4.5 sq.ft. were used to conduct the experiment.
- Commercial grade chemicals/auxiliaries were used for post tanning processes
- Dyes were procured from M/s Colourtex India Pvt. Ltd.

3.1.2 Leather processing equipments, Laboratory instruments and Apparatuses

- Testing (small scale) leather processing drums
- Model tannery mechanical machines
- Wet blue shaving machine
- Dry shaving machine
- Overhead drying machine
- Staking machine
- Laboratory equipment for measuring colour (Colour measurement instrument)

3.2 Methods

3.2.1 Method for Identification of factors for colour non-uniformity

In order to identify the factors that would affect the dyeing process, various experiments were designed, which are described in the below given sections. Initially, the wet blue sheep leathers were converted in to natural crust leathers by employing the process provided in Annexure 1.

3.2.1.1 Designing glove processing recipes

Five different glove processes were designed in order to understand the effect of the processes on the dyeing of leathers. The recipes are provided in Annexure 2 to 6. Annexure 2 is the dyeing process, which is currently being practiced in Ethiopian tanneries. Annexure 3, the recipe is designed such a way that the dye stuff is provided after retanning and fatliquoring. In annexure 4 recipe, the dyestuff is given before adding retanning and fatliquoring agents. In Annexure 5 recipe, the dye stuff is given in feeds, before and after adding the retanning and fatliquoring agents. In the final recipe provided in Annexure 6 the dye is given before adding the retanning and fatliquoring agents but was accompanied by the dye levelling agent. In all the experiments, the dyes used were the same with equal offer.

3.2.1.2 Standardizing the dyestuffs

For this study, two dye stuffs were selected, namely Coloderm Orange GS and Coloderm Red SG from M/s Colourtex India Pvt. Ltd. the characteristics of these two dyestuffs were studied by treating them with the leathers. The penetration rate of the dyestuff and the exhaustion characteristics of the dye stuff were taken as two parameters to characterize the dyestuff. The experiments were carried out in a sample testing drum. Small cut pieces of similar sizes were cut from the natural crust leathers. These leathers were then dyed using the recipe provided in Annexure 4 with varying offer of dyes. The offer of dye was varied from 1, 3, 5, 7 and 10%. The penetration of the dyes in to the leather were ascertained by visual examination by experienced personnel and rated in the scale of 1 to 5, where 5 indicated complete penetration and 1 indicates less penetration. The exhaustion behavior of the dyes were characterized using UV-Visible spectrophotometer. Standard graphs were prepared for two dyes, with concentration being the X axis and the optical density at Y axis. The standard graphs for both the dyes are provided in Fig. 3.1 and 3.2. The concentration of the dye in the exhaust liquor was determined using these standard graphs.

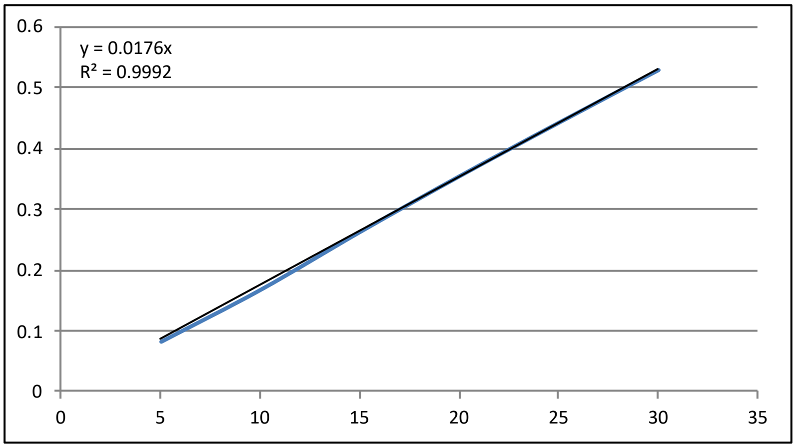

Fig. 3.1: Standard Graph for Coloderm Orange GS

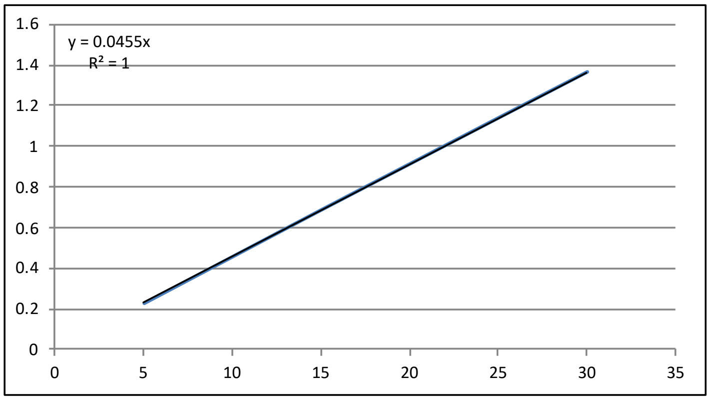

Fig. 3.2: Standard Graph for Coloderm Red SG

3.2.1.3 Identification of the Factors affecting the non-uniform dyeing

Among the various factors, that would lead to non-uniform dyeing, three factors such as the concentration of dye stuff used, substance or thickness of the skin and the float length of the dyeing operation were identified. The dye concentration was varied from 1, 3, 5, 7 and 10% and the recipe as per Annexure 4 was employed to study the effect of offer of dye stuff. In case of effect of thickness/substance, experiments were carried out on the samples cut from butt and belly areas, respectively. The effect of thickness was studied for all the dyeing recipes provided in Annexure 2-6. The effect of float length was studied by employing short float (500% on the crust weight) and long float (1000% on the crust weight). The effect of the float length was studied for all the recipes provided in Annexure 2-6.

3.2.1.4 Instrumental Colour Analysis

The dyed crust leathers were then analysed using the colour measurement instrument. The CIE Lab values of each sample of dyed crust after the dyeing trials were measured. The total colour difference (ΔE) was calculated for each type of experiments (CIE Lab values).

3.2.2 Method for Controlling and monitoring mechanism for colour non-uniformity

Based on the colour measurement data, the best recipe among the four-dyeing recipe with minimum total colour difference value (ΔE) was chosen for further studies. Dye trials were conducted on full skins using the recipe, which was best selected recipe among the four alternative dyeing recipes. The improvement of colour uniformity was analyzed using the dress glove leather samples obtained from ELICO-Awash tannery. Since, the leathers from the tannery were made following recipe as per Annexure 2.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of the dyes

Two dye stuffs were chosen for this study. The initial experiments were conducted to understand the exhaustion behavior of the dyes used in the study. The exhaustion results of Coloderm Orange GS and Coloderm Red SG are tabulated in Table 4.1 ad 4.2, respectively. In order to understand the exhaustion behavior, the dyeing recipe provided in Annexure 4 was followed. It could be observed from the table that both the dyes showed better exhaustion behavior. With increase in the offer of Coloderm Orange GS from 1 to 10%, the amount of dye present in the exhaust liquor varied from 13.73 to 95.41 ppm, respectively. Similar condition was observed with Coloderm Red SG (Table 4.2), where the amount of Red SG present in the exhaust liquor varied from 6.27 to 98.30 ppm for the increase in the offer of dye from 1 to 10%, respectively. Hence, it could be inferred that, with increase in the offer of the dyes, the exhaustion of the dyes decreased, but not very significant. However, it could be understood that, the chrome tanned sheep leathers have better affinity for the anionic dyes.

Table 4.1 Exhaustion characteristics of Coloderm Orange GS

% offer of dye	Initial dye offer (mg)	Concentration of exhaust Liquor (mg/L)
1	59.2	13.72
3	176.7	19.42
5	338.5	41.44
7	453.6	61.69
10	566	95.41

Table 4.2 Exhaustion characteristics of Coloderm Red SG

% offer of dye	Initial dye offer (mg)	Concentration of exhaust Liquor (mg/L)
1	74.4	6.27
3	221.1	23.39
5	336.5	36.07
7	506.8	65.17
10	716	98.03

Similarly, penetrative behaviors of the chosen dye stuffs have also been studied and the results of the experiments are tabulated in Table 4.3 and 4.4 for Coloderm Orange GS and Coloderm Red SG, respectively. Along with the rating of penetration, the colour levelness of the crust leathers and also the shade intensity of the crust leathers was also visually observed and recorded in the respective Tables.

Table 4.3: Penetration rates and colour qualities of Coloderm Orange GS

% of dye offer	Coloderm Orange GS		
	Penetration rating	Colour levelness	Intensity of Shade
1%	2	Good	Good
3%	2/3	Good	Good
5%	3	Good	Good
7%	4	Good	Good
10%	5	Good	Good

Table 4.4: Penetration rates and colour qualities of Coloderm Red SG

% of dye offer	Coloderm Red SG		
	Penetration rating	Colour levelness	Intensity of Shade
1%	1	Very good	Very good
3%	1/2	Very good	Very good
5%	1/2	Very good	Very good
7%	3	Very good	Very good
10%	4	Very good	Very good

It could be seen from the table that the penetration rating for Orange GS was better than Red SG, with increasing offer of dyes. However, it could also be observed that the with lower offer of dyes, the penetration rating was poor in both the dyes. This could be attributed to the fact that the at lower % offer of the dyes, sufficient quantity of dye is not available for achieving the complete penetration of the dyes in to the leather matrix. On the other hand, by increasing the % offer of dyes, more amount of dye molecules is available, whereby quick penetration was achieved.

On the other hand, with respect to the colour levelness and intensity of shade is concerned, it could be clearly observed from the table that Red SG had better levelness and also very good intensity of the shade than Orange GS. This could be attributed to the fact that, owing to the poor penetrating power of Red SG, the dye is remaining on the surface and gives a better intensity and levelness of shade. On the other hand, the Orange GS owing to the high penetrating power, has distributed itself uniformly in to the matrix and the surface seems to be less intense. Hence, these two dyes can be used in combination, we get a good penetrative dyeing and also result in crust leathers having better colour intensity and uniformity.

4.2 Identification of the Factors affecting the non-uniform dyeing

4.2.1 Concentration of dyestuff

The effect of concentration of dye on the final colour value of the dyed crust leather was conducted. The results of the CIE Lab values for the crust leathers dyed using Orange GS and Red SG for different % dye offers is provided in Table 4.5 ad 4.6, respectively.

Table 4.5: L, a and b values of leathers dyed using different % of Coloderm Orange GS

CIE Parameters	**% offer of Coloderm Orange GS**				
	1	**3**	**5**	**7**	**10**
L	65.05	63.33	61.20	61.99	58.87
a	29.01	32.16	35.25	35.57	38.47
b	29.32	35.36	41.97	43.06	49.27

It could be observed form Table 4.5, for increasing offer of Orange GS there is a change in the L, a and b values. It is clearly observed that, by increasing the % offer of dye from 1 to 10%, the L value decreased from 65 to 58, respectively, which ensures that the colour of the leather was darker for higher offer of dyes. Similarly, the a and b values also showed an increasing trend, from which it can be inferred that the colour intensity was also improved with increased offer of the dye.

Table 4.6: L, a and b values of leathers dyed using different % of Coloderm Red SG

CIE Parameters	% offer of Coloderm Red SG				
	1	3	5	7	10
L	50.75	46.10	45.76	45.09	45.88
a	49.84	52.02	52.20	51.94	51.90
b	34.62	37.99	38.40	38.03	37.36

From Table 4.6, it could be seen that unlike Orange GS, increasing offer of Red SG did not have much influence on the L, a and b values. Only the L value reduced by 4 units, confirming the darkening of shade. Otherwise the a and b values almost remined the same. This is in confirmation with our earlier finding that the Red SG gives rise to intense shade as it has less penetrating power. Hence, it could be inferred that, for obtaining brighter shades by mixing these two dyes, more amount of Orange GS and less amount of Red SG is sufficient. With both the dyes, the offer of 5% gave better colour values, which was also suggested as the optimal offer by the dye manufacturer, the same was used for subsequent experiments.

4.2.2 Substance/Thickness of the Skin

Effect of the substance/thickness of the skins on the dyeability of leathers were studied. The results of the studies using Orange GS and Red SG are provided in Tables 4.7 and 4.8, respectively. Four different recipes (Annexure 3 to 6) were used for this study.

Table 4.7: L, a and b values of butt and belly portion dyed using Coloderm Orange GS

CIE Parameters	Annexure 3		Annexure 4		Annexure 5		Annexure 6	
	Butt	Belly	Butt	Belly	Butt	Belly	Butt	Belly
L	60.37	55.59	60.34	58.84	59.08	58.16	64.91	59.84
a	42.39	46.51	38.76	41.43	40.88	42.01	35.50	40.81
b	49.33	56.87	47.54	54.08	50.53	53.35	40.49	50.09

From Table 4.7 it could be seen that for all the recipes employed, the L values of the butt regions were higher than the belly regions, implying belly regions are darker than the butt regions. Similarly, there were also differences in a and b values observed between the butt and belly regions for all the recipes employed. Where the belly portion had intense dyeing than the butt regions. This could be attributed to the fact that when compared to belly portion, the butt portions have more fiber density and higher hide substance. Hence, it could be inferred that, owing to the presence of higher fiber density in butt region and also due to the high penetrating power of Orange GS, the butt region was lighter and less intense than the belly region. In belly region, owing to the less amount of fibers, less amount of dye has penetrated and more amount of surface deposition has taken place, which has made the colour more intense on the fibers, irrespective of the process followed. Furthermore, the Recipe provided in Annexure 5 has given more intense shade than other three recipes.

Table 4.8: L, a and b values of butt and belly portion dyed using Coloderm Red SG

CIE Parameters	Annexure 3		Annexure 4		Annexure 5		Annexure 6	
	Butt	**Belly**	**Butt**	**Belly**	**Butt**	**Belly**	**Butt**	**Belly**
L	44.71	47.12	45.23	48.45	41.80	43.77	43.85	47.56
a	52.52	53.46	52.99	51.94	53.00	53.63	53.07	52.76
b	39.54	38.58	37.79	37.09	39.71	39.65	40.45	37.89

In Table 4.8, it is observed that Red SG has dyed the butt region more intense and darker than the belly region, for all the recipes followed. This has been proved in the earlier sections that the Red SG has less penetrating power. Hence, in the butt region, where the fiber density is higher, more intense dyeing has been obtained than the belly region, where the fiber density is less. Here also, it has been observed that recipe provided in Annexure 5 has more intense dyeing than the other three process recipe. Hence, could be inferred that, if the retanning is not proper, and there is a difference in filling between the regions of the leather, then it affects the uniform dyeablity of the leather. Hence, there is a chance of getting non-uniform dyeing within the same leather.

4.2.3 Effect of Float length

Effect of the Float length on the dyeability of leathers were studied. The results of the studies using Orange GS and Red SG are provided in Tables 4.9 and 4.10, respectively. Four different recipes (Annexure 3 to 6) were used for this study. The results obtained by using Orange GS is provided in Table 4.9.

Table 4.9: L, a and b values of leathers dyed using Coloderm Orange GS with different float length

CIE Parameters	Annexure 3		Annexure 4		Annexure 5		Annexure 6	
	Short	Long	Short	Long	Short	Long	Short	Long
L	40.59	43.77	45.09	48.45	46.88	47.12	45.36	47.56
a	52.01	53.63	53.18	51.94	53.03	53.46	53.20	52.76
b	37.56	39.65	38.23	37.09	37.94	38.58	38.34	37.89

It could be observed from the Table that the leathers dyed with long float has shown decrease in L values and the intensity, however, the values are not significant. Hence, for a penetrative type of dyes, the float length does not have any significant effect.

Table 4.10: L, a and b values of leathers dyed using Coloderm Red SG with different float length

CIE Parameters	Annexure 3		Annexure 4		Annexure 5		Annexure 6	
	Short	Long	Short	Long	Short	Long	Short	Long
L	46.25	48.75	44.98	50.31	41.73	45.98	45.66	50.80
a	53.47	49.10	53.60	51.67	53.79	53.78	53.46	51.74
b	37.77	31.84	37.83	33.33	39.01	37.63	37.59	34.04

In Table 4.10, it could be observed that, the change of float length had effect on the dyeing of leather using Red SG. It is clearly seen that in all the processes, not only the L value has changed, the intensity has also changed with the change in float length. Owing to the nature of Red SG used, at lower float length, more amount of dye has fixed to the surface. With long float, the dye gets diluted, hence the L value and the intensity is less. Thus, it could be inferred that for dye having more surface fixing power, optimal amount of float length needs to be employed across all the batches, else will result in colour variation between batches.

4.3 Monitoring and Controlling of colour non-uniformity

The recipes provided in Annexure 2 to 6 were employed to process 5 numbers each of sheep natural crust. The respective L, a and b values along with the change in colour value (ΔE) is provided in Table 4.11. Process recipe in Annexure 2 is taken as control. The other recipes employed can be briefly explained as follows.

- Annexure 3: Reverse dyeing recipe
  (Wet back, fatliquoring, dyeing, fixation)
- Annexure 4: Regular dyeing recipe
  (Wet back, dyeing, fatliquoring, fixation)
- Annexure 5: Multiple stage dyeing recipe
  (Wet back, dyeing, fatliquoring, fixation, dyeing, fixation)
- Annexure 6: Regular dyeing recipe with dye levelling agent
  (Wet back, dye levelling, dyeing, fatliquoring, fixation)

Table 4.11: Calculated total colour difference between different dyeing recipes

Type of dyeing recipes	**Calculated total color difference(ΔE)**	
	Orange GS	**Red SG**
Annexure 3	9.83	2.76
Annexure 4	7.22	4.34
Annexure 5	3.17	2.07
Annexure 6	12.09	4.51
Control was leathers processed using from Annexure 2 recipe		

It could be observed from the Table that the leathers processed using the recipe provided in Annexure 5 showed the least variation in colour difference (ΔE). This observation was true for both the dyes used in this study. From Table 4.11, it is clearly seen that the minimal colour difference obtained was 3.17 for leathers dyed using Orange GS and 2.07 for leathers dyed using Red SG. Hence, it could be concluded that Recipe provided in Annexure 5, wherein the dye was used before and after retanning/fatliquoring operations has given best results.

In order to ascertain the outcome of the study, the leathers processed using the optimal recipe (Annexure 5) and the leathers processed at ELICO Awash tannery, following the control recipe (Annexure 2) were compared among themselves using the colour measurement instrument. The results are provided in Table 4.12 and 4.13.

Table 4.12 CIE Lab values of leathers from ELICO-Awash tannery (Recipe-Annexure 2)

CIE values	Control	Leather 1	Leather 2	Leather 3
L*	18.98	18.2	19.1	15.24
a*	7.67	7.61	7.5	6.93
b*	7.58	7.44	6.57	6.3
DL*		-0.78	0.12	-3.74
Da*		-0.06	-0.17	-0.74
Db*		-0.14	-1.01	-1.28
dE*		0.79	1.03	4.02

Table 4.13 CIE Lab values of samples dyed using recipe from Annexure 5

CIE values	Control	Leather 1	Leather 2	Leather 3
L*	19.12	18.83	19.54	18.28
a*	8.63	8.22	8.05	9.36
b*	8.45	7.87	9.12	8.97
DL*		-0.29	0.42	-0.84
Da*		-0.41	-0.58	0.73
Db*		-0.58	0.67	0.52
dE*		0.77	0.98	1.23

It could be observed from the Table that, both the leathers produced at the tannery and by following the experimental processes had colour variations. It is seen that the overall colour difference between the leathers produced at tannery were 0.79, 1.03 and 4.02, the average deviation was 1.94. The overall colour difference between leathers produced employing the recipe (Annexure 5) were 0.77, 0.98 and 1.23, the average deviation was 0.99. Hence, it could be concluded that by following the experimental recipe developed in this study, the overall colour difference between the batches could be significantly minimized.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Leather is a difficult substrate to dye; it has structural differences as well as other imperfections. To achieve the target of a level and uniform dyeing the leather dyer needs to be experienced and to have a thorough understanding of the dyeing properties of the dyes. Uniformly tanned leather, a suitable selection of dyes and well-designed dyeing recipe are essential for an even shade.

A full chrome tanned sheep skin was selected as starting material as wet blue sheep skin is also a preferable input material for dress glove leather production. A common crusting recipe was designed to have the unique physical properties of dress glove, specially the run property.

Dyeing properties of the dyestuffs was investigated by choosing Coloderm Orange GS and Coloderm Red SG, which are anionic acidic dyestuffs from M/s ColourTex India, Ltd., India. Coloderm Orange GS has better penetration rate while Coloderm Red SG has less penetration rate. It was also inferred that colour levelness and intensity of shade of Red SG was better compared to that of Orange GS.

Factors of colour non-uniformity were identified by conducting dye trials on possible causes of colour non-uniformity with four different well-designed dyeing recipes. When concentration of dyestuff, substance of skin and length of dyeing float were varied individually keeping other factors as constant. It was observed that these factors did have significant effect on the development of leathers having uniform dyeing property.

Controlling and monitoring of colour non-uniformity is analyzed by conducting dye trials using four different well-designed dyeing recipes. The total colour difference (ΔE) values obtained using multiple stage dyeing recipe was smallest as compared to the other three recipes by varying all possible factors of colour non-uniformity. From these observations, multiple stage dyeing recipe is the best alternative way to manage colour non-uniformity.

It is concluded that by following the experimental recipe developed in this study, the overall colour difference between the batches could be significantly minimized.

5.2 Recommendation

Dyestuffs exhibit different exhaustion characteristics and penetration rates which influence the colour levelness and intensity of the shade. Therefore, leather dyers

are recommended to select suitable dyestuffs which have better exhaustion characteristics and penetration rates during colour matching before bulk production.

Concentration of dyestuff, substance of skin and length of dyeing float are identified as factors for colour non-uniformity. During dyeing, these factors need to be controlled and monitored to achieve the target level of colour uniformity.

Multiple stage dyeing recipe is better and well-designed dyeing recipe to manage all factors of colour non-uniformity for those samples that have deep shade colour. It may not work for lighter shade since it is difficult to bring the lighter shade with multiple stage dyeing recipes.

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ANNEXURES

Annexure 1. Crusting of wet blue sheep skin for dress glove leather

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, ^{o}Be, etc)
Wash/Drain/ Wash				
Add	150	Water, 40^{o}C		Check pH=3.0/3.3
	0.5	Acetic acid	60’	
Re-chroming	1	Relugan GT 50	30’	
	1	Acid bate	45’	
	3	BCS	30’	
	0.5	Sodium Formate	30’	
	0.5	Sodium Bicarbonate (Three feeds)	60’	
Leave Over Night (L/O/N) Keeping the skins under the bath				
Next day ,Morning		Run	10’	Check pH=4.0/4.2
Drain/Wash/Drain				
Neutralization	150	Water, 35^{o}C		
	2	Sodium formate	30	
	1.5	Sodium Bicarbonate	60	pH 6.0/6.5
Drain/Wash/Drain				
Fatliquoring	100	Water, 50^{o}C		
	4	Syncontan TL	20’	
	5	Synthol DT		
	5	Synthol GT 616		
	2	Lecithin		
Fixation	1	Formic Acid	10	
	1	Formic Acid	10	
	1	Formic Acid	20	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 2. Dyeing of natural crust for dress gloving leather

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, °Be, etc)
Washing	1000	Water, 50°C	10’	
Drain				
Wetting back	750	Water, 50°C	30’	
	2	Ammonia		
	0.5	Wetting agent		
Leave Over Night (L/O/N) ,Keeping the crust under the bath				
Next day, Morning		Run	10’	
Drain/Wash/Drain				
Dyeing	750	Water, 35°C	45’	
	10	Dyestuff		
Check dye Penetration				
Fatliquoring	5	Synthol DT	60’	
	5	Synthol GT 616		
	2	Corilene LFA		
	2	Fish oil		
	2	Synthol WP		
	5	Formic Acid	30’	
	300	Water, 60 °C	30’	
	5	Dyestuff		
	3	Formic Acid	30’	
	3	Dyestuff	20’	
	1	Formic Acid	30’	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 3. Dyeing of natural crust for dress gloving leather (Recipe-1)

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, °Be, etc)
Wetting back	1000	Water, 50°C	30’	
	2	Ammonia		
	0.5	Wetting agent		
Leave Over Night (L/O/N) ,Keeping the crust under the bath				
Drain				
Fatliquoring	750	Water, 60 °C	60’	
	5	Synthol GT 616		
	2	Corilene LFA		
	2	Fish oil		
	2	Synthol WP		
Dyeing	10	Dyeing	45’	
Check dye Penetration				
Fixation	10	Formic Acid	5x5’+20	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 4. Dyeing of natural crust for dress gloving leather (Recipe-2)

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, °Be, etc)
Wetting back	1000	Water, 50°C	30’	
	2	Ammonia		
	0.5	Wetting agent		
Leave Over Night (L/O/N) ,Keeping the crust under the bath				
Drain				
Dyeing	750	Water, 35°C	45’	
	10	Dyestuff		
Check dye Penetration				
	5	Synthol GT 616		
	2	Corilene LFA		
	2	Fish oil		
	2	Synthol WP		
Fixation	10	Formic Acid	5x5’+30’	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 5. Dyeing of natural crust for dress gloving leather (Recipe-3)

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, °Be, etc)
Wetting back	1000	Water, 50°C	’ 30’	
	2	Ammonia		
	0.5	Wetting agent		
Leave Over Night (L/O/N) ,Keeping the crust under the bath				
Drain				
Dyeing	750	Water, 35°C	45’	
	5	Dyestuff		
Check dye Penetration				
	5	Synthol GT 616		
	2	Corilene LFA		
	2	Fish oil		
	2	Synthol WP		
	5	Formic Acid	2x5’+10	
Top dyeing	5	Dyestuff	30’	
Fixation	5	Formic Acid	2x5’+30	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 6. Dyeing of natural crust for dress gloving leather (Recipe-4)

Date: ____________ Quantity: ________________ Size: _________________

Breed type: _____________ Weight: ____________ Process by: ____________

Process	%	Chemicals	Time (min.)	Parameters (pH, ^{o}Be, etc)
Wetting back	750	Water, 50^{o}C	30’	
	2	Ammonia		
	0.5	Wetting agent		
Leave Over Night (L/O/N) ,Keeping the crust under the bath				
Drain				
Dye levelling	750	Water, 35^{o}C	20’	
	2	Dye levelling agent		
Dyeing	10	Dyestuff	45’	
Check dye Penetration				
Fatliquoring	5	Synthol GT 616	60’	
	2	Corilene LFA		
	2	Fish oil		
	2	Synthol WP		
Fixation	10	Formic Acid	5x5’+30’	pH 3.4/3.6
Drain/Wash/Drain				

Annexure 7. Production samples from M/s ELICO-Awash Tannery, Addis Ababa