Addis Ababa University

School of Graduate Studies

Addis Ababa institute of Technology (AAiT)

Chemical and Bio-Engineering

Approaches to Near Zero Utilization of Water in the Post tanning Operations of Leather Processing

By

Solomon Fessehaye

Advisor:

Dr. K J Sreeram

Principal Scientist, Chemical Laboratory

Central Leather Research Institute

Chennai – 600 020

September, 2014

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

LEATHER TECHNOLOGY STREAM

STUDY ON THE SPECIALITY OF ETHIOPIAN HIGHLAND HAIR SHEEP SKIN TO MAKE GLOVE AND CABRETTA

A Thesis Submitted To the Graduate School of Addis Ababa University, Addis Ababa Institute Of Technology ,Department Of Chemical Engineering In Partial Fulfilment Of The Requirements For The Degree Of Masters Of Science In Chemical Engineering Under Leather Technology Stream.

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Approved by

Name of	_____	_____
Chairman,	Signature	Date

Department Graduate Committee

Dr. K J Sreeram	_____	_____
Advisors	Signature	Date

Name of	_____	_____
Internal Examiner	Signature	Date

Name of	_____	_____
External Examiner	Signature	Date

September 2014

Acknowledgements

First of I would like to Thank Almighty God for his helping hand in all my moves.

Secondly, I would love to thank Ato.Wondu Legesse Director of Leather Industry Development Institute for giving me this opportunity to pursue my dreams on expanding my knowledge on leather technology/chemical engineering.

I forward my deepest gratitude to my advisor Dr. K J Sreeram Principal Scientist in Chemical laboratory at Central Leather Research Institute for his relentless and unreserved support during the course of this project work. I also wish to express my sincere gratitude to Dr. J Rhagava Rao Chief Scientist of Chemical Laboratory of Central Leather Research Institute for his encouragement, precious suggestions and insightful advice. Thirdly, I would love to thank my on bench mentor Ms. N. Bhargavi Reddy without whom this project work would have not been realized.

I would love to offer my thanks to all the twinning program scientists specially the twinning program coordinators Dr. B Chandrasekaran and Mr. P. Saravanan, and also Dr. B. Madhan, Dr. R. Aravindhan, Dr. P. Thanikaivelan for their esteemed support.

Lastly I make grateful acknowledgements to all the staff members of Chemical Laboratory in CLRI.

And grateful acknowledgement is made to all the staff members of Testing Laboratory Directorate in LIDI, especially to Ato. Tsegab Bekele, Aster, tiegist, Bereket and Model Tannery members.

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Abstract

Any industrial activity would generate waste, whose form would be as solid, liquid and/or gas. While industrialization is important to a nation's economy, the wellbeing of human kind is even more important. The conflict for water between mankind consumption and industrial activity is increasing day by day as the population is increasing. An industrial activity like leather processing is a water intensive process, with most of the industries consuming 35 L of water to process every kilogram of hide/skin. While it is easy to wish away an activity like leather processing, an analysis of the relevance of this industry to Nation building would reveal that this is the only industry that uses a byproduct of meat industry, viz., skin and converts it into a fashion commodity. In the transformation, a host of rural men and women are involved directly or indirectly. For the nation, it is a good source of export income. This research work is one of an out-of-the-box thinking of systematic reduction and utilize known concepts of recycle, reduce or recovery of used water from processing. For this, the methodology has relied upon the replacement of water with environmentally benign and clean/green solvent for transporting chemicals into the skin matrix instead. The work consists of identifying the appropriate solvent or solvent mixture that a) did not have any adverse effect on the fibre structure, b) where a significant number of leather auxiliaries could be dissolved or dispersed and c) could be easily recovered and reused. The combination of solvents was selected from amongst reported clean/green solvents and the solubility / stability of the auxiliary dispersions determined by the measurement of the zeta potential of the system. The initial interaction of

the dispersed auxiliaries with skin matrix being one of adsorption, various models of adsorption can be fitted to understand the nature of binding. The physical and visual properties of developed leathers have also been compared.

1. INTRODUCTION

1.1. BACKGROUND FOR THE RESEARCH

Leading researchers and statisticians around the world have been suggesting time and again that unless severe measurers are adopted the essence of life on earth – water may not be available in sufficient quantity for meeting even our basic needs. This indication has come forward based on facts from UN[1-5] such as a) population in high water stress areas remaining at about 40%, b) influence of a possible shortage or even current levels of seasonal shortage of water on business of 40% of fortune 1000 has been catastrophic, c) only 1% of quality water is available for industrial processes as well as human consumption. With quality of water required for industrial processes that includes agriculture and for human consumption remaining more or less similar, the increasing population – more so in developing world puts additional stress. An analysis of three major manufacturing industries – viz., paper, textile and leather indicates water consumption levels of 150-200 cu.m, 200-250 cu.m and 35-50 cu.m respectively. They also contribute to a significant wastewater discharge with large emission factors – many a times into river bodies carrying quality water for human use.

1.1.1. Role of Water in Leather Processing

Hide or skin in a live animal provides for protection against the harmful effects of weather such as protection against UV radiations, thermostatic control by way of adjusting to temperature changes etc. However, when the neural networks connecting the skin to the body are removed on the death of animal and the skin is flayed, all these properties are lost. A flayed hide or skin has about 70% water by its

weight, which in order to protect against bacterial degradation is reduced to less than 35% through the process of curing. However, during leather processing the water levels are increased to enable diffusion of chemicals into a skin matrix, as water is used as the medium of transport. The quantum of water needed for the process was determined by the uniformity of penetration and fixation of the chemical - more so in the case of tanning and post-tanning. In recent years, with drop in ground water levels in and around the tannery regions, tanners have been forced to look at methodologies for water conservation and reuse.

While leather-processing activity can be predominantly grouped under pre-tanning, tanning and post-tanning, it is the post-tanning activity, which comprises of retanning, fatliquoring and dyeing steps that adds aesthetics and value to the leather. The penetration and fixation of the post-tanning chemicals is hugely influenced by the quality of water. A close look at the post -tanning auxiliaries also reveals that they are generally formulated assuming the use of quality water for processing. In recent years, keeping in mind the deteriorating quality of water, leather chemical manufacturers have resorted to development of auxiliaries that are soluble/dispersible in hard water, under saline conditions etc. The British Leather Corporation has classified the efforts made by researchers and tanners towards water consumption under five major categories, viz., a) performance of water balance studies, b) measuring and increasing control, c) stopping bad practices, d) reducing process water and e) water recycling. In spite of adopting much of these best practices, the water usage for a tannery processing wet-blue to finish ranges from 58-85 L/m^2 of leather.

Gradual increase in intellectual curiosity of using organic solvents as a transporting vehicle for diffusion of chemicals in to the skin matrix was evident in the later part of the 19thcentury. Acetone was one of the famous water-miscible solvents used in processing by Ushakoff [7], which was subsequently ruled out for its flammability. A process of tanning or curing of hides in alcohol was patented previously by William H. Towers (1865). Through the years, several solvents were employed in leather processing, with no renowned influence.

This research work addresses to the important aspect of minimization of water usage in post tanning processes by replacing the same with solvents. Recent endeavors from researchers at Central Leather Research Institute have been based on individual solvents for pre-tanning and post-tanning processes. Their preliminary reports suggested that much of the commercial leather auxiliaries were not soluble/dispersible in single solvent systems. The present research pays attention especially, to the technical aspects of solvent processing and the possibilities of its continuance for mass production in competition with the aqueous process.

1.2. STATEMENT OF THE PROBLEM

Fig. 1.1 portrays the current stress on usable water. This project addresses to a solution for the leather industry, when the stress on available water grows higher, say by the year 2050 [1-3]. By 2050, global water demand is projected to increase by 55%. This would be mainly because of growing demands from manufacturing (400%), thermal electricity generation (140%) and domestic use (130%). Consequently, freshwater availability will be increasingly scarce over this period and more than 40% of the global population is projected to be living in areas of severe

water stress through 2050. It is threatening to know that groundwater supplies are diminishing with over-exploitation of the world's aquifers reaching about 20%. Worldwide deterioration of wetlands is also reducing the capacity of ecosystems to purify water.

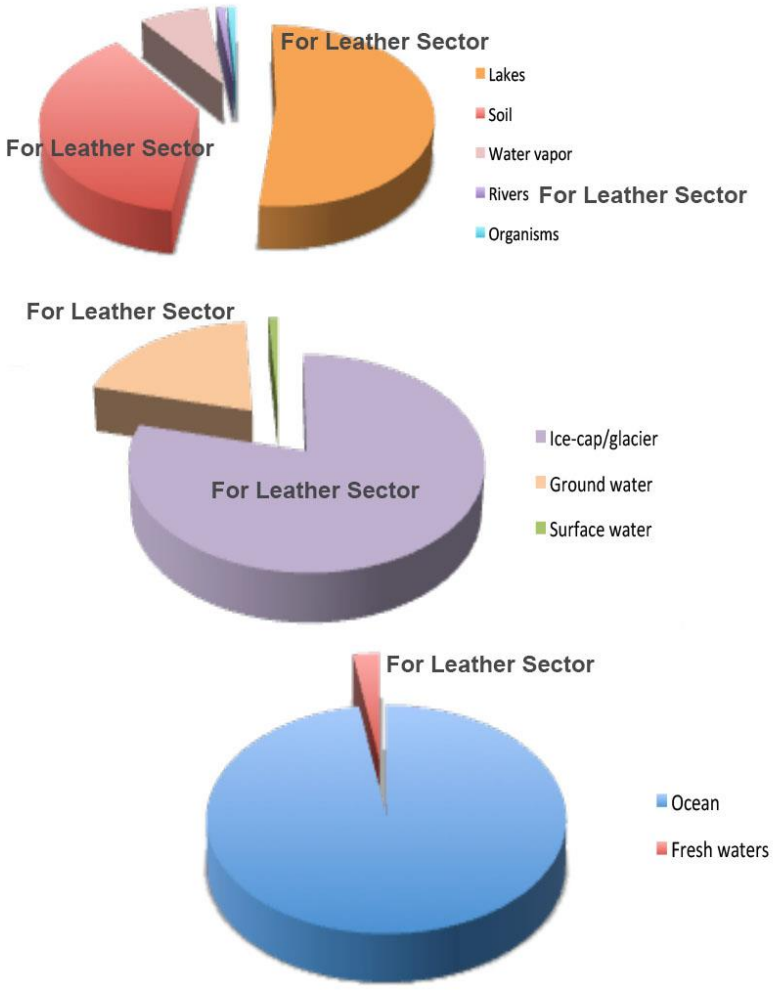


Fig. 1.1 Stress on usable water

Some aspects taken for consideration while designing this project are

- The industrial water use annually is increasing enormously. Industrial water use in 1995 was about 752 km^3/year and it is supposed to increase up to 1,170 km^3/year by 2025 [1-3].In other words, 24% of the total fresh water available is going to be utilized by the Industry
- Industries depend on water for all levels of production. It is mainly used as a raw material, as a solvent, coolant, transport agent, and energy source. It is astounding to know that many liters of water are used to produce glass, plastic, along with some fabric components according to Environment Canada's website [5]. Fresh water is not just for drinking anymore.
- The main concerns with regards to fresh water are:
    - For most industrial purposes, the water used needs to be freshwater, not salt water, because salt can corrode metal.
    - According to the UN World Water Development Report, some 300-500 million tons of heavy metals, solvents, toxic sludge, and other wastes accumulate each year from industry, most of which gets into the freshwater supply.
    - Another major concern about water use in industry is that the governments do not regulate or enforce the standards put in place to conserve water. Standards are put in place, however they are not closely followed.
    - Fresh water is needed for industries to survive, but it is also needed for humans to survive. While several management practices are in

place, the enormity of the problem demands development of several hitherto unknown methodologies.

In Ethiopian context the leather industry is one of the major drivers of the economy. But it is also considered as one of the most polluting industry. The main factors for pollution being a)excessive pollution due to the huge volume of aqueous media effluent, b) discharge of a significant amount of un reacted chemicals in the waste water and c) low concentration of chemicals contained by the conventional aqueous media. Presently there are different end- of-pipe wastewater treatment technologies to address the issue of pollution. To mention some, waste water treatment plants, advanced treatment systems like reverse osmosis, nano-filtration are commonly used but sustainability and the question of comprehensive solution are the main issues. Businesses are starting to be aware of reducing all forms of waste to improve profit, whether it is energy, raw materials or other resources. All water used must eventually come out as effluent, incurring a charge from the water company, based on its volume, chemical oxygen demand (COD) and total suspended solids (TDS).

In essence, the problem addressed to in this dissertation is the non-availability of quality potable water required for leather processing in the future, say by 2025, when current methodologies for water management such as reduced usage, recycling or recovery may not be sufficient enough to meet the needs of the industry. Reduced water availability is also likely to add up to increased cost of water treatment. To arrive at a completely new comprehensive solution for the current problems it is compulsory to use an alternative methodology for diffusion or mass transfer of chemicals in to the hide matrix in order to reduce or avoid the dependence on water.

1, 3, OBJECTIVES OF THE WORK

- Technology preparedness towards near zero utilization of water in post tanning processes through transition from water based chemical transport to clean/green solvent based methods

The objective is further sub-divided into

- Screening and selection of green solvent(s) to use as a transporting medium for post tanning auxiliaries.
- To study the interaction of leather auxiliaries with selected solvents and their mixture.
- Study the physico - chemical characteristics of the dispersions
- Understanding the leather making process in the minimized water scenario.
- study the adsorption properties of auxiliaries on to skin after transport through solvent medium
- Understand the overall feasibility of the methodology complete with parameters such as diffusion coefficient for the solvent mixture process

1.4. SIGNIFICANCE OF STUDY

The growing relevance of the leather sector to Ethiopian economy is well understood. The natural abundance of raw material, higher levels of unemployment, need for export earnings all favor the need to ensure sustainability of the leather sector. One of the aspects relevant to sustainability is the water consumption by the industry. Leather industry in the future will need to look at avenues for complete replacement of water with other solvents – more so for transport of chemicals in areas such post tanning that enhance the value of leather by over 350%. The present work looks at need to develop such a methodology through use of solvents for

chemical diffusion, thereby providing an easy methodology for recycle and reuse and avoidance of usage of water in leather processing.

2.0 LITERATURE SURVEY

2.1 DATA PERTAINING TO WATER BASED PROCESSES

Wastewater discharged and the emission load from each operation, quantified in terms of organic/inorganic loading is presented in Table 2.1

Table 2.1: Water discharge and emission loads from each unit operation in leather processing

	Soak	Lime	Delime	Tan	Post-tan	Finish	Total
Discharge (m^3/ton)	7 to 9	7 to 13	5 to 10	3 to 5	7 to 10	1 to 3	30 to 50
SS (Kg/ton)	11 to 17	53 to 97	8 to 12	5 to 10	6 to 11	0 to 2	83 to 149
COD (Kg/ton)	22 to 33	79 to 122	13 to 20	7 to 11	24 to 40	0 to 5	145 to 231
BOD (Kg/ton)	7 to 11	28 to 45	5 to 9	2 to 4	8 to 15	0 to 2	50 to 86
Cr (Kg/ton)	NA	NA	NA	2 to 5	1 to 2	NA	3 to 7
S (Kg/ton)	NA	3.9 to 8.7	0.1 to 0.3	NA	NA	NA	4 to 9
TKN (Kg/ton)	1 to 2	6 to 8	3 to 5	0.6 to 1.5	1 to 2	NA	12 to 18
Chlorides (Kg/ton)	85 to 113	5 to 15	2 to 4	40 to 60	5 to 10	NA	137 to 202
Sulfates (Kg/ton)	1 to 2	1 to 2	10 to 26	30 to 55	10 to 25	NA	52 to 110

A compilation of less water technologies reported in literature and relevant to this work is presented in Table 2.2

Table 2.2: Less water technologies and their significance

Less water technology	Significant contribution towards water reduction
Salt less preservation (Kanagaraj et., al 2005)	The process eliminates usage of salt in preservation process, thereby reducing the usage of water in soaking process
Counter current soaking process (Mariliz et., al 2010)	Water repeatedly used for the next batch, in the counter current way, which leads to reduction in usage of water for soaking process.
Enzymatic unhairing and fiber opening (Dettmer et., al 2013)	Usage of water for hair removal and the opening is very minimal (25 - 30%) when compared to conventional liming process (300%)
Direct chrome liquor recycling (Raghava Rao et., al 2003)	High exhaust chrome tanning leads to chromium uptake of above 80%. Because of consequent low chromium content, wastewater is used for pickling in subsequent batches, thereby reducing the usage of water for pickling system
Reverse leather processing (Saravanabhavan et., al 2005)	It avoids several do-undo processes thereby reducing usage of water.
Electrochemical oxidation (Sundarapandiyar et., al 2010)	The residual chemicals comes from each operation is oxidized and the wastewater again reused for the same operation

Minimization of water use for leather processing, which is copious, has been looked at seriously for the last two decades. One of the technologies includes adoption of

integrated cleaner technologies that provides a viable solution to the conservation of water. This requires both in-plant control as well as end of pipe treatment systems. The strategies employed the entire time to minimize water discharge and there by pollution load include searching alternative process [Mandal et al 2008; Thanikaivelan et al 2000] and or materials [Madhan et al 2003], recycle of wastewater and or reuse of treated wastewater [Saravanabhavan et al 2004], development of end-of-pipe treatment technologies [Kanth et al 2009, Sundarapandian et al 2010] and secured disposal of wastewater and sludge. Irrespective of the various solutions being available, the changes happening in leather industry are only incremental and yet the pollution problems are still the big challenge.

The suggestion of an organic solvent for leather processing is not new. Use of conventional organic solvents have been proposed but all suffered from the same fundamental drawback of flammability (Covington T., 2009). Kerosene was used for degreasing operation wherein the fat is removed [US Patent 1908116, 1933]. Generally solvents have been employed for operations such as drying, degreasing and dyeing [Sivakumar et al 2009, US patent 4147511, 1979, EP 0681054, 1995]. However, no work has been carried out to minimize water this far by using solvent mixture medium.

2.2 SOLVENT BASED PROCESSING

Solvents have a wide industrial application viz. cleaning, paints, adhesives, inks, pharmaceuticals etc. About 20 million tons per year is consumed by industries such as paints, surface cleaning, and pharmaceuticals, which is about 60% of the total solvent consumption[16]. Aliphatic, aromatic, terpenic, chlorinated hydrocarbons,

alcohols, esters, ketones, glycol ethers and other miscellaneous solvents are frequently used ones for industrial applications. Keeping in tune with the concerns – more so relating to health and accidental discharge related issues, several pharmaceutical companies have come out with their own internal guidelines for selection and usage of solvents. For instance, one of the leading pharmaceutical companies – M/s. GlaxoSmithKline (GSK) published its solvent selection guide in 1998, and followed it up with an expanded list in 2011[19]. The present version of the GSK solvent selection guide in addition to addressing their requirements of chemical synthesis also included factors with regards to process safety, reactivity with fire and explosion hazards. This guide has been split into solvents of different families, wherein the solvents have been ranked relatively in a scale of 1 to 10. Scores less than 3 have been categorized as red, yellow with score of 3 to 8 and green for greater than 8. Lesser scores on a particular count implied impending issues – mostly relating to its safety on use or toxicity.

While different agencies employed different criteria for solvent classification the general trend observed in such classification were

a. disposal – recyclability, incineration, volatile organics present, amenability to biological treatment
b. impact – fate and effect on environment
c. health – acute/chronic on exposure
d. flammability – flammability and explosion related issues on storage/handling
e. reactivity – under various conditions of storage and
f. life cycle – from aspects of producing the solvent to its final discharge

Based on the above criteria and employing screening tools like Environmental Health and Safety (for identification of potential hazard) and Life Cycle Analysis, Capello et al., 2007[16] evaluated 26 organic solvents under 9 categories such as release potential, fire/explosion and reactivity (representing safety hazard), acute toxicity, irritation and chronic toxicity (representing health hazard), air hazard and water hazard (representing environmental hazard). A typical output of such a study involving three solvents water, ethanol and ethyl acetate is presented in Table 2.3.

Table 2.3: Typical output of a solvent screening test (Capello et al., 2007)

S.N	Solvent name	LCA tool (Solvent cumulative Energy Demand (CED) per kg solvent/MJ-eq.)			EHS	Solvent Categorization
		Production	Distillation	Incineration		
1	Water	0	0	0	0	Most Green
2	Ethanol	50.1	-31.2	-31.7	About 2.5	Green Solvent
3	Ethyl acetate	95.6	-72.0	-27.6	About 2.9	Green with some issues
4	Ethanol-water (90:10) mixture	-	23	15	About 1.8	Green solvent mixture

In essence, survey of literature available in the public domain indicates a short-term option of reducing usage of water or its end-of-pipe treatment. While a complete radical change from water to any other benign solvent may not be possible immediately in pre-tanning (where most of the cleansing operations are performed), the same could be considered effective and advantageous in post-tanning processes. However, the challenge for such a process from the leather processing

angle would be the need to include water compatibility as an additional tool in the solvent selection guideline.

The forefront aim of the present work is to introduce, study and characterize application of ethyl acetate for the post tanning leather processing. Ethyl acetate is a colorless liquid with a fruity odor having a molecular weight of 88.10. It is slightly soluble in water and soluble in most organic solvents, such as alcohol, acetone, ether and chloroform. It finds use as a solvent in a wide range of applications due to its powerful solvency, high volatility and mild odor. It is used as a solvent for paints, coatings, adhesives, cellulose, plastics, fats, wood stains, across many industries, including: dissolvent for paints, varnishes, plastics and rubber. It is used as a solvent in, for example printing inks, varnishes and car care chemicals and in the manufacture of enamels, plastics and rubber. Ethyl Acetate is used in the food industry in the manufacture of flavoring and pharmaceutical industry as an extraction solvent.

Ethyl acetate has a very low dielectric constant (6.02 (63)) and water has high dielectric constant (78.54(63)). These two liquids are immiscible based on the fact that the columbic forces of attraction between water molecules are effectively inseparable by ethyl acetate. However, when ethanol (28.0(63)) which has a dielectric constant in between ethyl acetate and ethanol is added to the system a single phase is observed. This is explained by the relation between dielectric constant, polarity, intermolecular attractions and solubility. When ethyl acetate is added to water a clear separation is observed-with the denser water at the bottom. A red metal complex dye (Red 2BN) was added which went past the ethyl acetate layer and dissolved in the water layer, dyeing it red. But when ethanol was added

and the mixture stirred a single phase of uniform color was obtained. This explains the notion of solubility and miscibility of ethyl acetate, water and ethanol. Though ethanol is capable of forming a hydrogen bond, it also contains several relatively non polar carbon hydrogen bonds and therefore it is intermediate in polarity.

This mixture of solvents *per se* has a vast application viz. pharmaceutical, extraction process, food industry, cosmetics industry.

Most finger nail polish removers were originally acetone based but due to the high affinity of acetone for water, it tends to dry out the skin, cuticles and nails. On the other hand, chemists observed that ethyl acetate can remove fingernail polish just great, and since it was immiscible with water, it did not pull water out of skin, cuticles and nails which replaced acetone in the nail polish preparation commercially. Apparently, if the mixture can be applied on nails it is pretty obvious to be used as a leather processing medium with an appropriate personal EHS.

2.3. POST TANNING LEATHER PROCESSING

Leather attains important functional properties during the post tanning leather processing. This process interacts at skin architectural or macro-molecular level by imparting compaction (change of packing order) to the skin matrix unlike to tanning process which interacts at Armstrong or molecular level. Moreover, reduction of cohesion at inter fibril or fiber bundle level is obtained by incorporation of oils/fatliqours with aesthetic appeal bestowed mostly by coloration. To achieve the required functional property transportation and diffusion medium traditionally used is water. In the current investigation solvent mixture is used as a transporting medium. It is well known that wet blue substrate has certain charge that needs to be adjusted according to the final article requirement rescued by the process called

neutralization. This process gets rid of free acids, free sulfates and acid-chromium linkages. In the present work, the neutralization medium had an important impact in the current solvent processing of leather. Neutralization was done in water as well as in solvent mixture medium. The presence of water in the solvent mixture used has a great deal of importance in maintaining natural interaction of the leather auxiliaries as solvent acquire a dehydration potential.

2.4. ADVANTAGES OF USING THIS TECHNOLOGY

Any of the activity relating to water reuse or minimization involves an end-of-pipe treatment cost. Establishment of such facilities also need land, equipment and personnel costs. These are in addition to reduction in available water for human activities. Under such circumstances this project has the advantage of

a. Conserving portable water for future use/ generations
b. Looks at complete elimination of water without affecting the quality or salability of the leather
c. Uses low boiling solvents where energy for recovery is less than the energy for evaporation of water in soak beds
d. The loss of solvent is low due to use of a solvent mixture, wherein the cost of solvent and modifications to process drums is far offset from the cost for treatment
e. Leather drying costs are minimized
f. May contribute to lesser process time

3.0 MATERIALS AND METHODS

3.1. MATERIALS

3.1.1. Raw materials and Chemicals

Raw material: Conventionally processed wet blue goat skins, by cropping out the left and right sections of the butt area for experiment and control processes, were used for the study. All the chemicals used in the present study are of commercial and Analytical grade. Post tanning auxiliaries employed and their chemical nature are listed in Table 3.1.

Table 3.1 Post tanning Chemicals used for the study

Product	Classification	Chemical nature
$NaHCO_3$	Neutralizing salt	
HCOONa	Mild neutralizing salt	
Neutrigan	Neutralizing syntan	Naphthalene Sulphonic acid condensate
Relugan RE	Acrylic syntan	Aqueous solution of acrylic copolymeter
Basyntan FDI	Replacement Syntan	Phenol napthol condensate
Basyntan FB6	Melamine	Nitrogen containing resin
Lipoderm LP16	Lecithin Fatliqour	
Lipoderm BL2	Vegetable Fatliqour	
Replicker SX-25	Semisynthetic Fatliqour	
Replicker SX-E	Synthetic Fatliqour	
Wattle	Vegetable tanning material	
Brown RR	Dye	metal-complex
Green MBGL	Dye	metal complex
Brown GBT	Dye	acid dye
Black dye	Dye	acid dye
Red 2BN	Dye	metal complex
Blue dye	Dye	metal complex
Formic Acid		

3.1.2. Glassware and Accessories

Veils, Flasks, test tube, beakers, burette, pipette, measuring cylinders, separating funnel, glass rod, Erlenmeyer Flask, filter paper, spatula, laboratory retort stand, pH paper

3.1.3. Equipment used

Stainless steel tight fitting drums, Ultrasonic homogenizer, ZetasizerNano series(Malvern), UV-Visible Spectroscopy, Scanning Electron Micrograph (SEM), Fluoro Spectrophotometer(Model SS5100), , Kjeldehl distillation set (BUCHI-Evaporator R210), COD analysis digester, water bath, Centrifuge, Jisico drying oven, shaker SK-600, Oil Dynamic Micro Clicking Press(Guiliani), Digital Dynamometer(Giuliani), thickness tester(Guiliani), Ball Burst Test(Guiliani), Instron Universal Testing Machine, Analytical Balance, Thermometer, Digital pH measuring device, Dedicators.

3.1.4 Software for statistical study:

Design Expert Version 7 was used for statistical analysis of experimental data.

3.2 METHODS

3.2.1. Compatibility of mixture of solvents and post tanning chemicals: The preliminary experiments started with compatibility of solvents and their mixture with water. The compatibility of ethyl acetate in water was tested by keeping the amount of ethyl acetate and water as constant with gradual increase of ethanol until uniform homogenous mixture without any phase separation was got (Fig. 3.1).

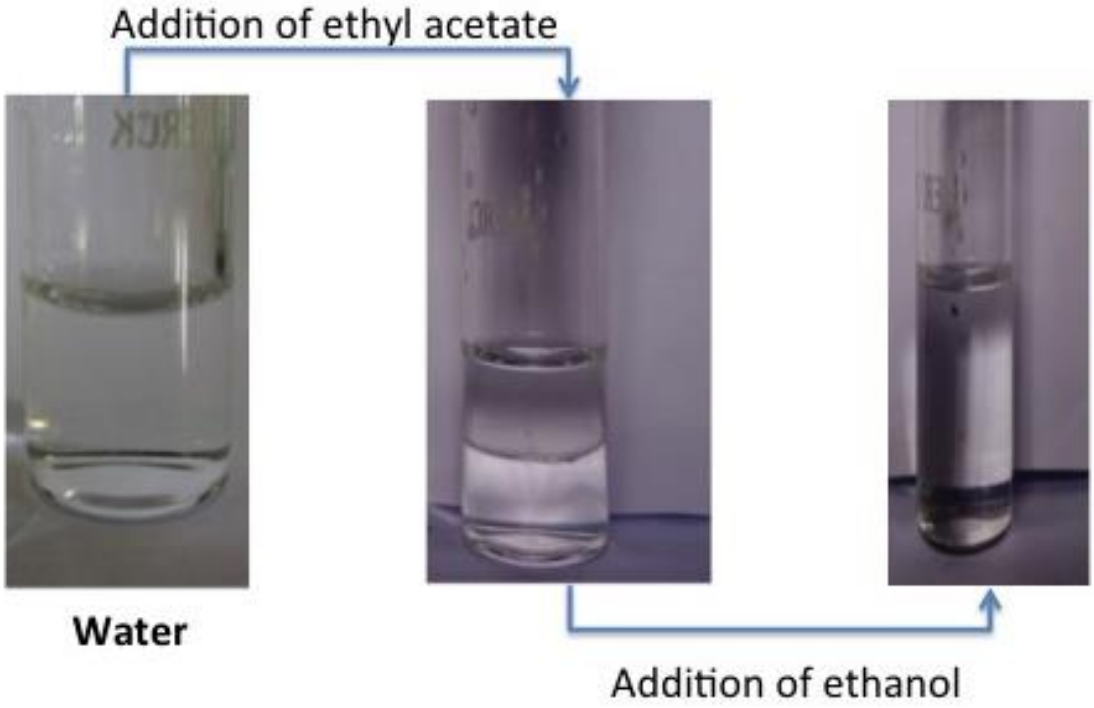


Fig 3.1. Pictorial presentation of the miscibility of water with ethanol and ethyl acetate (1:1:1)

All the post tanning chemicals were tested for their solubility in neat and mixture of solvents. A known amount of syntan/ Fatliquor/ Dye taken in to a transparent glass vial, known volume of water was added. To this, mixture of ethyl acetate/ ethanol/

ethyl acetate and ethanol mixture is added. This has been carried out starting from 0.1% to (10% w/v %). The ratio of solvent mixture and maximum solubility of chemicals in the solvent medium has been optimized. The general steps followed are presented in Fig 3.2.

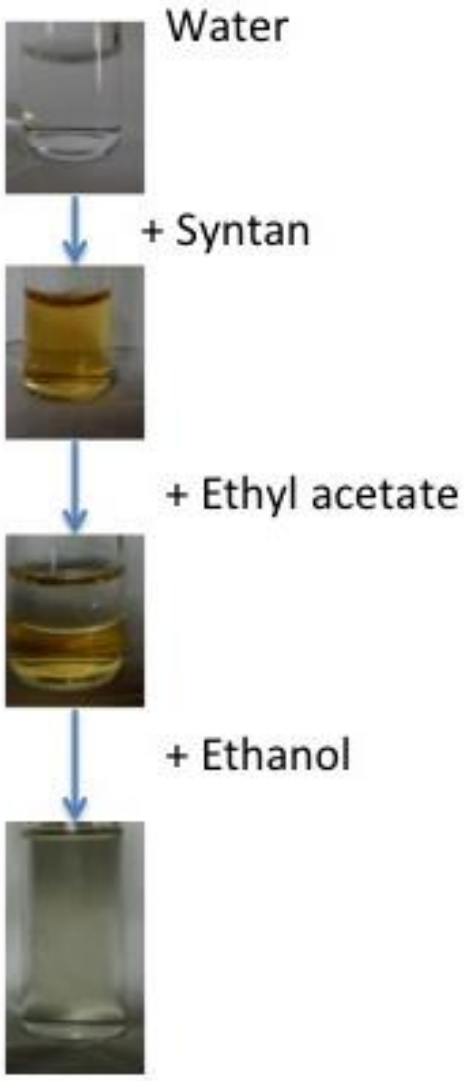


Fig 3.2. Typical pictorial presentation of solubility of a phenolic syntan in solvent mixture

3.2.2. Determination of particle size and charge: The dispersions of post tanning chemicals in solvents mixture and in water, were evaluated for physico-chemical characteristics. Dynamic Light Scattering method was used to determine hydrodynamic radii and charge of particles in a solution. A high performance particle sizer (Zetasizer Nano series, Malvern) at 25˚C that operates at 4 mW He-Ne laser power, scattering angle of 175˚C and wavelength of 633 nm was used. From the correlation function the diffusion coefficient, D, and the hydrodynamic diameter can be computed using the Stokes–Einstein equation. The zeta potential of dispersions was also obtained by conducting electro phoresis experiment in the solution. Converting electrophoretic mobilities by using Smoluchowski relation for aqueous, and Huckle relation for non-aqueous solutions zeta potential results were obtained.

3.2.3. Determination of moisture content: About 1g of experimental leather sample accurately weighed, dried in an oven at 100 - 105^{o}C for a period of 5hrs, cooled and weighed according to the *SLC - 3 methods*. The process of drying, cooling and weighing was repeated until constant weight is obtained. The moisture was then expressed as percentage of the weight of leather taken. This process was replicated three times.

Calculations:

$$\text{Moisture} = (\text{Loss in Weight} / \text{Weight of leather}) \times 100$$

3.2.4. Post Tanning processing in mixture of solvents: Tight-fitting stainless steel drums with RPM 15 were used for leather processing in a solvent medium. The butt

area of a wet blue goat skin was cut from the center and weighed separately. The left side was used for the solvent mixture processing while the right side was used for water control processing. After post tanning (Table 3.2), the crust leathers were hook dried, stake and buffed and were taken for organoleptic properties study and physical testing. Shaker SK-600 from JEIO Tech was also used for pieces of wet blue goat skins processing.

Table 3.2. Post tanning recipe for (a) Shoe upper (b) Garment Leather

Process	Chemicals	%	Time (minutes)	Remarks
Washing	Water	100	10	Drained
Neutralisation	Water Neutralizing syntan (Neutrigan)	100 0.7	20	pH-adjusted to 5.2 - 5.4 Drained
Retanning, Dyeing& Fatliquoring	Mixture of solvents Acrylic syntan (RE) Dye Lecithin fatliqour Phenolic syntan(LP - 16) Melamine syntan(FB-DI) Vegetable fatliquor Semi synthetic fatliquor Synthetic fatliqour Formic acid	150 2 2 3 5 5 3 3 3 2 1	 20 20 30 40 60 3x10+30	

a

Process	Chemicals	%	Time (minutes)	Remarks
Washing	Water	100	10	Drained
Neutralisation	Water Neutralizing syntan (Neutrigan)	100 0.7	20	pH-adjusted to 5.8 - 6.0 Drained
Retanning, Dyeing& Fatliquoring	Mixture of solvents Acrylic syntan (RE) Dye Lecithin fatliqour Phenolic syntan(LP - 16) Melamine syntan(FB-DI) Vegetable fatliquor Semi synthetic fatliquor Synthetic fatliqour Formic acid	150 1 2 3 2 2 3 4 4 1	 20 20 30 40 60 3x10+30	

b

The methodology employed for various trials, wherein the medium for neutralization as well as the neutralization auxiliary (Neutralization syntan (NS) or NS with mild alkali) is detailed in Table 3.3

Table 3.3. Methodology employed for processing - role of solvent medium

Goat crust leathers (CL) designation	Neutralization medium	Neutralizing auxiliary	Retanning medium	Dye stuff
CL1	Solvent mixture	NS	Solvent mixture	Brown RR
CL2	Water	NS	Solvent mixture	Green MBGL
CL3	Water	NS	Solvent mixture	Brown GBT

CL4	Solvent mixture	NS+Na_2HCO_3	Solvent mixture	Black dye
CL5** (total recipe offer)	Water	NS+Na_2HCO_3	Solvent mixture	Red 2BN
CL5*** (50%recipe offer)	Water	NS+Na_2HCO_3	Solvent mixture	Red 2BN
CL6	Water	NS	Solvent mixture	Brown RR
CL7	Ethyl acetate	NS+Na_2HCO_3	Ethyl acetate	Navy blue
Respective water control are represented by one asterisk (*) Except for *CL6* (garment) all the samples are for shoe upper purpose				

The post tanning process was done in a tight fit solvent resistant stainless steel drum. This avoids the loss of solvent in the form of vapor. The solvent in the vapor form condenses and goes to the bulk medium and again goes to vapor which gives rise to the circulation of the solvent between the vapor and liquid phase.

3.2.5. Adsorption properties study: Tight-fit stainless steel drums were used for adsorption studies. The butt area of wet blue goat skins (wt. 45gms) were taken and drummed in a red metal complex anionic dye of different concentrations (0.05%, 0.1%, 0.2%, 0.3% and 0.307%). The dimensions of the skins were taken to be similar to the experimental skins used for solvent processing. After weighing the skins were water neutralized using a neutralizing syntan to the required pH (pH = 2.5). The skins were washed and dipped in to a mixture of solvents (water: EtAC: EtOH-1:1:2). Then a specified amount of dye stuff was added and the drum was run at 12rpm. Liquors were collected every 20minutes for 2 hours. Then these liquors were quantified by using UV- Visible spectroscopy.

3.2.5.1. UV-Vis spectroscopic studies for dye adsorption: The liquors containing red metal complex dye used in adsorption isotherms, collected at regular intervals for quantitative study by using UV-Visible spectroscopy. UV-Vis Spectroscopy is one of the most important quantitative spectroscopic techniques. Shimadzu UV

spectrophotometer (UV-1800) with scanning wavelength range from 800 to 200nm was used for the present study. To quantify the amount of dye present in the spent liquor, the standard solutions with known concentrations 0.01ppm, 0.02ppm, 0.04ppm, 0.06ppm, 0.08ppm and 0.1ppm of red metal complex dye in the solvent mixture were prepared. The sample was scanned through the entire wavelength (200nm to 800nm) of the UV-Vis and the Lambda maximum (λ_{max}) was identified. Based on this, different unknown concentrations, collected from drum processing for Langmuir isotherm study, were evaluated at the identified λ_{max}. Taking a large number of known concentrations of the red metal complex dye and running them in the UV-Vis plotted standard graph, the slope of the standard graph was calculated.

3.2.6. Diffusion coefficient measurements: The PMI Capillary Flow Porometer was used for the present diffusion coefficient study. Primarily a wetting liquid (Galwick) was used to fill the pores of a wet blue goat skins. The pores were filled because the liquid-solid interfacial free energy was less than the solid-gas interfacial free energy that gives rise to reduction of the free energy system by spontaneously filling the pores of the sample (Fig. 3.3). The wetting liquid cannot come out voluntarily. Thus, a non-reacting gas is applied under pressure on the wetting liquid in the pore in order to displace it. The gas pressure and flow rates through wet and dry samples are accurately measured. The gas pressure required to remove liquid from the pores and cause gas to flow is given by

$$D = 4 \gamma \cos \theta / p$$

Where D is the pore diameter, γ is the surface tension of liquid, θ is the contact angle of liquid, and p is the differential gas pressure. From measured gas pressure and

flow rates, the pore throat diameters, pore size distribution, and gas permeability are calculated.

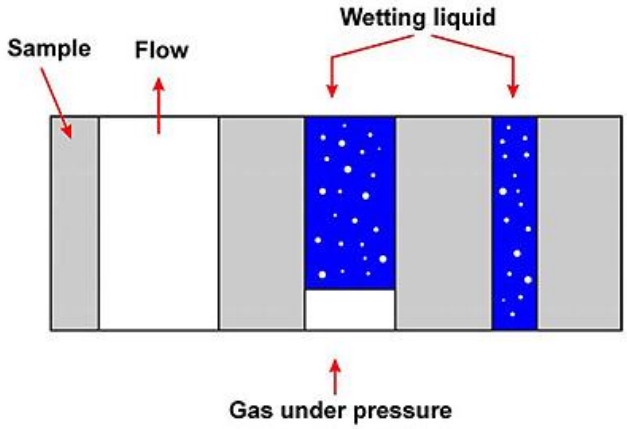


Fig. 3.3 Illustration of the principle of Capillary Flow Porometry

3.2.7. Physical strength parameters: All measurements were performed using International standard – viz., IUP. The physical properties such as tensile strength, % elongation at break (IUP 6, 2000), tear strength (IUP 8, 2000) and grain crack index (IUP 12, 2000) were examined for leather produced from solvent and water based post tanning processes. Specimens were conditioned at 20±2°C and 65±2°C R.H. over a period of 48 hours. The thickness of the specimen was taken as average of the three positions measured (two rear and one center).

3.2.8. Analysis of fastness properties: Color fastness properties to and pro rubbing of the dyed crust leathers was tested according to ISO 11640:1993(E) test method. Dry rub fastness was measured using Giuliani Rub Fastness tester.

3.2.9. Color value of the processed crust leather: Quantification of color were carried out by reflectance measurements using Techkon SpectroDrive (TKSDEB) and Premier Color scans Instruments Fluoro Spectrophotometer, Model SS5100 in order to know intensity of dye on grain side of the leather surface.The L*, a*, b* and **c** values recorded are the values in the CIELAB colour space. More negative value of L* denotes darker shade where as more positive value of L* shows lighter shade of the color. More negative value of a* implies more green color and more positive value of a* for more red color. Negative value of b*means more blue color and positive value of b* for more yellow color. The sample was first spread on a horizontal table and the device was taken from the horizontal track to be positioned on a leather sample for color measurement. The spectral measurement gives densitometric and colourimetric data of the spot measurement powered by ExPresso software.

3.2.10. Scanning electron micrograph (SEM) analysis: A sample from experimental and control crust leathers were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pre-treatment. All specimens were then coated with Gold using Edwards E306m sputter coater. A Leica Cambridge Stereoscan 440 Scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20kv with different lower and higher magnification levels

3.2.11. Total Solids of effluent liquors: The spent liquor from control and experiment post tanning processes were collected and evaluated for total solids. A known volume of filtered liquor was concentrated by using rotavapor, the semi dried sludge was then evaporated to dryness on a water bath. The beaker was then shifted

to desiccator, the sample was weighed at regular intervals, until getting the concurrent values.

Total solids = (Wt of the solids after drying/ Volume of the liquor) X 100

4.0 RESULTS AND DISCUSSION

4.1 SOLVENT SCREENING

The essential aim of this work was to find a solvent or solvents alternative to conventionally employed water as a transport medium for post-tanning chemicals. Boundaries for selection of solvents from the GSK Solvent Selection Guide (SSG) was set as follows: a) polarity, b) boiling point, c) vapor pressure, d) flammability, e) toxicity, f) changes to collagen conformation, g) miscibility with water present in the skin and h) cost. The same according to the manner in which the SSG is tabulated can be rephrased as a) boiling point, b) waste c) environmental impact, d) health impact, e) flammability and emission and f) reactivity/solubility (as obtained from SSG) along with information sourced from open sources such as a) polarity, b) changes to collagen conformation, c) miscibility and d) cost.

Repetitive iterative analysis of the SSG resulted in the identification of four solvents. A comparative assessment of these solvents vis-à-vis SSG tabulated scores in a scale of 0 – 10 is presented in Table 4.1 and annexure III.

Table 4.1: Comparative assessment of shortlisted solvents

S.no	Solvent	Melting point (°C)	Boiling point(°C)	Waste	Environmental Impact	Health	Flammability and emission	Reactivity /solubility	Life cycle score	Cumulative score
1	Water	0	100	4	10	10	10	10	10	54
2	Ethanol	-114	78	3	8	8	6	9	9	43
3	Ethyl acetate	-84	77	4	8	8	4	8	6	38
4	Propylene carbonate	-55	242	6	7	5	8	9		35

5	Ethyl lactate	-23	154	7	5	4	8	10		34

In addition to these parameters the $LD_{50,}$ dielectric constant and vapor pressure were compared. Adding the parameter of cost, propylene carbonate and ethyl lactate were dropped from the list.

The selected solvents acquire cumulative score >70% (cut off value ≥38, for water 54). The short listed solvents are given in annexure I. According to the HMSI (Hazardous Materials Identification Systems) standard, solvents which are having LD_{50} > 5,000 are classified as less toxic substances. So the screening cut-off for the selected solvents was found to be beyond 5,000. As a matter of fact the selected solvents are hugely utilized in pharmaceutical, cosmetics and as a flavoring in food industry. The short listed solvents based on LD_{50} values are presented in annexure II.

In order to broaden the scope of research and also the practical application, in addition to studies on solvent – water mixtures, solvent – solvent – water mixtures were also included in the studies. Knowledge of thermodynamic properties and phase equilibrium of ethanol, water, and ethyl acetate are important and have practical application such as fluid flow, heat transfer, mass transfer and study on molecular interactions in solutions. These properties are dependent upon the hydrogen-bond strength of hydroxyl groups, chain length, isomeric structures, and molecular interactions. Through various trials as mentioned in Chapter 3, a 1:1:1 mixture of the three solutions were found to be uniform. Theoretically, when alcohols are mixed with esters the H-bond structure of the alcohols break and a new H-bonded molecular species are

formed due to the interaction between the alcohols and esters. On the other hand, a hydrogen bond is initiated between the molecules of ethanol and water during mixing due to the polar hydroxyl group of ethanol and polar nature of water. These binary mixture characteristics are useful for ternary mixture predictions. It is proved that a three dimensional structure of polar molecules are obtained for the ternary mixture of ethyl acetate, water and ethanol [37-40]. The non-ideal behavior of real mixtures was characterized by a property referred to as excess molar volumes (V_m^E). V_m^E is expressed by the difference between the partial molar property of a component in a real mixture and that of a component in an ideal mixture [38]. This property can be thought of to occur from interactions between component molecules of mixtures 1) dispersion forces or weak dipole-dipole interactions which have a +ve impact, taken as a physical interaction 2) chemical interactions, which can be due to charge transfer, H-bond formation and other complex forming interactions, this have a –ve contribution, and 3) structural contribution resulting from difference in size and shape of the component molecules that gives rise to fitting of the component molecules of the mixture in to each other hereby reducing volume and compressibility giving a +ve value (4). V_m^E was obtained as negative for the binary mixture of ethanol and water, but volumetric expansion was observed for ethyl acetate and ethanol mixture, which was positive in value. For the ternary mixture, molecular packing between ethanol and water by undergoing intermolecular association and weak polar interaction and relative steric hindrance for the ethyl acetate ester group showed opposite effect. With

respect to viscosity, 1) deference in size and shape of component molecules and dipolar association lead to decrease in viscosity likewise 2) unlike molecules interaction such as H-bond forming and charge transfer lead in increase in viscosity in mixtures rather than in pure components. The calculated excess molar volumes from literature data is presented in Table 4.3.

4.1.1. Statistical analysis for solvents compatibility

The composition of each component during the mixture of solvents optimization determines the ultimate viscosity (at room temperature) of the mixture which was investigated by using mixture design software of Design Expert (Version 7.0 Stat-Ease Inc., Minneapolis, Minnesota, USA). The experimental design consisted of 14 design points, three component compositions and a dependent variable viscosity (Table 4.3). The statistics look very good (annexure IV). The model has a high F value, low probability values (Prob > F) and more than adequate precision (>4). The probability values show the significance of each term. R^2 approaching unity signifies that the model fits well. From the analysis of variance the R^2 value was found to be 0.9262 which shows that the system is well defined by the regression model (Figure 4.1).

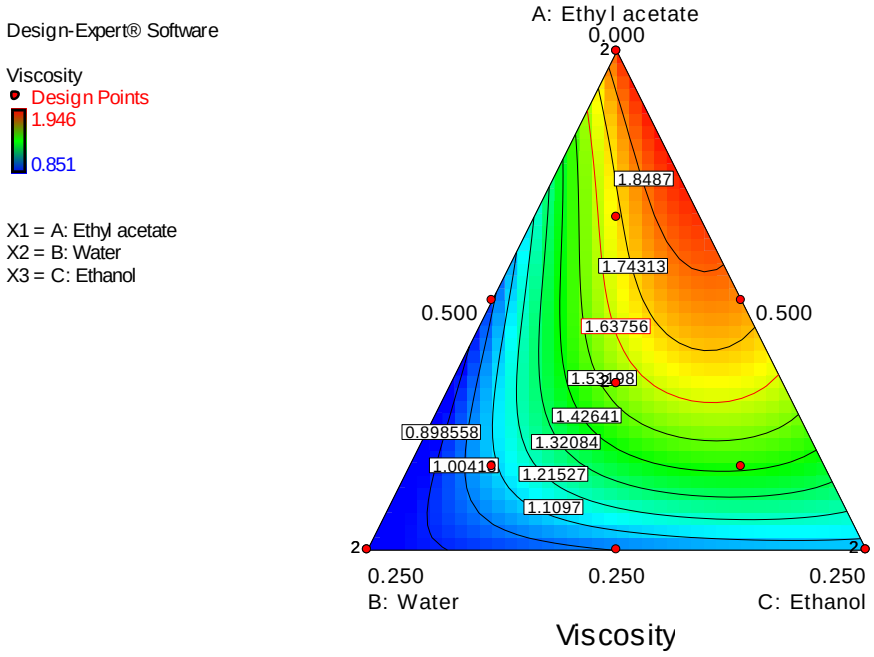
It was observed that the increase of water composition or decrease in ethyl acetate or ethanol increases the viscosity of final mixture. While the vice versa had an opposite effect in the final viscosity. The design point at 0.25:0.25:0.5 water, ethyl acetate and ethanol respectively was the selected based on its dissolution capability though other uniformly miscible component ratios are available at different mixing proportions. The viscosity obtained was 0,851 near to the viscosity of plain water at room temperature about 0.8902.

Table4.2. Mixture compatibility designs and viscosity values

Design points	Component Compositions (μl)			Viscosity mPa.s	Miscibility
	Ethyl acetate	Water	Ethanol		
1	0.000	0.500	0.500	1.946	Miscible
2	0.125	0.375	0.500	1.052	Immiscible
3	0.125	0.500	0.375	1.74	Immiscible
4	0.250	0.250	0.500	0.851	Miscible
5	0.250	0.375	0.375	0.977	Immiscible
6	0.250	0.500	0.250	1.027	Immiscible
7	0.083	0.458	0.458	1.67	Immiscible
8	0.208	0.333	0.458	0.968	Immiscible
9	0.208	0.458	0.333	1.67	Immiscible
10	0.167	0.417	0.417	1.56	Immiscible
11	0.000	0.500	0.500	1.946	Miscible
12	0.250	0.250	0.500	0.851	Miscible
13	0.250	0.500	0.250	1.027	Immiscible

14	0.167	0.417	0.417	1.56	Immiscible

Data source *Pires m. R. et al.* (35), the excess molar volume was obtained from measured viscosity at 25°C given in annexure VIII



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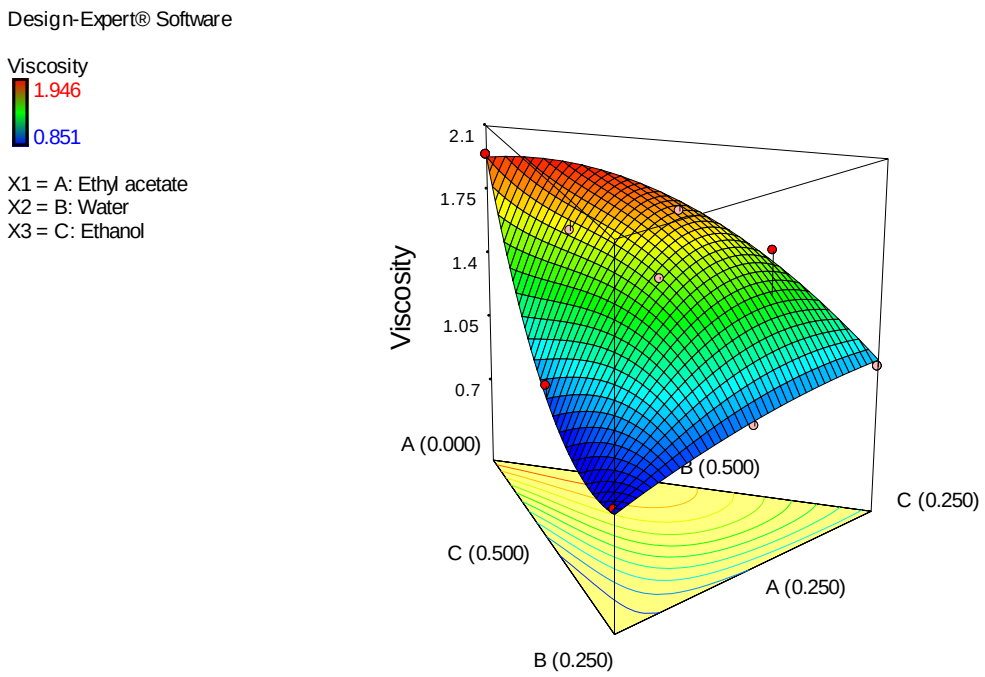


b

Fig.4.1. surface plot of mixture design (a) 2D, (b) 3D

4.2 INTERACTION OF POST TANNING LEATHER AUXILIARIES WITH THE OPTIMIZED SOLVENT MIXTURE

The solubility of commercial syntans, fatliquors and dyes were evaluated in the optimized ternary mixture of 1:1:2 (water: ethyl acetate: ethanol). Table 4.4 provides a detailed analysis.

Table 4.3: Excess molar volumes for solvents and their mixtures at varying temperatures*

Solvent	Temperature 298.15K			Temperature 318.15K		
	ρ (g·cm^{-3})	η (mPa·s)	V^E_m (cm^3.mol^{-1})	ρ (g·cm^{-3})	η (mPa·s)	V^E_m (cm^3.mol^{-1})
Water	0.99704	0.8902		0.99017	0.5961	
Ethanol	0.78510	1.102		0.76811	0.7461	

Ethyl acetate	0.89445	0.4260		0.86990	0.346	
Ternary mixture (Water:Ethylacetate:Ethanol-1:1:2 ratio)	0.84275	0.78467	-1.03	0.86350	0.58858	-0.54908

*Data source *Pires m. R. et al.* (35), the excess molar volume was obtained from measured density by the formula $V_m^E = \rho^{-1}(\Sigma x_i M_i) - \Sigma x_i M_i \rho_i^{-1}$, where x_i, M_i, and ρ_i are mole fraction, molecular weight and measured density respectively.

Table 4.4: Solubility of auxiliaries in solvents/ternary mixtures

Nature		**ETHYL ACETATE**	**ETHANOL**	**Water: EtAc: EtOH (1:1:2 ratio)**
Synthetic Tanning agents				
Phenol condensation product	Observation (before sonication)	Settles down	Settles down	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.1 %)	Insoluble (0.1 %)	Soluble (1.5%)
Naphthalene sulphonic acid condensate	Observation (before sonication)	Settles down	Settles down	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.1 %)	Insoluble (0.1 %)	Soluble (1.5%)
Complex aminoplast resin of medium polymeric size	Observation (before sonication)	Settles down	Settles down	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.1 %)	Insoluble (0.1 %)	Soluble (1.5%)

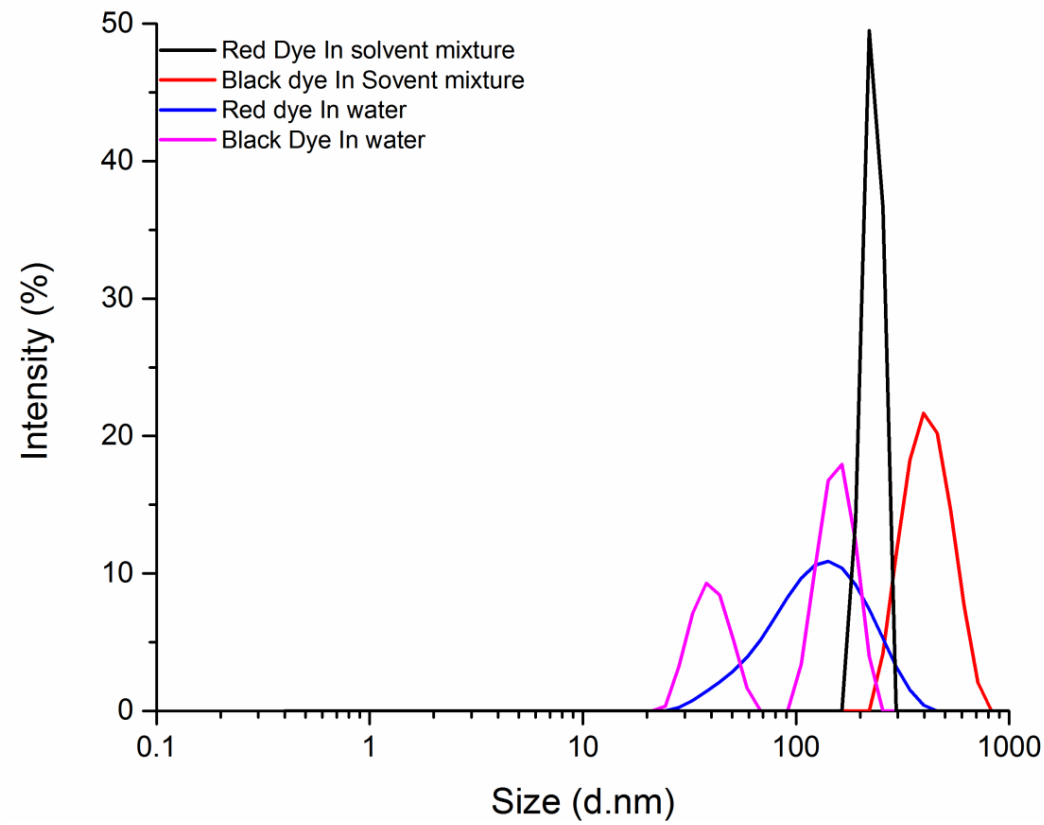
Nature		ETHYL ACETATE	ETHANOL	Water: EtAc: EtOH (1:1:2 ratio)
Acrylic Syntan Liq.	Observation (before sonication)	Settles down	Settles down	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.2 %)	Insoluble (0.2 %)	Soluble
Melamine	Observation (before sonication)	Settles down	Insoluble	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.2 %)	Settles down	Soluble (1.5%)
Vegetable Tannin Extracts				
Wattle	Observation (before sonication)	Settles down	Settles down	Soluble
	Observation (after sonication)	Settles down	Settles down	Soluble
	Inference	Insoluble (0.01%)	Insoluble (0.01%)	Soluble (1.5%)
Fatliquors				
Vegetable (anionic)	Observation	Particles settled down	Translucent	Soluble
	Inference	Insoluble	Soluble (10%)	Soluble
Synthetic (anionic)	Observation	Particles settled down	Particles settled down	Soluble
	Inference	Insoluble	Insoluble	Soluble
Synthetic (anionic)	Observation	Precipitation formed, settled down	Clear solution	Soluble
	Inference	Insoluble	soluble (3.3%)	Soluble

Nature		ETHYL ACETATE	ETHANOL	Water: EtAc: EtOH (1:1:2 ratio)
Synthetic (anionic)	Observation	Particles stick to walls	Large precipitate formed	Soluble
	Inference	Insoluble	Insoluble	Soluble
Synthetic (anionic)	Observation	precipitate formed, settled down	Solution	Soluble
	Inference	Insoluble	Insoluble	Soluble
Other Auxiliaries				
Sodium carbonate	Observation	Settles down	Settles down	Soluble
	Inference	Insoluble (0.2%)	Insoluble (0.2%)	Soluble
Sodium carbonate solution	Observation	Clear solution	Spontaneous separation	Soluble
	Inference	Soluble (0.2%)	Insoluble	Soluble (1%)
Sodium formate	Observation	Settles down	Settles down	Soluble
	Inference	Insoluble (0.2%)	Insoluble (0.2%)	Soluble
Sodium formate solution	Observation	Clear solution	Spontaneous separation	Soluble
	Inference	Soluble (0.2%)	Insoluble	Soluble (1%)
Acid black	Observation	Settles down	Settles down	Soluble
	Inference	Insoluble (0.2%)	Insoluble (0.2%)	Soluble (0.67%)
Acid black + water (soluble)	Observation	Clear solution	Spontaneous separation	Soluble
	Inference	Soluble (0.2%)	Insoluble	Soluble (0.67%)

From the results presented in the above table, it can be inferred that most of the leather auxiliaries, though in some cases to a small extent, were soluble in the mixture of solvents than individual solvents.

Under conditions were absolute solubility was observed; the size of the particles dispersed in a given solvent was also measured. The data presented in Fig. 4.2 provides a direct comparison between conventional system – water as dispersant and that of solvent mixture.

The figures below show the size distribution plotted %intensity as a function of size for the syntan and dyes.



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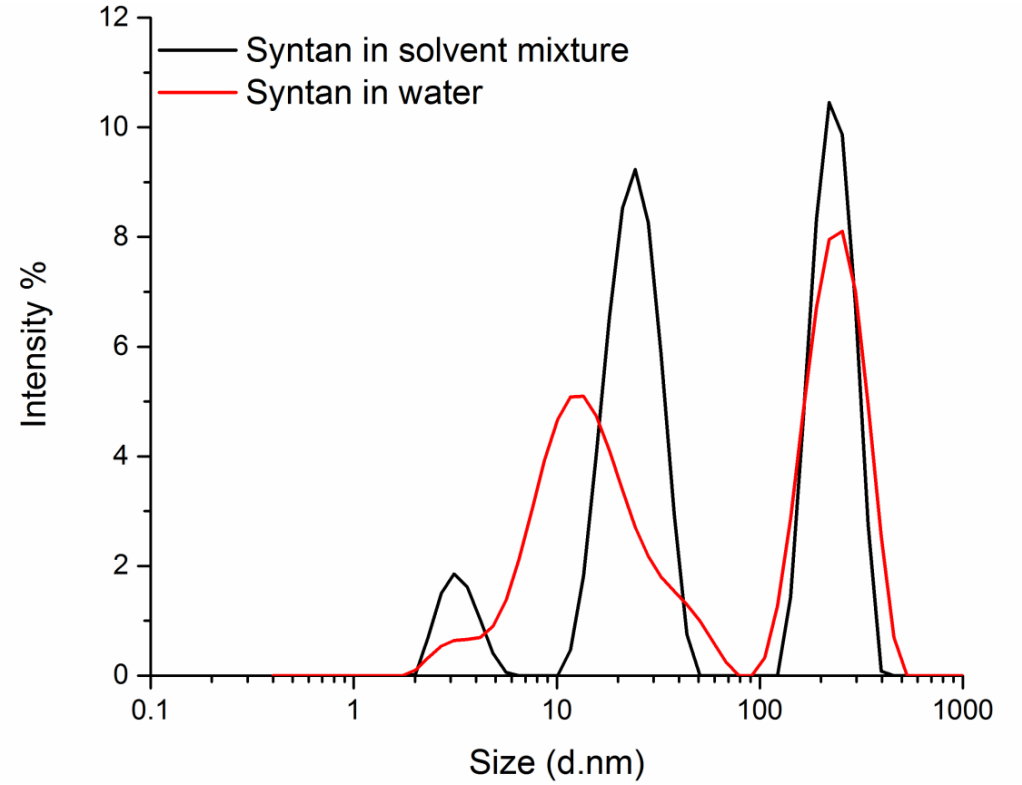


b

Fig. 4.2. Particle size distribution (intensity vs. average diameter) as measured for the dispersion of (a) dye in a given solvent (b)syntan in solvent mixture

Diffusion and penetration are the two main factors that depend on the particle size of the dispersions. It can be seen from Fig 4.2 that a monodispersed system is observed for dye dispersed in solvent, indicating a homogeneous dispersion and thus a uniform hue when used as a dye for leather. The red dye evaluated was a metal complex dye, which binds to the leather by coordinate covalent bond and the black acid dye binds to the collagen through electrostatic interactions. In tune with the size observed, visual assessment by experts indicated good penetration, color uniformity, depth of shade and dry rub fastness for leathers post-tanned using solvent as the diffusion medium.

No significant difference was however observed in the case of the syntan. The average particle size of the syntan in both systems was around 260 nm.

4.3. DIFFUSION COEFFICIENT

To obtain an understanding of the diffusion coefficient of the dye (metal complex – red) when solvent was the diffusion medium, the pore size and pore size distribution was measured. It is known that the pore sizes in hides/skins change not only with the species but also with respect to the origin and kind of processing. In this study, wet salted goatskins sourced from Tamil Nadu, India was employed as raw material.

Pore structure governs kinetics of physicochemical processes and flow of auxiliary dispersions into the skin matrix. Quantitative measurement of pore structure is essential for design, development and performance evaluation. Pore structure and distribution also determines adsorption, diffusion phenomena, fluid flow, and thermal conductivity properties.

The pores are identified by flow porometry when the wetting liquid is displaced from the pores and gas starts taking over. At the pore throat maximum pressure is required to remove the liquid completely, beyond which the presence of the pore is revealed as gas under pressure starts flowing through it. The pore diameter calculated from the differential pressure is the *diameter at its constricted part* as demonstrated in Fig. 4.3.

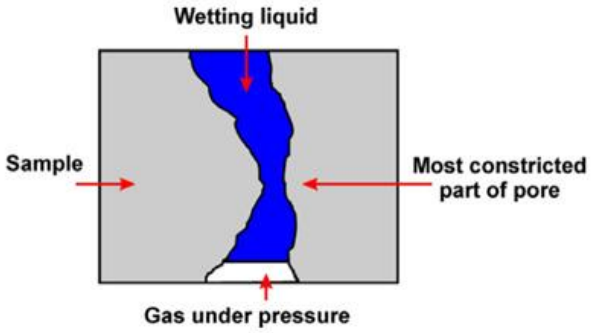


Fig. 4.3. Cross-sectional view of a typical pore

Measured differential pressures and flow rates can be used to determine all the pore structure characteristics. Initially the flow rate is zero. Flow starts when the largest pore is emptied under pressure. This pressure is called *bubble point pressure*. When the differential pressure is small, the gas flow tends to increase linearly with differential pressure. Flow increases with increasing pressure and becomes equal to dry flow at high pressures. The highest pressure corresponds to the *smallest pore size*.

The random weave of the collagen fiber in hides and skins develop a physical structure that is highly “porous”. This porosity depends upon the tightness of the weave and location within the skin. The radius of the pore is larger than 20000 Å. About one million number of pores is available in an area of 25 mm^2[40].The ability of the individual collagen fibres to reorient under stress and return to its original position after removal of stress – thus providing an elastic effect can be related to the porosity and voids present in the leather. Continuous pores also help transmit water vapor pressure across the substance. Under increasing pressure, a cumulative flow, expressed as the percentage of total

flow is obtained. As information on pore size distribution was scanty, a comparison of the sizes before and after tanning was made and detailed in Table 4.5. For the wet blue goat skin of our current concern, mean flow pore size of 0.18 μ was obtained that signifies about 50% of flow occurring through pores larger than that. The smallest pore diameter was 0.11 μ while the largest pore diameter 3.82 μ. This shows a broad size distribution for accommodating dispersions of syntans/dyes and emulsions of fatliqours.

Table 4.5. Pore size distribution observed before and after chrome tanning.

Parameter	Pickled pelt	Chrome tanned leather
Tortuosity	0.715	0.715
Smallest detected pore diameter	0.17 μ (@98% CFF)	0.11 μ (@98% CFF)
Mean flow pore diameter	1.53 μ	0.18 μ
Largest detected pore diameter	9.54 μ	3.82 μ
Std. deviation of average pore diameter	1.5	0.60
Bubble point pressure	0.69 PSI	3.9 PSI
Bubble point pore diameter	9.6 μ	3.82 μ
Maximum pore size distribution	140.4	4354.1
Diameter at maximum pore size distribution	0.16 μ	0.17 μ

To determine diffusion coefficient of dye through a wet blue goat skin having the above pore distribution, the solvent mixture with an initial dye concentration y_o (mg/mL) was brought into contact with the porous wet blue goat skin. The initial concentration of the dye was fixed at $2x10^{-3}g.cm^{-3}$. Diffusion coefficient

was measured using the formula: $F = 2y_0\sqrt{\frac{Dt}{\pi}}$, where *F* represents the amount of dye diffused across a unit area of leather at time *t*. For the measurements, wet blue goat skin with an area of 154cm^2 was loaded into a sample run containing the dye solution and run for one hour. Concentration of dye in the bath was determined by intermittent collection of sample. From the plot of dye uptake versus t$^{0.5}$, the slope of the straight line passing through origin was found to be 5.41576 x 10^{-7} and the apparent diffusion coefficient for diffusion of dye in to the skin matrix in solvent mixture medium was determined as 5.759 x 10^{-8} cm^2.s^{-1} (Figure 4.4). The diffusion coefficient of dyes in water is recorded as 10^{-8}-10^{-6} [41, 42] which puts the current analysis in a feasible position by maintaining uptake of chemicals.

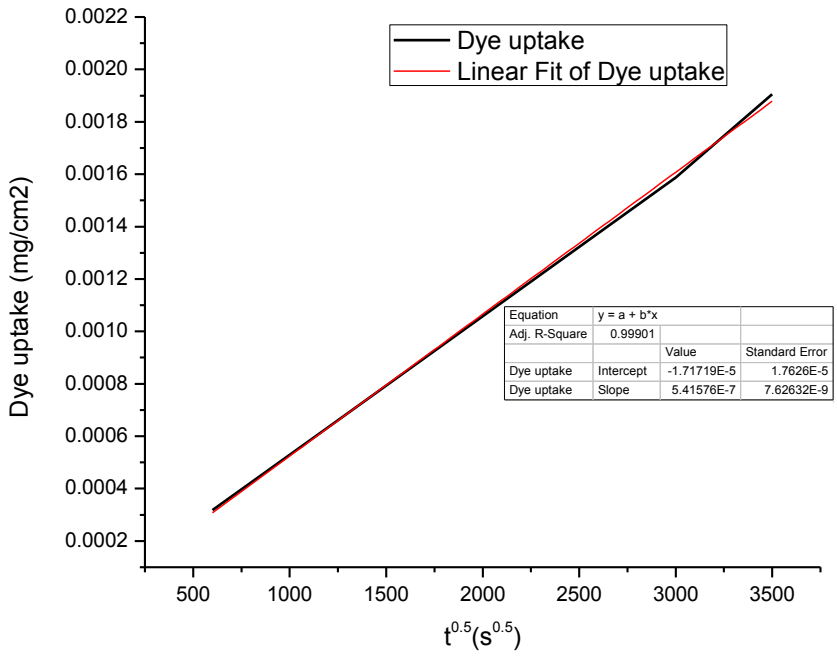


Fig. 4.4 Dye uptake per unit area Vs $\sqrt{t}$

Adsorption of dye to the surface of the leather is limited by the number of active sites (-NH_4^+) available. Accordingly, as the dye concentration increases, adsorption increases till all of the active sites covered, following which the same remains stagnant. The adsorption capacity (A/m) can be calculated as the difference between the dye concentration before and after equilibrium, divided by the mass of wet blue goat skin used, according to the equation $\frac{A}{m} = (C_0 - C_e)V/m$, where C_o is the initial concentration of the dye in solution (mgL^{-1}), C_e is the equilibrium dye concentration (mgL^{-1}), V is the volume of solution (L) and m is the mass of the adsorbent (mg). The adsorption capacity was determined for C_o values ranging from 22.5 mg/ml to 138.2 mg/ml and the A/m values computed (Table 4.6). The Langmuir isotherm was constructed from the plot of C_e against A/m (Fig. 4.5). The maximum adsorption capacity (B) and the equilibrium constant (K) was calculated according to the formula $\frac{C_e}{A/m} = \frac{C_e}{B} = \frac{1}{B} K$

The maximum adsorption capacity (B) for the dye in solvent medium was estimated as 307.1 mg/g and the equilibrium constant was 0.0183 L/mg.

Table 4.6. Determination of adsorption capacity of dye for varying initial dye concentration

	C_o (mg/ml)	**C_e (mg/ml)**	**Percent removal (%)**	**Adsorption Capacity (A/m)**	**C_e/(A/m)**
1	22.5	21.252258	49.98	0.059756996	355.407436
2	45	15.693939	65.12	0.06512458	240.983343

3	90	5.922241	93.41	0.186839464	31.696949
4	135	4.701401	97.25	0.289552442	12.685821
5	138.17	0	100	0.30704444	0

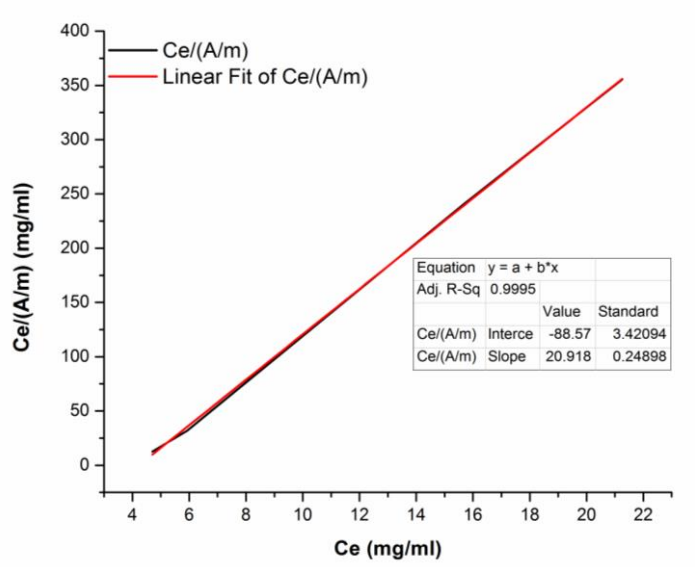


Fig. 4.5. Langmuir isotherm fit for solvent mixture medium

4.4. CHARACTERIZATION OF LEATHERS PROCESSED IN THE MINIMIZED WATER SCENARIO

4.4.1 Visual Assessment

Experts have evaluated the crust leather from both control and experimental processes. Their evaluation in a scale of 0-10, with 10 being the highest is presented in Table 4.7. It can be seen that post-tanning in solvent medium provides for comparable properties with that in water medium. The metal complex dye with a mono dispersed particle size character (as seen from the

particle size measurements) was rated better for dye penetration and uniformity as against the acid dye. Sample CL7 processed in ethyl acetate alone provided the poorest bulk properties because of insolubility of chemicals. Referring to *CL1* and *CL4* which were neutralized in a solvent mixture medium, *CL1* shows better softness, dye penetration and shade indicating that the choice of neutralization agent and medium was critical to obtain appropriate bulk properties. This is further exemplified from the fact that CL5** which was neutralized in water medium employing neutralization syntan and bicarbonate was rated to have good bulk properties. Nevertheless, bicarbonate as a neutralization salt was observed to create uptake problems which might be explained by its mild electrolytic properties breaking water-ethanol hydrogen bond. Consequently, possible salt concentration build up in water medium might lead to surface aggregation.

Loose grain is an undesirable defect especially for upper leathers as wrinkles are formed due to flexing during use as finished product. It was found that grain tightness of solvent processed leathers were comparable to that of water controls.

Table 4.7. Bulk properties of leather as evaluated by experts

Sample code	Full ness	Softness	Grain tightness	Grain smoothness	Dye penetration	Dye uniformity	Shade
CL1	**7**	**8**	**8**	**8**	**8**	**8**	**7**
CL1*	**8**	**8**	**8**	**7**	**8**	**8**	**8**
CL2	**5**	**7**	**7**	**6**	**7**	**7**	**8**

CL2*	**7**	**8**	**8**	**9**	**9**	**9**	**8**
CL3	**8**	**7**	**7**	**6**	**8**	**5**	**5**
CL3*	**8**	**7**	**7**	**8**	**8**	**8**	**8**
CL4	**7**	**6**	**7**	**7**	**5**	**7**	**6**
CL4*	**7**	**7**	**7**	**7**	**7**	**7**	**7**
CL5**	**8**	**8**	**8**	**8**	**8**	**8**	**8**
CL5***	**8**	**8**	**8**	**8**	**8**	**8**	**7**
CL6	**8**	**8**	**8**	**8**	**8**	**8**	**8**
CL7	**4**	**5**	**5**	**6**	**5**	**4**	**6**

4.4.2 Physical properties

Tensile strength of the leathers processed in solvent medium matched with that of standard norms (Table 4.8). Minor variations in the values have to be attributed to the improper penetration of the acid dye as well as improper neutralization in solvent medium when a combination of neutralization syntan and sodium bicarbonate was employed. The prescribed norms are 15 N/mm^2 at 40% elongation at break for a 1 mm thick leather.

Table 4.8. Physical properties of the leathers processed in solvent medium

Sample code	**Tensile strength and % elongation**	**Tear strength (double edge tear)**

	Tensile strength (N/mm^2)	**Percentage elongation at break (%)**	**Average tear load (N)**	**Tear strength (N/mm)**
CL1	22.4 (0.81)	84.0	47.3	47.6 (1.00)
CL1*	24.9 (1.13)	83.9	60.9	51.0 (1.20)
CL2	23.1 (0.06)	66.7	65.8	49.7 (0.94)
CL2*	29.0 (0.93)	97.1	58.4	58.1 (1.01)
Cl3	14.4 (1.00)	52.7	35.8	34.2 (1.05)
CL3*	9.2 (1.00)	95.0	32.6	32.9 (0.99)
CL4	18 (0.84)	47.7	33.15	33.1 (0.85)
CL4*	18.2 (0.98)	51.4	34.55	34.6 (0.82)
CL5**	17,5 (1.07)	65.7	31.6	29.3 (1.08)
CL5***	17.5 (1.12)	70.1	32.1	29.9 (1.08)
CL6	13.0 (1.00)	67.5	34.2	31.6 (1.08)
CL7	14.8 (0.83)	52.9	35.5	40.5 (0.82)

*values in parenthesis indicate sample thickness in mm

A higher tensile strength observed in solvent processed leathers is an indication of the uniform distribution of the syntan/fatliquor. Above 40% elongation at break indicates permanent elongation under stress – a plastic character – which indicates no further loosening of leather would occur once stretched and fixed to the sole, in the case of an upper. Although, the syntan distribution in solvent medium and water are similar, tensile strength of *CL1* is still greater than *CL4* which could be due to the heterogeneity of acid dye creating problems for further diffusion of the retanning auxiliaries. Also the effect of Na_2HCO_3 have to be doubted as leathers incorporating the very salt for neutralization are showing inferior physicochemical properties. All leathers complied with the tear

strength norms of 40 N/mm^2 for a sample of 1 mm thickness. Variations in values, similar to the case of tensile strength has to be attributed to the inhomegenity in distribution of syntan/fatliquor due to improper neutralization.

Table 4.9 details the grain crack strength properties of the leathers. Grain crack is effected due to weak grain surface characteristics of leather by more filling and loading of tanning and retanning materials in the grain side. Simple folding and flexing cannot visualize grain crack failure. Thus, grain crack load and distension tests are normally done using standard test equipment called lastometer. The grain crack strength (IUP 9, 2000) measurement values reveal enhanced resistance to crack for solvent processed leathers. This implies that strength properties were not affected rather enhanced, in some cases, by using mixture of solvents as a medium for post tanning processing.

Table 4.9. Grain crack properties of the leathers processed in solvent medium

Sample code	Load at grain crack (Kg)	Distension at crack (mm)
CL4	13.0	5.9
CL4*	17.6	6.6
CL7	18.0	7.1
CL5**	22.6	6.7
CL5***	18.7	6.9

4.4.2.1. Dry rub fastness properties

The leather products often are subjected to mild and constant abrasion by contact materials. Abrasion properties of leather surfaces are mostly related to unreasonable application of retanning materials in the post tanning processing of leather. Table 4.10 displays dry rub fastness values for control and experimental leathers. Dry-rub fastness obtained is maximum for an acid dye used solvent processed leather while relatively minimum value is obtained for the ethyl acetate processed crust leather owing to the poor solubility and dispersion properties of dyes. All in all, dry rub fastness values acquired were very good which implies that colour of the leathers dyed in solvent mixture medium can withstand dry rub conditions in a better way.

4.4.3. Color measurements

The color measurement values presented in Table 4.11 reveal solvent processed leathers exhibit better values to that of water control. Color measurement values shown in Table 4.11b quantify that leather dyed with Brown RR (metal complex dye) processed using solvent mixture show greater richness and greenness of color compared to that of control leathers. Thus, a lighter and brighter yellow brown color is obtained

Table 4.10. Dry rub fastness properties of solvent processed and water control crust leathers

Sample	Dry rub at 100 cycle		
	Test piece	Test pad	Average fatness
CL1	4	4	4
CL1*	4	4	4
CL2	4/5	4/5	4/5

Sample	Dry rub at 100 cycle		
	Test piece	Test pad	Average fatness
CL2*	4/5	4/5	4/5
CL3	5[a]	5[a]	5[a]
CL3*	¾	4	¾
CL4**	4	4	4
CL6	4/5	4	4/5
CL7	3	4/5	¾

[a]3- fastness is bad, [a]5- excellent rub fastness

Referring to the table, higher L* values for experimental leather show augmented depth of shade. Similarly higher a* value is for the more redness and increased b* value denote more yellowish leather with respect to the water control. From Table 4.10a, ΔE^*_{ab} value for *CL1*is maximum revealing obvious difference of color which can be related to dispersion homogeneity of metal complex dye. On the other hand, values *CL2* and *CL3* possess values in the range of 3 – 4 which reveals very small to medium difference with respect to water control. While CL4 shows small shade difference from the water control. As a whole, color measurement values depict that no huge difference exist between solvent processed and water control leathers. On the other hand, chroma (saturation) expresses the dominance/strength of hue which shows the sample has intensely saturated hue than the control. This higher values correlates with the fact that metal complex dyes behavior of maximum dispersion.

Table 4.11. Color measurement values for the solvent mixture processed and water control using a. Techkon SpectroDrive b. Fluoro Spectrophotometer model ss5100

Sample code	% Dye	Measured values								
		C	L*	a*	b*	ΔC	ΔL*	Δa*	Δb*	ΔE^*_{ab}
CL1	2	.49D	54.02	20.29	20.73					
CL1*	2	.64D	45.59	21.01	19.13					
						-0.15D	8.43	-0.72	1.60	8.61
CL2	2	1.04D	39.81	-8.27	2.93					
CL2*	2	.97D	43.15	-9.21	1.35					
						0.07D	-3.34	0.94	1.58	3.81
CL3	2	.80D	43.72	6.78	8.83					
CL3*	2	.87D	40.46	7.06	9.12					
						-0.07D	3.26	-0.28	-0.29	3.28
CL4	2	1.13D	33.99	1.71	-8.20					
CL4*	2	1.12D	31.12	1.39	-7.74					
						0.08D	2.37	0.32	-0.48	2.93
CL5**	2	0.32D	56.12	44.77	-6.95					
CL5***	1	0.29D	63.39	33.11	-6.11					

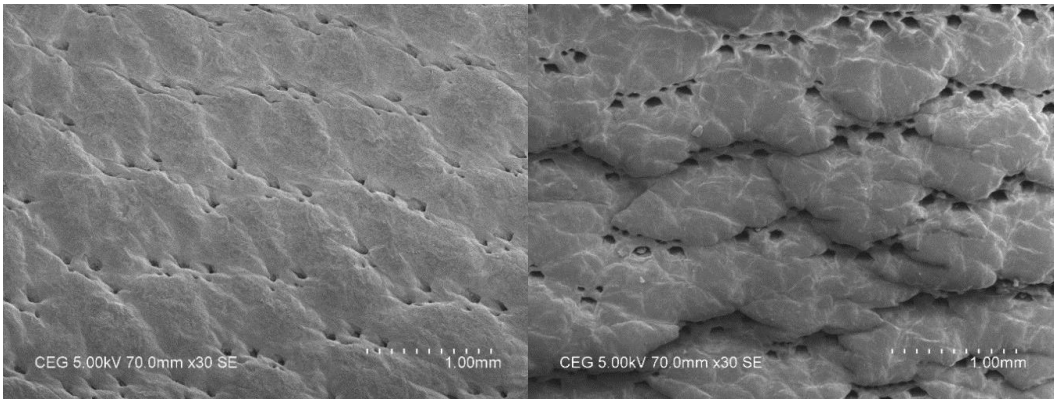
a. Techkon SpectroDrive results

	L*	a*	b*	C	H	ΔE_{ab}
CL1	55.173	19.391	21.492	28.947	47.923	-
CL1*	44.680	17.744	16.585	24.288	43.049	-
Respective Δ values	11.493	1.647	4.906	4.659	4.874	12.6

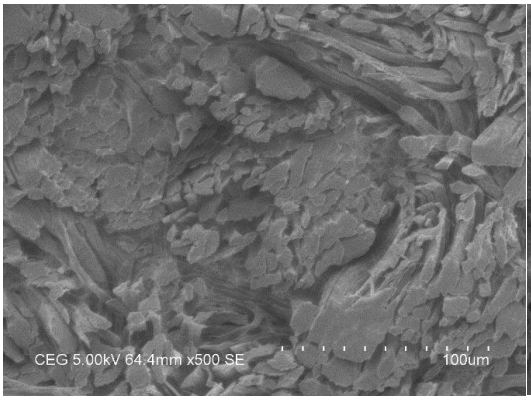
b. Fluoro Spectrophotometer model ss5100

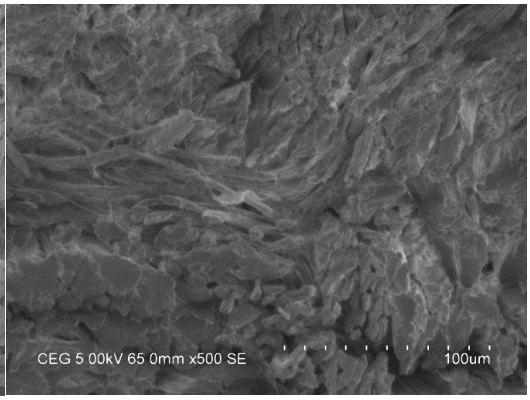
4.4.4. Scanning Electron Microscopic analysis of crust leather

A morphological study was carried out for crust leathers post tanned in solvent mixture as well as water (control) using scanning electron micrograph. The grain surface and cross-section of the control and experimental leathers at magnification of X30 and X500 are given in Figures 4.6. It is seen that the grain surface is clean without any foreign particles for both water and solvent processed leathers (Fig. 4.6 a,b and e). This could be due to the optimal solubilization and dispersion of post tanning auxiliaries especially syntans and fatliqours. Cross sectional images obtained through scanning electron micrographs of crust leather samples from control and experimental post tanning processes show well separated and opened up fibers for both solvent and water processed leathers (Fig. 4.6 c,d). Thus, it can be deduced that solvent processed leathers show a comparable result to that of control leather.

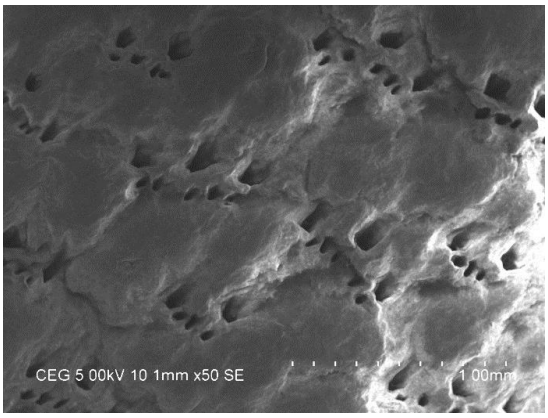


a **b**





c **d**



e

Figure 4.6. Scanning Electron Micrographs showing the grain surface of (a) solvent processed (CL1), (b) Water control (CL1*) and crossection view of (c) solvent processed (CL1), (d) water control (CL1*) and grain surface of (e) solvent processed (CL5)**

4.4.5. Chemical test of leather-Moisture Content Analysis

Water in leather is present in three different forms namely structural water, bound water and bulk water. Structure and function of collagen fibers routinely depend upon the water molecules present. The water may affect properties like strength, permeability and resistance to heat of collagen based materials. Poor organoleptic properties are mainly an indication of high amount of water. On

the other hand, low amount of water gives rise to low strength properties viz. tensile strength, tear strength. A dried leather shall have a moisture content as low as 10% provided thickness and other determinant factors are taken under consideration. The optimum moisture content for a properly dried leather is documented to be around 14%. Moisture content values of solvent processed leathers are given with respect to their respective water control in Table 4.12. There is no much divergence from the optimum value and also no much difference in value between sample and control leathers. The smallest value observed is for the solvent mixture neutralized and solvent mixture post tanning processed leather.

Table 4.12. Moisture content of the processed crust leather

Sample code	**Moisture content (%)**		**Moisture loss (%)**
	Wet blue goat skin	**Processed crust leather**	
CL1	60.2	15.2	45
CL1*	60.2	14.8	45.4
CL2	58.4	15	43.4
CL2*	58.4	13.8	44.6
Cl3	59	15.6	43.4
CL3*	59	14.2	44.8
CL4	59.8	17.6	42.2
CL4*	59.8	17.1	42.1
CL4**	57.37	15.7	41.67
CL4***	57.37	16.5	40.87

CL6	58.5	16.05	42.45
CL7	58.4	12.9	45.5

4.5 Spent liquor analysis

Fig. 4.7 displays images of spent liquor collected after processing at different offer of chemicals and water control.

4.5.1 Chemical oxygen demand (COD)

The Chemical Oxygen Demand of spent liquor for both experimental and control trials were determined and are given in **T**able 4.13. From the table it can be observed that COD of the spent liquor processed using solvent mixture was found to be quite high. The COD value increases as the offer of chemicals increase. COD values with respect to water extremely high. This is why solvent recovery is the main prerequisite for the solvent medium processing.

Table 4.13. COD test results for solvent processed and water control processed using (a) SK-600 Shaker (b) stainless steel drum

Post tanning chemicals offer	**COD (mgO_2/L)**		**Total Solids (mg/L)**	
	Trial 1	**Trial 2**	**Trial 1**	**Trial 2**
¼ of total offer	575,859.9	7704497.2	5100	19700
½ of total offer	700370.1	857564.3	7400	12200
¾ of total offer	856007.8	926044.9	12000	11300
Total recipe offer	887135.5	972736.3	8500	13400
Water control	6058.5	18287.4	13900	10020

Sample	Average COD values (mg/l)
CL5**	89217.66
CL5***	44853.3
CL7	240960

b

a **b**

Fig. 4.7. Images of spent liquor collected (a) trial 1 (b) trial 2

4.5.2 Total solids analysis

Total solids refers to the residue left in a container after evaporation of a sample under subsequent drying at a defined temperature until dried cake is obtained. The term total solids is summation of total dissolved solids and total suspended solids. Table 4.13a and Table 4.14 values imply that the total solids are in the safe side for disposal. But amount of chromium available shall be doubted.

Table 4.14: Total solids for solvent processed and water control crust leather

Sample code	Total solids (%)
CL2	4.2
CL2*	3.2
CL3	4.53
CL3*	3.66
CL4	5.33
CL4*	3.34
CL5**	2
CL***	3

4.6. UNDERSTAND OVERALL PRELIMINARY FEASIBILITY

Ethyl acetate, ethanol, and water have a tendency to produce an azeotropic mixture at various mixing compositions because of their closer boiling points and large difference in polarity (51). The azeotropic boiling point (70.4^{o}C) of the mixture of our concern is below each of the pure components' boiling point known as minimum boiling azeotrope. This kind of mixtures cannot be separated by simple distillation due to the fact that an identical composition of constituent formation in the liquid and vapor phase (52). Fortunately different means of separation and recovery of solvents are available viz. pressure swing distillation, azeotropic distillation, separation by chemical action, distillation using a dissolved salt, extractive distillation, pervaporation and other membrane methods.

In our current investigation we have managed to recover more than 96% of the bath liquor after processing using a lab scale rotary evaporator. Moreover, separation using an electrolyte - K_2CO_3 was also possible which can be explained by formation of ionic force which makes the water unavailable for hydrogen bonding decreasing the solubility of ethanol in water (53).

For processing wet blue skin 100grms of weight 4 liters of processing medium is initially required. The cost incurred is about 1000birr (solvents used were imported high quality analytical grade). But for the following batches the cost decreases tremendously as 0.16litres of solvent mixture are required.

Table 4.15 shows overall spent liquor characteristics which allows us to dispose dried cake abstained after evaporation. However, the accumulation of chromium might be of a concern until a standard disposal norms are published.

Table 4.15. Spent liquor characteristics

	Effluent liquor value
Ph	4.19
Chromium trivalent, Cr^{3-}, mg/l	85.5
Pollution load in g/ton	46.41

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Based on the globally known solvent selection guide (GSK), all the selected solvents scored >38 with LD_{50} >1500 and appropriate polarity for post tanning leather processing. Although the solvents selected were from individual performance analysis, a uniform mixture of solvents was optimized in 1:1:2 – water, ethyl acetate and ethanol respectively- ratio for a greener solvent medium utilization.

The solubility of syntans was found to be as much as 1.5%, neutralizing salts 1%, acid dyes up to 0.67% and there was no insolubility observed with fatliqours. Hence, post tanning leather auxiliaries were found to be soluble in solvent mixture used as a medium.

Metal complex dyes in solvent mixture were found to have a homogenous and narrow particle size distribution compared to water medium which was also confirmed with respect to penetration, depth of dye and dry rub fastness on processed leather.

Adsorption isotherm was determined at the optimum operating conditions. It was seen that adsorption equilibrium data fit very well to the Langmuir model in the studied concentration range. The isotherm parameters have also been calculated which gave promising results.

Strength properties tensile, tear, grain crack resistance and color measurements were not affected rather enhanced, in some cases, by using the mixture of solvents for post tanning processing.

The leather processed in ethyl acetate alone showed the poorest bulk properties. This might lead to a conclusion that ethyl acetate in solvent mixture function as a transporting medium while ethanol and water dissolve the post tanning chemicals. And this gives rise to quick transportation to the leather matrix in effect enhancing processing time.

SEM analysis indicates better fullness for the solvent processed with neutralization in a solvent medium while better grain smoothness and compactness is observed for water neutralized one.

Laboratory scale separation and recovery is possible.

5.2. Recommendation

We recommend a detailed feasibility study to be conducted for the present work

The current solvent mixture processing has given a promising result in all aspects. Thus applying the same for the rest of the tannery unit operations would be much more feasible. However, for an enhanced quality of leather, synthesis of a neutralizing syntan and fixing agent which can be utilized in a solvent medium should be looked at.

Good stainless steel drums that give ease of draining and refilling without solvent lose should be looked at.

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ANNEXES

ANNEX I

Shortlisted Solvents Based on Selection Cumulative Score

Family	Name	Family	Name
	2-Ethyl hexanol		Ethyl acetate
	Glycerol		t-butyl acetate

Alcohol	Cyclohexanol	Esters	n-butyl acetate
	Ethylene glycol		Ethyl lactate
	1,4-Butanediol		Propyl acetate
	Isoamyl alcohol		Propylene carbonate
	1,2-Propanediol		Dimethyl carbonate
	1,3-Propanediol		n-Octyl acetate
	Benzyl alcohol	Ketones	Cyclopentanone
	1-Pentanol		Acetone
	Ethanol		Cyclohexanone
	Methanol	Ethers	Triethylene glycol
	1-Butanol		PEG-200/400

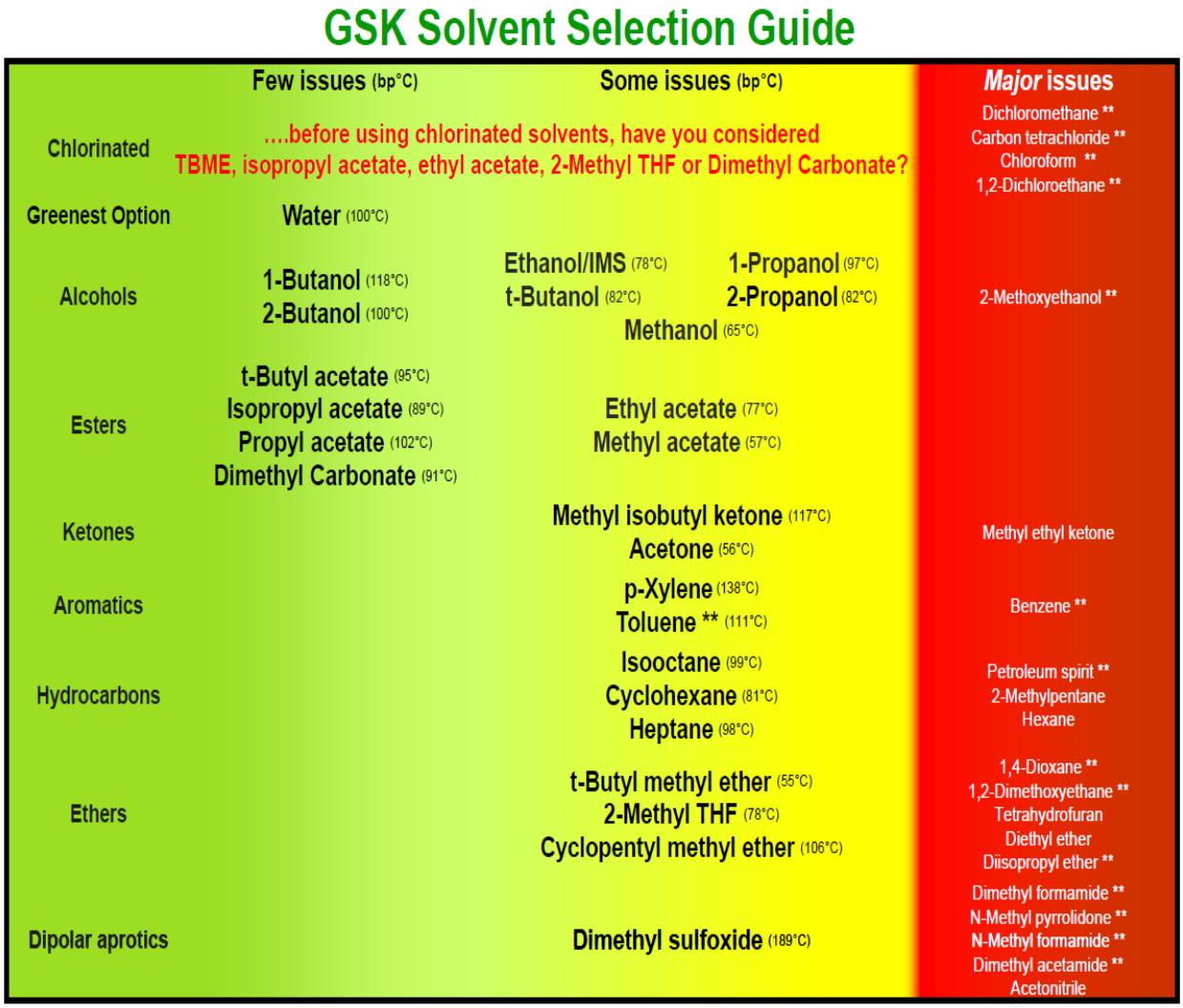
ANNEX II

Short Listed Solvents Based on LD_{50}

Family	Name	LD_{50} value (mg/Kg) of rat (oral acute toxicity)	Family	Name	LD_{50} value (mg/Kg) of rat (oral acute toxicity)
Alcohols	Methanol	5629		Ethyl acetate	5620
	Ethanol	7060		Ethyl lactate	25000
	1,2-Propanediol	20000		Propyl acetate	9370
	1,3-Propanediol	15000	Ethers	Triethylene Glycol	20000
	1,4-Butanediol	18000		PEG-200	31700
	Glycerol	12600			
Esters	n-Butyl acetae	10768			
	Propylene carbonate	20700			

	Dimethyl carbonate	13000			

ANNEX III GSK solvent selection guide



Classification	Solvent click on solvent name for hyperlink to more detail	Cas number	Melting point °C	Boiling Point °C	Waste	Environmental Impact	Health	Flammability & Explosion	Reactivity/ Stability	Life Cycle Score	Legislation Flag	EHS Red Flag
Water	Water	7732-18-5	0	100	4	10	10	10	10	10		
Alcohol	2-Ethyl hexanol	104-76-7	-76	185	9	5	6	9	10	6		
	Glycerol	56-81-5	18	290	6	7	8	10	9	8		
	Cyclohexanol	108-93-0	25	161	6	6	7	9	9	8		
	Ethylene glycol	107-21-1	-13	197	5	8	7	10	9	9		
	1,4-butanediol	110-63-4	20	235	6	6	8	10	10	4		
	Isoamyl alcohol	123-51-3	-117	131	6	6	7	9	10	6		
	1,2-propanediol	57-55-6	-60	188	6	6	10	10	10	3		
	1,3-propanediol	504-63-2	-27	214	6	6	9	10	10	3		
	Benzyl alcohol	100-51-6	-15	205	6	6	7	10	7	6		
	2-Pentanol	6032-29-7	-50	119	6	6	6	8	8	6		
	1-Butanol	71-36-3	-89	118	5	7	5	8	9	5		
	2-Butanol	78-92-2	-115	100	4	6	8	7	9	6		
	Ethanol IMS	64-17-5	-114	78	3	8	8	6	9	9		
	t-Butanol	75-65-0	25	82	3	9	6	6	10	8		
	Methanol	67-56-1	-98	65	4	9	5	5	10	9		
	2-Propanol	67-63-0	-88	82	3	9	8	6	8	4		
	1-Propanol	71-23-8	-127	97	4	7	5	7	10	7		
	2-Methoxyethanol	109-86-4	-85	124	3	8	2	7	6	7		
Ester	t-Butyl acetate	540-88-5	-78	95	6	9	8	6	10	8		
	n-octyl acetate	112-14-1	-39	210	8	5	5	8	10	6		
	Butyl acetate	123-86-4	-77	126	7	7	8	8	10	5		
	Ethylene carbonate	96-49-1	36	248	6	7	5	10	9			
	Propylene carbonate	108-32-7	-55	242	6	7	5	8	9			
	Isopropyl acetate	108-21-4	-73	89	5	7	7	6	9	7		
	Ethyl lactate	97-64-3	-23	154	7	5	4	8	10			
	Propyl acetate	109-60-4	-92	102	5	7	8	6	10	4		
	Dimethyl carbonate	616-38-6	-1	91	4	8	7	6	10	8		
	methyl lactate	547-64-8	-66	144	5	9	4	8	9	5		
	Ethyl acetate	141-78-6	-84	77	4	8	8	4	8	6		
	Ethyl propionate	105-37-3	-74	99	5	7	4	6	6			
	Methyl acetate	79-20-9	-98	57	3	9	7	4	9	7		
	Ethyl formate	109-94-4	-80	54	4	6	5	4	9			
Ketone	Cyclohexanone	108-94-1	-32	155	6	8	6	8	9	6		
	Cyclopentanone	120-92-3	-51	131	7	6	6	8	10	6		
	2-Pentanone	107-87-9	-78	102	5	6	6	7	10	4		
	3-Pentanone	96-22-0	-42	102	5	6	8	7	6	4		
	Methylisobutyl ketone	108-10-1	-84	117	6	6	6	7	8	2		
	Acetone	67-64-1	-95	56	3	9	8	4	9	7		
	Methylethyl ketone	78-93-3	-87	80	3	7	8	4	8	3		
Acid	Propionic acid	79-09-4	-21	141	4	8	6	8	8	7		
	acetic anhydride	108-24-7	-73	140	5	8	4	8	6	6		
	Acetic acid	64-19-7	17	118	4	8	6	8	7	8		
Aromatic	Mesitylene	108-67-8	-45	165	8	3	7	6	10	7		
	Cumene	98-82-8	-96	152	7	5	6	8	5	7		
	p-Xylene	106-42-3	-13	138	7	2	6	5	10	7		
	Toluene	108-88-3	-95	111	6	3	4	4	10	7		
	Benzene	71-43-2	6	80	5	6	1	3	10	7		
Hydrocarbon	cis-Decalin	493-01-6	-43	196	7	3	7	6	7	7		
	ISOPAR G	64742-48-9	-60	163	8	2	9	6	10			
	Isooctane	540-84-1	-107	99	6	4	8	3	10	7		
	Methyl cyclohexane	108-87-2	-127	101	6	5	8	3	10	7		
	Cyclohexane	110-82-7	7	81	5	5	7	2	10	7		
	Heptane	142-82-5	-91	98	6	3	8	3	10	7		
	Pentane	109-66-0	-130	36	5	6	8	2	10	7		
	Methylcyclopentane	96-37-7	-142	72	6	4	5	2	9	7		
	2-Methylpentane	107-83-5	-153	60	5	4	7	2	10	7		
	Hexane	110-54-3	-95	69	5	3	4	2	10	7		
	Petroleum spirit	8032-32-4	-73	55	6	2	2	3	10	7		
Ether	Di(ethylene glycol)	111-46-6	-10	246	6	8	7	9	9	8		
	Ethoxybenzene	103-73-1	-29	170	8	4	7	10	10			
	Tri(ethylene glycol)	112-27-6	-7	285	6	8	6	10	9	7		
	Sulfolane	126-33-0	28	282	5	9	6	10	10			
	DEG monobutyl ether	112-34-5	-68	231	6	7	7	9	6	7		
	Anisole	100-66-3	-38	154	6	6	7	7	6	5		
	Diphenyl ether	101-84-8	27	258	8	5	4	8	6			
	Dibutyl ether	142-96-1	-95	140	7	7	4	5	5	4		
	t-Amyl methyl ether	994-05-8	-80	86	5	5	5	5	9	8		
	t-Butylmethyl ether	1634-04-4	-109	55	4	5	5	3	9	8		
	Cyclopentyl methyl ether	5614-37-9	-140	106	6	4	4	5	8	4		
	t-Butyl ethyl ether	637-92-3	-74	70	5	5	4	4	9	8		
	2-Methyltetrahydrofuran	96-47-9	-137	78	4	5	4	3	6	4		
	Diethyl ether	60-29-7	-116	35	4	4	5	2	4	6		
	Bis(2-methoxyethyl) ether	111-96-6	-68	162	4	5	2	8	4	6		
	Dimethyl ether	115-10-6	-141	-25	3	5	7	1	4	7		
	1,4-Dioxane	123-91-1	12	102	3	4	4	4	5	6		
	Tetrahydrofuran	109-99-9	-108	65	3	5	6	3	4	4		
	1,2-Dimethoxyethane	110-71-4	-58	85	4	5	2	4	4	7		
	Diisopropyl ether	108-20-3	-86	68	4	3	8	1	1	9		
Dipolar aprotic	Dimethylpropylene urea	7226-23-5	-23	247	7	7	4	9	7	3		
	Dimethyl sulphoxide	67-68-5	19	189	5	5	7	9	2	6		
	Formamide	75-12-7	3	220	4	7	2	10	8	8		
	Dimethyl formamide	68-12-2	-61	153	4	6	2	9	9	7		
	N-Methylformamide	123-39-7	-4	200	4	6	2	10	10	7		
	N-Methyl pyrrolidone	872-50-4	-24	202	5	6	3	9	8	4		
	Propanenitrile	107-12-0	-93	97	3	6	4	6	9			
	Dimethyl acetamide	127-19-5	-20	165	5	6	2	10	8	2		
	Acetonitrile	75-05-8	-45	82	3	6	6	6	10	3		
Halogenated	1,2-Dichlorobenzene	95-50-1	-17	180	7	4	6	10	9	8		
	1,2,4-Trichlorobenzene	120-82-1	17	214	7	4	4	9	10	8		
	Chlorobenzene	108-90-7	-45	132	6	6	4	8	10	8		
	trichloroacetonitrile	545-06-2	-42	83	5	6	6	7	10			
	Chloroacetic acid	79-11-8	61	189	4	6	6	10	8	7		
	trichloroacetic acid	76-03-9	58	197	3	6	6	10	6	7		
	Perfluorotoluene	434-64-0	-66	104	5	3	4	5	10			
	Perfluorocyclohexane	355-68-0	51	53	5	5	3	5	10			
	Carbon tetrachloride	56-23-5	-23	77	4	5	3	4	10	7		
	Dichloromethane	75-09-2	-95	40	3	6	4	6	9	7		
	Perfluorohexane	355-42-0	-86	57	4	4	3	5	10			
	Fluorobenzene	462-06-6	-42	85	5	3	6	5	9	1		
	Chloroform	67-66-3	-64	61	3	6	3	6	9	6		
	Perfluorocyclic ether	335-36-4	-88	103	5	3	3	7	10			
	Trifluoracetic acid	76-05-1	-15	72	3	5	6	7	8			
	Trifluorotoluene	98-08-8	-29	102	5	4	1	5	9			
	1,2-Dichloroethane	107-06-2	-36	84	4	4	2	6	10	7		
	2,2,2-Trifluoroethanol	75-89-8	-43	74	3	5	2	6	9	7		
Base	N,N-Dimethylaniline	121-69-7	3	194	7	5	4	8	8	3		
	Triethylamine	121-44-8	-115	89	4	5	3	4	8	7		
	Pyridine	110-86-1	-42	115	3	4	4	7	9	2		
Other	Nitromethane	75-52-5	-29	101	3	8	4	7	2			
	carbon disulfide	75-15-0	-111	46	4	6	2	1	6	8		

Legislation Flag	
	Substitution recommended - There are no current restrictions but future regulatory restrictions may apply
	Substitution recommended - existing regulatory restrictions apply
	Must be substituted - A regulatory ban applies

GlaxoSmithKline

Classification	Solvent	CAS number	Melting point °C	Boiling point °C	Waste recycling, incineration, VOC, and biotreatment issues	Environmental impact fate and effects on the environment	Health acute and chronic effects on human health and exposure potential	Flammability & Explosion storage and handling	Reactivity/ Stability factors affecting the stability of the solvent	Life Cycle Score Environmental impacts to produce the solvent	Legislation Flag alerts regulatory restrictions
Greenest	Water	7732-18-5	0	100	4	10	10	10	10	10	
Alcohols	1-Butanol	71-36-3	-89	118	5	7	5	8	9	5	
	2-Butanol	78-92-2	-115	100	4	6	8	7	9	6	
	Ethanol/IMS	64-17-5	-114	78	3	8	8	6	9	9	
	t-Butanol	75-65-0	25	82	3	9	6	6	10	8	
	Methanol	67-56-1	-98	65	4	9	5	5	10	9	
	2-Propanol	67-63-0	-88	82	3	9	8	6	8	4	
	1-Propanol	71-23-8	-127	97	4	7	5	7	10	7	
	2-Methoxyethanol	109-86-4	-85	124	3	8	2	7	6	7	
Ester	t-Butyl acetate	540-88-5	-78	95	6	9	8	6	10	8	
	Isopropyl acetate	108-21-4	-73	89	5	7	7	6	9	7	
	Propyl acetate	109-60-4	-92	102	5	7	8	6	10	4	
	Dimethyl carbonate	616-38-6	-1	91	4	8	7	6	10	8	
	Ethyl acetate	141-78-6	-84	77	4	8	8	4	8	6	
	Methyl acetate	79-20-9	-98	57	3	9	7	4	9	7	
Ketone	Methylisobutyl ketone	108-10-1	-84	117	6	6	6	7	8	2	
	Acetone	67-64-1	-95	56	3	9	8	4	9	7	
	Methylethyl ketone	78-93-3	-87	80	3	7	8	4	8	3	
Organic Acids	Propionic acid	79-09-4	-21	141	4	8	6	8	8	7	
	Acetic acid (glacial)	64-19-7	17	118	4	8	6	8	7	8	
Aromatics	p-Xylene	106-42-3	-13	138	7	2	6	5	10	7	
	Toluene	108-88-3	-95	111	6	3	4	4	10	7	
	Benzene	71-43-2	6	80	5	6	1	3	10	7	
Hydrocarbons	Isooctane	540-84-1	-107	99	6	4	8	3	10	7	
	Cyclohexane	110-82-7	7	81	5	5	7	2	10	7	
	Heptane	142-82-5	-91	98	6	3	8	3	10	7	
	2-Methylpentane	107-83-5	-153	60	5	4	7	2	10	7	
	Hexane	110-54-3	-95	69	5	3	4	2	10	7	
	Petroleum spirit	8032-32-4	-73	55	6	2	2	3	10	7	
Ethers	t-Butyl methyl ether	1634-04-4	-109	55	4	5	5	3	9	8	
	Cyclopentyl methyl ether	5614-37-9	-140	106	6	4	4	5	8	4	
	2-Methyl THF	96-47-9	-137	78	4	5	4	3	6	4	
	Diethyl ether	60-29-7	-116	35	4	4	5	2	4	6	
	Bis(2-methoxyethyl) ether	111-96-6	-68	162	4	5	2	8	4	6	
	1,4-Dioxane	123-91-1	12	102	3	4	4	4	5	6	
	Tetrahydrofuran	109-99-9	-108	65	3	5	6	3	4	4	
	1,2-Dimethoxyethane	110-71-4	-58	85	4	5	2	4	4	7	
	Diisopropyl ether	108-20-3	-86	68	4	3	8	1	1	9	
Dipolar aprotics	Dimethyl sulfoxide	67-68-5	19	189	5	5	7	9	2	6	
	Dimethyl formamide	68-12-2	-61	153	4	6	2	9	9	7	
	N-Methylformamide	123-39-7	-4	200	4	6	2	10	10	7	
	N-Methyl pyrrolidone	872-50-4	-24	202	5	6	3	9	8	4	
	Dimethyl acetamide	127-19-5	-20	165	5	6	2	10	8	2	
	Acetonitrile	75-05-8	-45	82	2	6	6	6	10	3	
Chlorinated	Carbon tetrachloride	56-23-5	-23	77	4	5	3	4	10	7	
	Dichloromethane	75-09-2	-95	40	3	6	4	6	9	7	
	Chloroform	67-66-3	-64	61	3	6	3	6	9	6	
	1,2-Dichloroethane	107-06-2	-36	84	4	4	2	6	10	7	

Legislation Flag	
	Substitution recommended - There are no current restrictions but future regulatory restrictions may apply
	Substitution recommended - existing regulatory restrictions apply
	Must be substituted - A regulatory ban applies

ANNEX IV Size distribution and zeta potential of red metal complex dye

Size Distribution Report by Intensity

v2.2

Malvern

Sample Details

Sample Name: red dye solv 1

SOP Name: mansettings.nano

General Notes:

File Name:	15 2 14.dts	**Dispersant Name:**	Ethyl acetate
Record Number:	8	**Dispersant RI:**	1.370
Material RI:	1.37	**Viscosity (cP):**	0.4200
Material Absorbtion:	0.000	**Measurement Date and Time:**	Saturday, February 15, 2014 ...

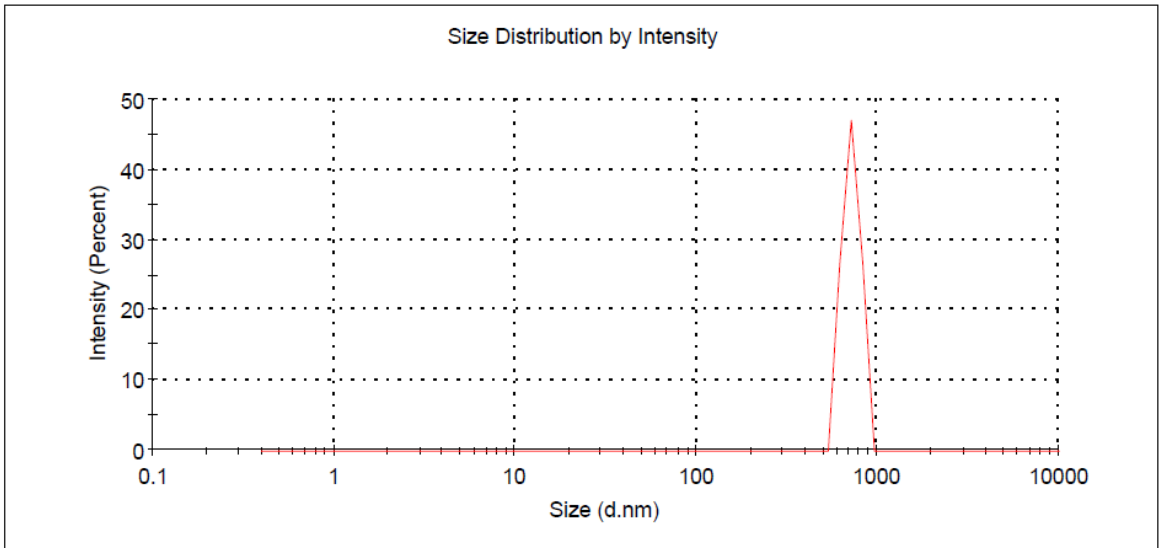
System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	290.4	**Measurement Position (mm):**	4.65
Cell Description:	Glass cuvette with square apert...	**Attenuator:**	8

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	1141	**Peak 1:**	716.4	100.0	76.49
PdI:	0.443	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.949	**Peak 3:**	0.000	0.0	0.000

Result quality : Refer to quality report



Zeta Potential Report

v2.3

Sample Details

Sample Name: red dye water zeta 1

SOP Name: mansettings.nano

General Notes:

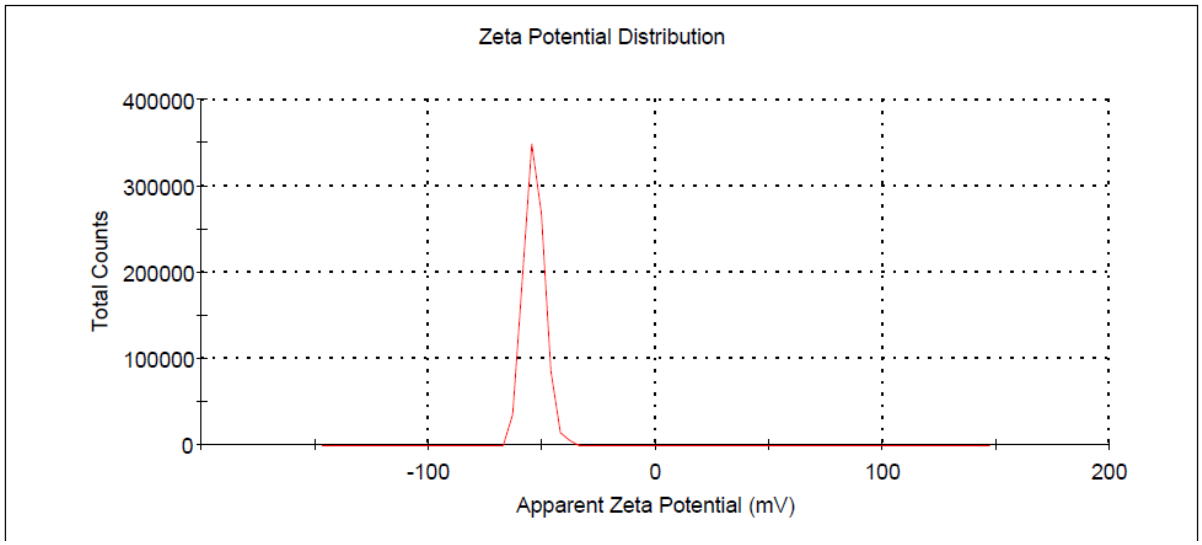
File Name:	15 2 14.dts	**Dispersant Name:**	Water
Record Number:	6	**Dispersant RI:**	1.330
Date and Time:	Saturday, February 15, 2014 7:52:...	**Viscosity (cP):**	0.8872
		Dispersant Dielectric Constant:	78.5

System

Temperature (°C):	25.0	**Zeta Runs:**	12
Count Rate (kcps):	66.3	**Measurement Position (mm):**	4.50
Cell Description:	Zeta dip cell	**Attenuator:**	8

Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-53.5	**Peak 1:**	-53.5	100.0	4.54
Zeta Deviation (mV):	4.54	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.803	**Peak 3:**	0.00	0.0	0.00
Result quality :	Good				



ANNEX V UV-Vis concentrations obtained at 545nm

S.N		Absorbance @ 545nm			
		UV – 1	UV – 2	UV – 3	UV – 4
1	0.0005		0.134		
2	0.00075				0.106
3	0.00075				0.283
4	0.00125				0.168
5	0.0015	0.467	0.104		
6	0.00175				0.235
7	0.002	0.349			
8	0.0025				
9	0.00325				0.239
10	0.0035	0.356	0.149		
11	0.00375				
12	0.00425		0.154		0.307
13	0.005	0.418		0.065	0.460
14	0.0075	0.490			
15	0.01	0.440	0.249		0.446
16	0.0125			0.138	
17	0.015				0.579
18	0.02	0.490	0.247		0.451
19	0.025		0.283	0.231	0.484
20	0.03	0.593			0.481
21	0.05		0.285	0.353	0.479
22	0.1			0.435	
23	0.15			0.537	
24	0.25				

ANNEX VI ANOVA analysis for Mixture design

Response 1 Viscosity

ANOVA for Mixture Special Cubic Model

***** Mixture Component Coding is U_Pseudo. *****

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	2.15	6	0.36	30.07	0.0001
Linear Mixture	*1.75*	*2*	*0.88*	*73.50*	*< 0.0001*
AB	*0.13*	*1*	*0.13*	*10.93*	*0.0130*
AC	*0.072*	*1*	*0.072*	*6.00*	*0.0442*
BC	*2.988E-003*	*1*	*2.988E-003*	*0.25*	*0.6321*
ABC	*0.091*	*1*	*0.091*	*7.67*	*0.0277*
Residual	0.084	7	0.012		
Lack of Fit	*0.084*	*3*	*0.028*		
Pure Error	*0.000*	*4*	*0.000*		
Cor Total	2.24	13			

Std. Dev.	0.11	R-Squared	0.9626
Mean	1.35	Adj R-Squared	0.9306
C.V. %	8.11	Pred R-Squared	0.4864
PRESS	1.15	Adeq Precision	14.330

Componen t	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
A-Ethyl acetate	1.94	1	0.076	1.76	2.11
B-Water	0.83	1	0.076	0.65	1.01
C-Ethanol	1.06	1	0.076	0.88	1.24
AB	-1.58	1	0.48	-2.71	-0.45
AC	1.17	1	0.48	0.040	2.30
BC	0.24	1	0.48	-0.89	1.37
ABC	8.51	1	3.07	1.24	15.78

VIF

1.55
1.55
1.55
2.16
2.16
2.16
2.99

Final Equation in Terms of U_Pseudo Components:

Viscosity =
+1.94 * A
+0.83 * B
+1.06 * C
-1.58 * A * B
+1.17 * A * C
+0.24 * B * C
+8.51 * A * B * C

Final Equation in Terms of Real Components:

Viscosity =
-100.75509 * Ethyl acetate
-27.09340 * Water
-39.05340 * Ethanol
+247.08639 * Ethyl acetate * Water
+291.16411 * Ethyl acetate * Ethanol
+140.03572 * Water * Ethanol
-544.81067 * Ethyl acetate * Water * Ethanol

Final Equation in Terms of Actual Components:

Viscosity =
-100.75509 * Ethyl acetate
-27.09340 * Water
-39.05340 * Ethanol
+247.08639 * Ethyl acetate * Water
+291.16411 * Ethyl acetate * Ethanol
+140.03572 * Water * Ethanol
-544.81067 * Ethyl acetate * Water * Ethanol

ANNEX VII Excess molar volume and Viscosity data from open source

Table 2. Experimental Densities, ρ, and Excess Molar Volumes, V_m^E, for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 298.15 K and Atmospheric Pressure

x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}
0.0269	0.9731	0.89532	−0.039	0.2091	0.3036	0.85688	−0.466
0.0469	0.9531	0.89613	−0.081	0.1798	0.4012	0.86415	−0.364
0.0722	0.9278	0.89709	−0.124	0.1500	0.5005	0.87056	−0.267
0.0892	0.9108	0.89790	−0.168	0.1200	0.6004	0.87623	−0.178
0.1045	0.8955	0.89848	−0.189	0.0899	0.7006	0.88129	−0.099
0.1249	0.8751	0.89950	−0.240	0.0600	0.8002	0.88585	−0.032
0.9051	0	0.96551	−0.506	0.0300	0.9001	0.89010	0.014
0.7992	0	0.93360	−0.893	0.0894	0.1001	0.81245	−0.239
0.7005	0	0.90469	−1.031	0.0795	0.2002	0.82585	−0.149
0.6205	0	0.88556	−1.115	0.0696	0.3004	0.83760	−0.069
0.5001	0	0.85865	−1.056	0.0596	0.4006	0.84814	−0.011
0.4145	0	0.84326	−1.004	0.0497	0.5002	0.85782	0.010
0.3085	0	0.82673	−0.895	0.0397	0.6003	0.86624	0.055
0.2018	0	0.81078	−0.645	0.0298	0.7001	0.87430	0.048
0.0998	0	0.79760	−0.376	0.0199	0.8002	0.88143	0.057
0	0.1000	0.80150	0.062	0.0095	0.9047	0.88844	0.038
0	0.1992	0.81625	0.087	0.0980	0.0902	0.81203	−0.274
0	0.3006	0.82952	0.120	0.1999	0.0800	0.82398	−0.561
0	0.3949	0.84061	0.147	0.2989	0.0701	0.83694	−0.785
0	0.5001	0.85204	0.147	0.4009	0.0599	0.85192	−0.953
0	0.5987	0.86164	0.154	0.4989	0.0501	0.86726	−1.003
0	0.7000	0.87079	0.141	0.5999	0.0400	0.88645	−1.027
0	0.7981	0.87906	0.110	0.6970	0.0303	0.90890	−1.006
0	0.9000	0.88696	0.074	0.8000	0.0200	0.93352	−0.778
0	0.9501	0.89081	0.034	0.9000	0.0100	0.96227	−0.454
0.6303	0.1000	0.90340	−0.990	0.1000	0.2700	0.83804	−0.203
0.5573	0.2042	0.90200	−0.921	0.2003	0.2401	0.84760	−0.476
0.4902	0.2999	0.90104	−0.857	0.3006	0.2100	0.85816	−0.691
0.4202	0.4000	0.89974	−0.755	0.3972	0.1810	0.86948	−0.837
0.3501	0.5000	0.89862	−0.647	0.5004	0.1500	0.88297	−0.914
0.2802	0.5999	0.89768	−0.536	0.6003	0.1200	0.89927	−0.967
0.2100	0.7001	0.89670	−0.405	0.6996	0.0902	0.91701	−0.890
0.1401	0.8000	0.89577	−0.265	0.8002	0.0600	0.93809	−0.704
0.0700	0.9000	0.89489	−0.116	0.9001	0.0300	0.96529	−0.448
0.4503	0.1001	0.86609	−0.914	0.1000	0.4500	0.85899	−0.151
0.4003	0.2000	0.87181	−0.783	0.2004	0.3998	0.86677	−0.409
0.3503	0.2999	0.87656	−0.669	0.3000	0.3500	0.87539	−0.614
0.3002	0.3999	0.88033	−0.552	0.4000	0.3000	0.88549	−0.786
0.2500	0.5004	0.88341	−0.434	0.4998	0.2501	0.89653	−0.869
0.2001	0.6000	0.88598	−0.318	0.6000	0.2000	0.91013	−0.916
0.1500	0.7001	0.88823	−0.206	0.1000	0.6300	0.87643	−0.127
0.1000	0.8001	0.89016	−0.095	0.1999	0.5601	0.88273	−0.358
0.0500	0.9001	0.89198	0.001	0.3059	0.4859	0.89062	−0.582
0.2700	0.1008	0.83752	−0.707	0.4000	0.4200	0.89852	−0.728
0.2400	0.2007	0.84791	−0.583				

Table 4. Experimental Viscosities, η, for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 298.15 K and Atmospheric Pressure

x_1	x_2	η / mPa·s	x_1	x_2	η / mPa·s
0.0258	0.9742	0.436	0.1798	0.4001	0.653
0.0450	0.9550	0.444	0.1499	0.5001	0.579
0.0748	0.9252	0.456	0.1199	0.6000	0.523
0.0853	0.9147	0.460	0.0899	0.7001	0.487
0.1053	0.8947	0.468	0.0599	0.8001	0.460
0.1258	0.8742	0.476	0.0300	0.9000	0.442
0.2009	0	1.407	0.0902	0.1000	1.042
0.3001	0	1.558	0.0802	0.2000	0.810
0.4016	0	1.761	0.0701	0.3000	0.691
0.5001	0	1.946	0.0600	0.4012	0.605
0.6000	0	2.166	0.0501	0.5000	0.551
0.7000	0	2.342	0.0401	0.6000	0.512
0.8000	0	2.390	0.0301	0.7000	0.476
0.9000	0	1.923	0.0200	0.8000	0.450
0	0.1000	0.848	0.0100	0.9000	0.435
0	0.2000	0.707	0.2000	0.0800	1.132
0	0.3000	0.614	0.3008	0.0699	1.283
0	0.4000	0.560	0.4000	0.0600	1.461
0	0.5000	0.513	0.5003	0.0500	1.654
0	0.6000	0.488	0.6000	0.0400	1.868
0	0.7000	0.465	0.7001	0.0300	2.069
0	0.8000	0.448	0.8000	0.0200	2.119
0	0.9000	0.434	0.9000	0.0100	1.834
0.5529	0.2101	1.153	0.1002	0.2700	0.713
0.4900	0.3000	0.946	0.2000	0.2400	0.821
0.4200	0.4000	0.791	0.3000	0.2100	0.948
0.3446	0.5078	0.666	0.4002	0.1800	1.107
0.2800	0.6001	0.594	0.5000	0.1500	1.268
0.2098	0.7002	0.529	0.6000	0.1200	1.464
0.1401	0.7999	0.480	0.7000	0.0900	1.679
0.4499	0.1001	1.363	0.8000	0.0600	1.844
0.3999	0.2000	1.052	0.9000	0.0300	1.681
0.3500	0.3000	0.854	0.1001	0.4500	0.579
0.3002	0.3999	0.708	0.2003	0.3999	0.661
0.2502	0.4999	0.628	0.3002	0.3499	0.762
0.2001	0.6000	0.557	0.4001	0.3000	0.887
0.1501	0.7000	0.510	0.5002	0.2499	1.027
0.1000	0.8000	0.477	0.6002	0.1999	1.226
0.0500	0.9001	0.450	0.1003	0.6297	0.506
0.2697	0.1002	1.151	0.3002	0.4898	0.646
0.2398	0.2001	0.914	0.4000	0.4200	0.745
0.2098	0.3000	0.756			

ANNEX VIII

Description of some of the major equipments used:

- Tight-fitting stainless steel drums were used for leather processing in a solvent medium. If wooden drums were used loss of the solvent medium would be significant. Apparently, butt area of the skins were cut in to half and weighed separately. The left side was used for solvent processing while the right side for water control. After neutralizing in water/solvent mixture, the solvent mixture optimized above was fed through the doors of the drum followed by the weighed skins. Different controlling buttons are displayed on the control board for instance the RPM was adjusted about 15.
- Dynamic Light Scattering was used to determine hydrodynamic radii of particles in a solution. A high performance particle sizer (Zetasizer Nano series, Malvern) at 25˚C that operates at 4 mW He-Ne laser power, scattering angle of 175˚C and wavelength of 633 nm was used. For measurement, a transparent solution in solvent mixture and water was prepared from the post tanning chemicals. Filtration was also done when dust particles were present in the solution. Zeta potential of the solutions was also obtained with the Zeta Nanosizer.
- UV - Vis Spectroscopy refers to absorption spectroscopy of light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved by undergoing electronic transitions. Three different

concentrations (25μl, 50μl and 100μl in 1ml each) from collected liquor for adsorption study were taken to the UV-Vis for concentration analysis. But primarily standard solutions of red dyes were analyzed to set the wavelength of the solvent mixture and draw a standard graph.

- Instron Universal Testing Machine was operated after samples for various physical tests from experimental and control crust leathers were obtained as per IULTS methods (IUP 2, 2000).Specimens were conditioned at 20±2° C and 65±2°C R.H. over a period of 48 hours. Physical properties such as tensile strength, Percentage elongation at break (IUP 6, 2000), grain crack strength (IUP 9, 2000) and tear strength (IUP 8, 2000) were measured as per standard procedures.
- Rotary evaporator with a digital heating bath can be adjusted from +20°C to +180°C. The motorized quick-action jack is easily activated at the touch of a button. The effluent liquors were evaporated at 40 to 45°C by adjusting the solvent to ethanol. The dried solid is taken to a decicator before final weighing.
- Leica Cambridge Stereoscan 440 Scanning electron microscope was used to study the surface morphology and cross section of samples taken from experimental and control crust leathers. Samples were directly cut into specimens with uniform thickness without any pre-treatment. All specimens were then coated with Gold using Edwards E306m sputter coater. The micrographs for the grain surface and cross

section were obtained by operating the SEM at an accelerating voltage of 20kv with different lower and higher magnification levels.

a) Tight-fit stainless steel drums for solvent processing

b) UV - Vis spectroscopy (*Evolution 300*)

c) Nano-ZS Zetasizer (MALVERN)

d) Rotary evaporator, BUCHI-R210

e) Ultrasonic homogenizer

g) Instron Universal Testing Machine

h) Leica Cambridge Stereoscan 440 SEM