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TARA (Cæsalpinia spinosa):
The sustainable source of tannins for innovative tanning processes

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Erratum:

Section 10, figures 49, 50, 51, 52, 53, 54, 56, X-Axis, NaCOOH instead NaCOH.

Abstract:

This thesis considers the fruit of the tara tree (Caesalpinia spinosa) as a sustainable source for tanning agents and proposes alternatives to the commercial mineral salts and vegetable extracts to comply with an increasing demand that concerns lower carbon footprint and health safety. Taxonomy of the tree is described and the substances contained in the fruit are chemically characterized in order to justify that tara farm forestry is economically viable and to secure a potential worth. The value chain is fully described from fruit collection in remote Andean regions to the export for the most important leather markets.

Although tara tannins have been used in the leather industry and its properties being well known, the experimental part of the work aims to optimize innovative formulations using tara as wet-white pre-tanning agent. Combinations with a selected syntan used for wet white and final article recipes are proposed.

Key words: Tara, tannins, leather, wet-white, vegetable-tanning, sustainability

Resumen:

Esta tesis considera el fruto del árbol de tara (Caesalpinia spinosa) como fuente sostenible de taninos para la curtición del cuero y propone alternativas para las sales minerales y los extractos vegetales como respuesta a la creciente demanda para reducir el impacto medioambiental y la seguridad de los artículos de consumo. Se describe la taxonomía del árbol así como la caracterización de su fruto para justificar la silvicultura como práctica económicamente viable y asegurar su valor y la cadena desde la recolección de los frutos en las regiones andinas hasta la exportación a los mercados más importantes de la industria del cuero.

Aunque los taninos de la tara ya se usan para la fabricación de cueros desde épocas remotas y sus propiedades están reconocidas, la sección experimental de este trabajo se orienta a optimizar fórmulas innovadoras utilizando la tara como agente de curtido wet-white. Se proponen fórmulas para artículos finales.

Palabras clave: Tara, taninos, cuero, wet-white, curtición vegetal, sostenibilidad.

Original is to return to the simplicity of the origin by the new means.

ANTONI GAUDÍ. ARCHITECT.

Plant a tree

WANGARI MAATHAI. PEACE NOBEL PRIZE

Preface

Since pre-Hispanic eras, plants were used for tanning and dyeing the hides and skins from the animals hunted for food. With the development of the knowledge and the technologies, humans have researched substances with specific properties to replace those from nature.

Consumers concern today on the impact that the industry is causing to the environment and the health of the users, as well on social aspects, and claims for a just commerce and tackling poverty.

The tannins from tara are well known in the leather industry and they are appreciated because their light color and lightfastness compared with other traditional vegetable tannins. For this reason, demand of tara increased during the last decades at the time high performance leather production for automobile upholstery has experienced a growing demand. However, there are no specific promotions and researches for the use of tara tannins. Its application as tanning agent remains in the technical departments of the chemical suppliers. Tannery technicians obtain very little information from their technical product information-sheets that only specify few recommendations and provide minimum quality values such as concentration of tannins, solids and humidity.

Therefore, the technical and scientific scope of this thesis is to fulfill the lack of specific literature and research focused on tara tannins. Also, it aims to provide technical information for its promotion to leather technicians.

Cæsalpinia spinosa (Molina) Kuntze, commonly known as tara, is a small leguminous tree or thorny shrub. Tara is cultivated as a source of high value products from its pods as tannins based on a gallotannin structure used in the leather industry and seeds as gum for food industry. Having its origin in the Andean Region, pre-Incas civilizations used the fruits of the tree to produce dyes for textiles and ceramics, tannins for leather and medicines. Known, therefore, as "Incas green gold", there is a strategic interest in Peru, Bolivia and Ecuador, supported by international organizations for cooperation, to promote productive processes under environmental sustainability criteria and social benefit.

Beyond the technical and scientific objectives of this research work, the two implicit pillars in the scope are:

- Environment: The study focus on the tannins obtained from the pods of the tara fruits. Tara is a tree, thus contributes to fix carbon and nitrogen, and, contrary to other vegetable tannins, production does not depend from other industries or requires deforestation. Regulations of chemicals, mainly in Europe, recognize the use of non-hazard substances from natural origin not chemically treated.
- Social: It demonstrates that tara tree is suitable for agro forestry and represents a source of economical activities for Andean Regions by exporting products to the leather markets. Also, other products from the fruit of tara are very valuable in other industries as gum for food and industrial applications and polyphenols with properties in medicine. The research has started as a cooperation work to engage in poverty in rural areas in Bolivia.

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Glossary

Term	**Definition**
Agro forestry	Integrated approach of using the interactive benefits from combining trees and shrubs with crops and/or livestock. It combines agricultural and forestry technologies to create more diverse, productive, profitable, healthy and sustainable land-use systems
Auxiliary syntan	A synthetic tannin not suitable for use alone as a tanning agent, but designed for use with vegetable tannins to assist tannage, e.g. to accelerate penetration, or to improve the leather, e.g. its color and fastness.
Beamhouse	The section of the tannery where hide and skins are prepared for tanning.
Caesalpinia spinosa	Scientific denomination for tara tree
Chrome tanned leather	Any leather article tanned mainly with chromium salts (usually chromium sulphate). Near 80% of commercialized leather is chrome leather.
Collagen	The protein composing the white fibers of vertebrate connective tissue, e.g. dermis of skin.
Corium	A kind of connective tissue forming the inner or the two layers of the skin of vertebrates, which is isolated for conversion into leather. Built-up essentially of collagen fibers, interspersed with small amounts of elastin and reticulin fibers, and with various kinds of cells.
Double-face	Clothing or glove leather from wool sheep skins, usable in both sides or reversible, one having a finished nap, the other the wool that has not been removed during the beamhouse operations.
Elongation (stretch)	A measure of the stress needed to produce a certain increase in

resistance	the length of a body
FOB	International Commercial Term (Incoterm) from the Internation Chamber of Commerce, used for international commercial transactions, that stands for “Free On Board” and means that shipment and loading costs are not included in the selling price.
Grain	The surface of a hide or skin exposed by removal of the hair or wool and epidermis.
Grain tightening	The increase of the tightness or firmness of the grain of a leather, e.g. by application of a high molecular compound.
Hide	The outer covering of a mature, or fully grown, animal of the larger kind.
Horse up, to	To place a hide or skin in process over the bar of a special stand, or horse, to drain or/and age
International standardization body	Any organization whose primary activities are developing, coordinating, promulgating, revising, amending, reissuing, interpreting, or otherwise maintaining standards that address the interests of a wide base of users outside the standard-developing organization.
Isoelectric point	pH at which a particular molecule or surface carries no net electrical charge.
Light fastness	Ability to endure long exposure to normal light conditions without serious deterioration of properties, especially color.
Lining	A layer of leather, fabric or other material applied to the inside of a shoe upper, garment, glove, handbag, etc.
Nappa	A soft, full-grain, smooth finish, through-dyed, gloving or clothing leather, made from unsplit sheep, lamb, goat or kid skins or split cattle hide. Formerly tawed and vegetable, or chrome, retanned, but now usually full chrome tanned. Also made from side leather for footwear and leather goods.

Syntan	Molecules obtained by organic synthesis with specific properties similar to the vegetable tannins
Tannin	A type of biomolecule. It is an astringent, bitter plant polyphenolic compound that either binds and precipitates or shrinks proteins and various other organic compounds including amino acids and alkaloids.
Tear resistance	Ability of a sheet of material, e.g. leather, to resist a shearing, or tearing, force applied merely by shearing one area across a second adjacent, firmly-held, area as in the tongue-tear test.
Tensile strength	The tensile force required to break, or rupture, a material, expressed as newtons (N) of cross section. ($kg*m/s^2$).
Replacement syntan	A synthetic tanning agent which can largely, or entirely, replace the vegetable tannins without fundamentally altering the tannin process or the character of the finished leather.
Samming	Bringing leather to uniformly partly- dry state necessary for certain finishing operations, e.g. by partially drying-out, by passing it through the sammying machine or by pressing.
Shrinking temperature	The temperature at which a skin or leather decreases in dimensions when heated under special conditions, e.g. when heated in water fibers shrunk..
Skin	The more or less thick, tough, flexible covering of human and other animal bodies
Suede	A generic term for leathers whose wearing surface, either the grain or the flesh side, has been finished to have a more or less fine, velvet-like nap.
Sustainability	To meet the needs of the present generation without compromising the ability of future generations to meet their our needs.
Syntan	An abbreviation of the term synthetic tannin.

Vegetable tannin	A tanning agent contained in, and obtained by extraction of, the barks, fruits, galls, leaves, roots or wood of certain plants
Wet blue	Term for a hide, or skin, which has been subjected to the usual beamhouse processes, chrome-tanned and left wet; may be stored or exported in this state.
Wet white	Term for a hide, or skin, which has been subjected to the usual beamhouse processes, chrome free and left wet, may be stored or exported in this state.

Introduction

The role of the tanning science is probably the key of the success for a dynamic and innovative business supplying a noble and natural material to the chain of consumer goods that include shoe, upholstery, apparel, car interiors, bags, travel suitcases, flexible gadgets for tools and machinery and many other applications. Being one of the oldest industries since humans live on the Earth, leather activities are driven by commercial indicators, but technology has been always the essential support to allow creating new markets and fulfilling the performing requirements and rigorous demands from consumers.

The leather industry is the solution to the disposal for a waste of the meat industry and transforms hides and skins from slaughterhouses into a high value material. Nevertheless, tanning is a potentially pollution-intensive activity. The environment effects that have to be taken into account comprise not merely the loan and concentration of the classic pollutants, but also the use of certain chemicals.

This thesis aims to validate the compliance of the two hypotheses already implicit in the title of the work. The fruit of the tara tree is proposed as a source of sustainable tannins. Thus, experiments are designed to prove that the application of such tannins, well known since remote eras, can respond as newest technologies of tanning leather that comply quality article standards at the time to meet the highest exigencies of chemical auxiliaries used in the consumer goods supply chains.

Concepts on sustainability from recent forums and expert publications are appraised in Section 1 and the model based on the Triple Bottom Line of social, economic and environmental dimension is chosen to support the first hypothesis. Section 2 and related annexes describe tara tree taxonomy and the contribution of its agro-forestry to the environment as a renewable source of active substances to be economically exploited in industries such tanning, food, pharmaceutical and other business while improving quality life for remote rural Andean communities. Section 3 analyses the supply chain of tara fruit components and their derivates, production and market, and concludes that opportunities depend on availability and price consistency. Thus, tara agro-forestry should replace the current practices of harvesting tara wild trees. The section concludes that tara products, if they are not chemically treated, are exempt of costly safety tests and registrations according to European Regulations such the REACH.

The hypothesis of tara pre-tanning process as innovative technology in the leather making is proven with the analysis of the performance of the pelts submitted to the treatment with tara, blended with general synthetic tannin groups, at different ratios and application conditions.

Section 4 reports the theoretical scientific fundamentals to be considered to design and understand the results of the Experimental Part, based mainly on literature from classic works among well known researchers highly recognized by the leather technician community. The collagen, Type I, is the constituent of the hides and skins. This protein consists in a fibril net of chains of amino acids, mainly glycine, proline and hydroxyproline. The tanning process consists on the stabilization of collagen through the bonding of the amino acid functional groups and the tanning agents to avoid the phenomena of parchment. Hydrothermal stability is used as the main indicator to control the degree of tanning. General current tanning practices are briefly described and chemistry of vegetable tannins and synthetic tanning agents as well as analytical characterization are summarized at the end of this section.

Section 5 introduces de main goals of the experimental designs to prove the second hypothesis of innovation. Section 6 analysis commercial tara powder from different leather chemical suppliers by means of content of water, soluble and insoluble matter, tannins, non-tannins and pH analytical solution. Limits of these parameters are statistically established within the normal distribution. These limits are useful for comparing, in section 7, further characterizations of tara powder processed in the laboratory from fruits obtained in different regions of Bolivia. This section concludes that, despite the natural origin of tara powder, composition of ingredients maintain consistent ratios. This section analyzes the correlation of non-tannins content and the Gallic acid hydrolyzed from tannin molecule. In this case, the null hypothesis cannot be rejected and such correlation cannot be proven, while a hydrolysis of Gallic acid is explained after the treatment of tara powder exposed to time and temperature.

Section 8, 9 and 10 statistically analyze the results of the experiments designed with the support of the Statgraphics Plus software, version 5.0 from Statpoint Technologies, Inc (Warrenton, VA, USA). In all cases, the considered dependent variables are the shrinkage temperature, the measurement of the tensile strength and elongation and the measurement of the tear load. All these physical properties are common required for most of the leather article quality specifications.

Blending tara powder with syntan for pretanning process, section 8, is designed with a Simplex with centroids method. Tara powder with naphthalene sulphonic syntan is found as the most suitable for tara tanning acting as a dispersant and aiding tannins to go through the inner layer of the pelt.

Section 9 optimizes the blend composition ratios of tara powder and naphthalene sulphonic syntan. Design II is based on quadratic, orthogonal, centralized and rotatable model to analyze best fitted variable response surface. The mean of the optimal values is calculated to obtain the ratio of 12% of tara powder and 7 % of naphthalene sulphonic syntan.

This composition is then applied under certain conditions, by means pH measurement previous and after pretanning operation, Section 10. Design III is also based on quadratic orthogonal, centralized and rotatable model to analyze best fitted variable response surface and the mean of optimal values of sodium formate and formic acid, as pH regulator agents, are calculated obtaining initial pH of 5,23 and final pH of 3,64.

Section 11 describes the manufacturing of an automobile-interior leather article from wet-white processed with tara, at pilot scale and according the results of the experiments. The leather is treated later with a regular recipe of retanning, fatliquoring, dyeing, mechanical operations and finished by coating. The leather article is tested for physical properties according the ISO standards of article specification and the results demonstrate the feasibility of the pretanning with tara as a sustainable and innovative source of tannins that can meet the quality leather requirements for consumer goods.

The research work was initially supported by the funding project:

- “Aprofitament sustenible de la tara, per la generació i diversificació de rendes en el medi rural bolivià”, Consorci de promoció Comercial de Catalunya, COPCA, Generalitat de Catalunya, Programa de cooperación pel desenvolupament. Referencia 53695/2008.

Results of this research are included in the:

- project labeled E! 6565, “Low carbon products to design leather processes based on Sustainable Tannins to improve leather manufacture, LOWEST” supported by the EUROSTARTS program powdered by EUREKA R&D platform Organization and the European Community.

During the execution of the research, partial results have been published in indexed scientific journals or national and international congresses:

- “Optimizing a Sustainable and Innovative Wet-White Process with Tara Tannins” presented at the 107th Annual Meeting of the American Leather Chemists Association, June 9 - 12, 2011, Treasure Islane Resort, Red Wing, MN. Published in Journal of the American Leather Chemist Association (JALCA), Vol 106, 2011, pages 278- 286. Authors: J.C. Castell, C. Fabregat, S. Sorolla, D. Solano, Ll. Ollé, A. Bacardit.
- “Tara (Caesalpinia spinosa): The sustainable source of tannins for innovative tanning processes”. XXXI IULTCS Congress. Valencia, September 2011. Authors: J.C. Castell, S. Sorolla, M. Jorba, J. Aribau, Ll. Ollé, A. Bacardit. Publication is foreseen in JALCA.

- “Antioxidant activity of tara pods” VI National Congress of Food Science and Technology. Valencia, 8-10 June, 201. Authors M. Skowyra, M. Davila, C. Fabregat, J.C. Castell, M.P. Almajano.

PART ONE

1. State of the art of Sustainability

1.1. General concept of sustainability

Sustainability is a widely-used term and is gaining attention in many parts of society, including government, business, academia, and in the public. However, it is hardly an agreed-upon concept. Even, among scientists there are numerous definitions.

Many people interpret it in the sense of continuous growth and the idea of sustainability focuses on depletion of resources. Others consider that sustainability covers also irreversible pollution, conservation of nature and other environmental an ecological aspects. Some also include the aspects of quality of human life.

Therefore, to be able to support a sustainable way of living in our planet, a clear definition of sustainability is required.

The word sustainability is derived from the Latin *sustinere* (tenere, to hold). Dictionaries provide more than ten meaning for sustain: “maintain”, “support”, “endure”…

Gro Harlem Brundtland, physician, former Prime Minister of Norway and international leader in sustainable development and public health, analyzed in 1987 the world situation demonstrating that the consequences of the development of the humanity were the environmental degradation, the increase of poverty and vulnerability of certain societies.

She introduced for the first time the term of sustainability or sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”[1].

Much of the contemporary discussion over sustainability starts from the ideas of resource scarcity and the transformation of the planet by humanity, emphasized by rapid population growth and industrialization.

Critical natural capital assets provide humans with goods and services that cannot be replaced, reproduced or substituted. Sustainability implies that there are limits that must be respected and these assets shall always be respected.

Another perspective is characterized by dynamic systems that maintain themselves overtime compromising three elements:

1 U.N. Documents. Report of the World Commission on Environment and Development: Our Common Future. Chapter II: Towards Sustainable Development. UN Documents: Gathering a Body of Global Agreements has been compiled by the NGO Committee on Education of the Conference of NGOs from United Nations web sites

- Depletion of resources, in order not to leave future generations empty-handed
- Environmental and ecological aspects, in order to enable present and future generations to live in a healthy environment, in harmony with nature
- Quality of life, in order to ensure human well-being for present and future generations.

Economy is not explicit included, though politicians often use the term "sustainable economy". During the last decade of the Twentieth Century, a lot of academic debates on concepts and definitions were taken about Corporate Sustainability (CS) and Corporate Social Responsibility (CSR). "In academic debates and business environments hundreds of concepts and definitions have been proposed referring to a more humane, more ethical, more transparent way of doing business"[2]. Marcel Van Marrewijk and Marco Werre, based on historical perspectives, philosophical analysis, impact on changing contexts and situations and practical considerations concluded on abandoning a "one-solution-fits-all" definition [3].

According to the US National Research Council, sustainability is "the level of human consumption and activity, which can continue into the foreseeable future, so that the systems those provide goods and services to the humans, persists indefinitely".

Professor Robert N. Stavins[4], included other concepts like dynamic efficiency consisting on accounting for intergenerational equity or total welfare, representing the consumption of market and non-market goods and services.

The concept of Sustainability has become a common goal for many national and international organizations including industry, governments, NGOs and universities.

This research work justifies the concept of Sustainability based on the Triple Botton Line (TBL), from Professor Andrew W. Savitz[5]. For businesses, sustainability is a powerful and defining idea: a sustainable corporation is one that creates profit for its shareholders while protecting the environment and improving the lives of those with whom it interacts. It operates so that its business interests and the interests of the environment and society intersect. A sustainable business stands an excellent chance of being more successful tomorrow than it is

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2 Marcel van Marrwijk, Concepts and Definitions of CSR and Corporate Sustainability: Between Agency and Communion. Journal of Business Ethics, 44, 95-105, 2003. Netherlands.

3 Marcel van Marrwijk and Marco Werre, Multiple Levels of Corporate Sustainability. http://www.vanmarrewijk.nl/pdf/021206131353.pdf. September 2002

4 Robert N. Stavins, Post-Kioto International Climate Policy. Summary for policymarkets. Research for the Harvard Project on International Climate Agreement. Cambridge. MA. USA. 2009. ISBN:9780521138000

5 Andrew W. Savits. The Triple Botton Line. Business/Management. Wiley. CA. 2006. ISBN-10: 0787979074 | ISBN-13: 978-0787979072

today, and remaining successful, not just for months or even years, but for decades or generations.

Increasingly, businesses are expected to find ways to be part of the solution to the world's environmental and social problems. The best companies are finding ways to turn this responsibility into opportunity. We believe that when business and societal interests overlap, everyone wins.

Thus, TBL objectives approach economic (profit), environmental (planet) and social (people) terms: "The triple bottom line (abbreviated as TBL or 3BL, and also known as people, planet, profit or the three pillars) captures an expanded spectrum of values and criteria for measuring organizational (and societal) success: economic, ecological and social. With the ratification of the United Nations and ICLEI[6] TBL standard for urban and community accounting in early 2007, this became the dominant approach to public sector full cost accounting. Similar UN standards apply to natural capital and human capital measurement to assist in measurements required by TBL, e.g. the ecoBudget standard for reporting ecological footprint."[7]. (Figure 1):

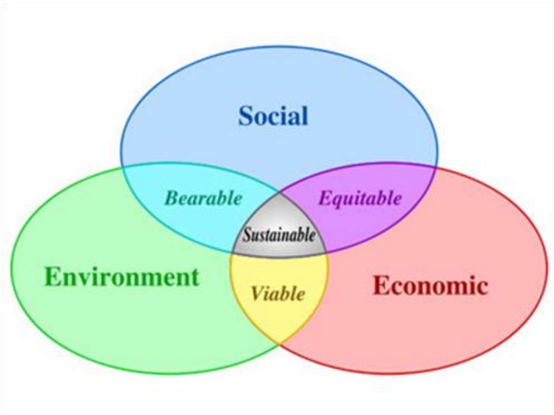

Figure 1: Three Pillars of Sustainability according to A. Savitz

1.2. The tara tree, a sustainable source of tannins

1.2.1 Environmental dimension. Planet

The environmental (planet) dimension of sustainability denominates those terms that describe environmental performance in order to minimize the use of hazardous or toxic substances, resources and energy.

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6 International council for local Environmental initiatives (ICLEI) founded in 1990, is an association of over 1220 local government Members who are committed to sustainable development See web page www.iclei.org

7 http://en.wikipedia.org/wiki/Triple_bottom_line. Date of consultancy March, 15th, 2010

These terms, arranged from preventive to control principles, are:

- renewable resources
- resource minimization
- source reduction
- recycling
- reuse
- repair
- regeneration
- recovery
- remanufacturing
- purification
- end-of-pipe
- degradation

Environment dimension on this research refers mainly to the renewable supply of the tara. Renewable resources are available in a continually renewing manner, supplying materials and energy in more or less continuous ways. Renewable resources do not rely on fossil fuels of which there are finite stocks.

The term emerges as a response to increased carbon dioxide emissions. The research focus on the tannins obtained from the pods of the tara fruits. Tara is a tree, thus contributes to fix carbon and nitrogen, and, contrary to other vegetable tannins, production does not depend from other industries or requires deforestation. Regulations of chemicals, mainly in Europe, recognize the use of non-hazard substances from natural origin not chemically treated.

Minimization of resource usage is understood as conservation of natural resources. It is an activity that can be applied to any reduction of usage of resources. Therefore, the term encompasses not only raw materials, water and energy, but also applies to natural resources such as forestry, watersheds, other habitats, hunting, fishing, etc. All these resources and processes which enable ecosystems to survive and are essential for helping societies to make progress toward sustainability must be addressed. Thus, resources can be conserved, their availability improved and maintained. Reduction in the usage of materials and energy, such as tanning mineral salts, syntans and some other vegetable extracts, can result in dramatic cost savings.

1.2.2. Economic dimension. Profit

The economic dimension of sustainability includes terms like Environmental Accounting, Eco-efficiency and Ethical Investments[8].

Environmental accounting is designed to bring environmental costs to the attention of the corporate stakeholders who may be able and motivated to identify ways of reducing or avoiding those costs while at the same tame improving environmental quality and profitability of the organization. Environmental accounting can be applied at the national, regional and corporate levels. National accounting refers to physical and monetary accounts for environmental assets and the costs of their depletion and degradation. Corporate environmental accounting refers to environmental auditing, but may also include the costing of environmental impacts caused by the corporation.

The term of eco-efficiency was perceived within numerous definitions of cleaner production. Eco-efficiency is the delivery of competitively priced goods and services that satisfy human needs and bring quality of life, while progressively reducing ecological impacts and resource intensity throughout the life cycle, to a level at least in line with the earth's estimated carrying capacity. It is based on the concept of "doing more with less" representing the ratio between economy and environment, with the environment in the denominator. It is about efficient use of materials and energy in order to provide profitability and the creation of added value.

Ethical investments or socially responsible investments are financial instruments (mortgages, bank accounts, investments, utilities and pensions) favoring environmentally responsible corporate practices and those, supporting diversity as well as increasing product safety and quality.

In the scope of this research work is a demonstration of the economical viability of agro forestry as a new trading of supplying tannins for the tanning industry, stabilizing production and prices to satisfy an increasing demand concerning the impact of the industry to the environment, the security of the employees in the tanneries and the health end users of leather articles. This is enhanced with regulations like the European REACH or restrictions from international companies as alternative to other chemicals substances that shall comply complex and costly registrations.

8 Glavic, Peter, Lukman Rebeka, University of Maribor, Demartment of Chemistry and Chemical Engineering, Slovenia. Review of Sustainability terms and their definitions. Journal of Cleaner production. 15 (2007). 1875-1885.

1.2.3. Social dimension. People

Social dimension of sustainability is composed of terms such Social Responsibility, health and safety. “polluter pays” principle (taxation) and reporting to the stakeholders.

Social responsibility refers to safe, respectful, liberal, equitable and equal human development, contributing to humanity and the environment. Furthermore, the term health and safety usually refers to the working environment and includes responsibilities and standards.

Tara tree is suitable for agro forestry and represents a source of economical activities for Andean Regions by exporting products to supply leather markets. Also, other products from the fruit of tara are very valuable in other industries as gum for food and industrial applications and polyphenol source with properties in medicine.

The research started as a cooperation work to engage in poverty in rural areas in Bolivia.

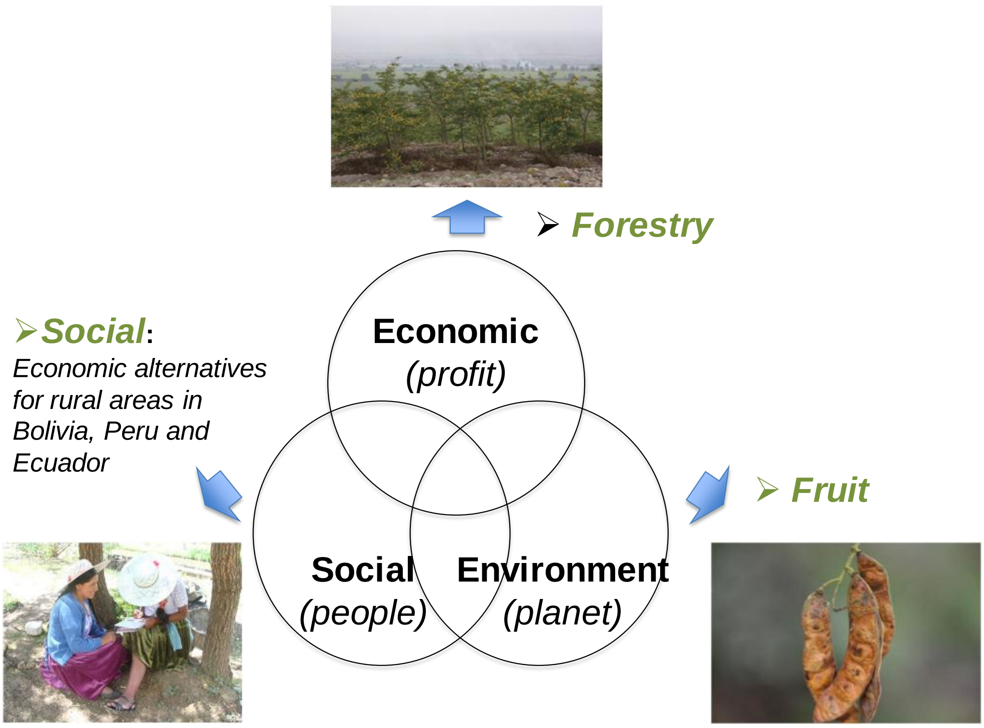


Figure 2: The three dimensions of sustainability for the tara sourcing of tannins

2. Description

2.1. Tara: a sustainable forestry resource from the Andean Region

Cæsalpinia spinosa (Molina) Kuntze, commonly known as tara[9], is a small leguminous tree or thorny shrub. Tara is cultivated as a source of high value products from its pods and seeds as tannins based on a galloylated quinic acid structure, used in the leather industry, and gum for food industry. It is also grown as an ornamental plant because of its large colorful flowers and pods.

Photo 1: Caesalpinia spinosa. Tree, flowers and pods.

Having its origin in the Andean Region, pre-Incas civilizations used the fruits of the tree to produce dyes for textiles and ceramics, tannins for leather and medicines. Known, therefore, as "Incas green gold", there is a strategic interest in Peru, Bolivia and Ecuador, supported by international organizations for cooperation, to promote productive processes under environmental sustainability criteria and social benefit.

The tara name comes from Aimara language and means flat because the shape of the pods.

Cesar Barriga[10] resumes this specie as:

- Plastic: it is able to adapt to several climates and soils
- Rustic: it is not exigent and can grow in superficial, acid and low fertility soils
- Multiple uses: the fruit is profitable, fixes the nitrogen, produces pollen and nectar, and can grow in agro-forestry systems together with other crops.

9 Known names (Jones, 1987 and De la Cruz (2004): "Tara", "Taya" (Peru), "Guarango" (Ecuador), "Cuica", "Serrano", "Vinillo", "Acacia Amarilla" (Yellow acacia), "Andean Dividivi"

Synonyms: Caesalpinia victoria (H.B.K.) Bentham ex Reiche; Poinciana spinosa Molina; Caesalpinia pectinata Cavanilles; Coulteria victoria HBK, Tara Spinosa (Molina) Britt & Rose; Caesalpinia stiulata (Sandwith) J.F.

10 Cesar Barriga: PEBAVI – Peru. Personal interview in June 2010

Due to its wildness, there exists a variety of plants according the regions and the living conditions, thus the content of tannins can vary from 30% to 80%. Currently, institutions and universities carry out researches to characterize the genetic variability[11].

2.2. Distribution and habitat

Cæsalpinia. spinosa can be found growing throughout northern, western and southern South America, from Venezuela to Argentina, subtropical and semitropical regions between 4º to 20º South latitudes. It has been introduced in dry parts of Asia, the Middle East and Africa and has become naturalized in California.

Normally tara grows in areas with a yearly rain of 400 to 1,100 mm, and on sanded or degraded soils. It is a wild tree, normally isolated, but sometimes, can form small forests. Generally resistant to most pathogens and pests, it lives between 0 and 3,000 meters above sea level. Trees begin to produce after 4–5 years. If well irrigated, they can continue to produce for 80 years, though their highest production is between 15 and 65 years of age.

2.3. Botanic characteristics

Annex 1 describes the Caesalpinia spinosa features.

Taxonomic classification by USDA[12]:

Kingdom	***Plantae***	**Plants**
Subkingdom	*Tracheobionta*	Vascular plants
Superdivision	*Spermatohyta*	Seed plants
Division	*Magnoliophita*	Flowering plants
Class	*Magnoliopsida*	Dicotyledons
Subclass	*Rosidae*	
Order	*Fabales*	
Family	*Fabaceae*	Pea family
Genus	*Caesalpinia*	Nicker
Species	*Caesalpinia spinosa (Molina) Kuntze*	Spiny holdback

11 RAPDs (Random Amplifies Polymorphic DNAs) molecular makers is the most common technique to characterize the genetic variability.

12 United States Department of Agriculture (USDA). Natural Resources Conservation Services. Plants Profile. Caesalpinia Spinosa (Molina) Kuntze. (Date of consultancy December, 13, 2009)
http://www.plants.usda.gov/java/nameSearch

2.4. Tara agro forestry. Environment and economical contribution

Lorena Mancero[13] goes over the contribution (↑) and the risks (↓) to the environment of the production of tara. Table 1 summarizes them:

	Factor of the chain affecting the environment	How?	
Production	Clone method of propagation	Risk of lower resistance to blight and sicknesses	↓
	Land selection for forestry	Risk of replacement for native species	↓
		Reforestation of desolated areas to create economic alternatives Protection of sloping soils or degraded ecosystems	↑
	Forestry management	Strong and healthy trees, growing in proper areas Better profit of nutrition, sunlight and water Better control of harvest, blights and sicknesses Increase of pod production	↑
		Replacement of species in natural forest, affecting fauna populations	↓
	Plantation	Supplies nitrogen to the soil Nitrogen associates to other crops like corns, potatoes, barley or	↑

13 Programa Regional ECOBONA-INTERCOOPERACION. "La Tara (Caesalpinia spinosa) en Perú, Bolivia y Ecuador: Análisis de la Cadena Productiva en la Región". Serie Investigación y sistematización. Vol. 02. Quito. 2009. Pag. 33

		sorghum. Ideal to protect soils erosion, mainly in arid or semiarid areas Does not require much water (600 mm rain or 4.000-6.000 m^3/ha/year). Good resistance to large dry seasons Proper to combine with apiculture Leaves are good for animal feed Possibilities as economic alternative Production of tannins does not need deforestation	
Transforming	Production of tara powder	Industrial risk. Needs protection for employers	↓
	Production of tara gum	High requirements of control for the food industry	↑
Consumption	Application of tara powder for tanneries	**As alternative to other tanning substances, specially chromium salts, or vegetable tannins from wood that require deforestation**	↑
	Application of tara powder in artisanal tanneries	Water pollution from the tanning process Low protection to employers for manipulating tara power, and low education of chemical uses.	↓

Table 1: Tara forestry: a sustainable source of high value products

The fruit of tara tree and its derivates have a high interest in a number of industries and, thus, a great worldwide economical potential for commerce. The properties of pods and seeds result in a sustainable and quality raw material for several applications.

The weight of the fruit of tara contains 60-64 % of pods, 34-38 % of seeds and 2 % of non-valuable residues. Annex 2 shows the industrial flow chart of by-products obtained from tara fruits. It is important to point out that tara powder contains 45- 50% tannins, and the seeds 24% tara gum.

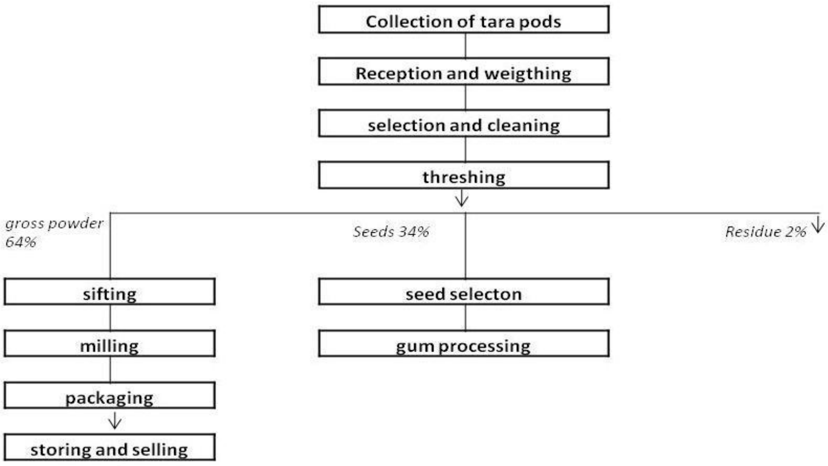


Table 2: Tara fruit processes

The pods are threshed and the seed separated. Tara powder is obtained by simply mechanically milling and sifting the gross powder, as can be seen in figure 3:

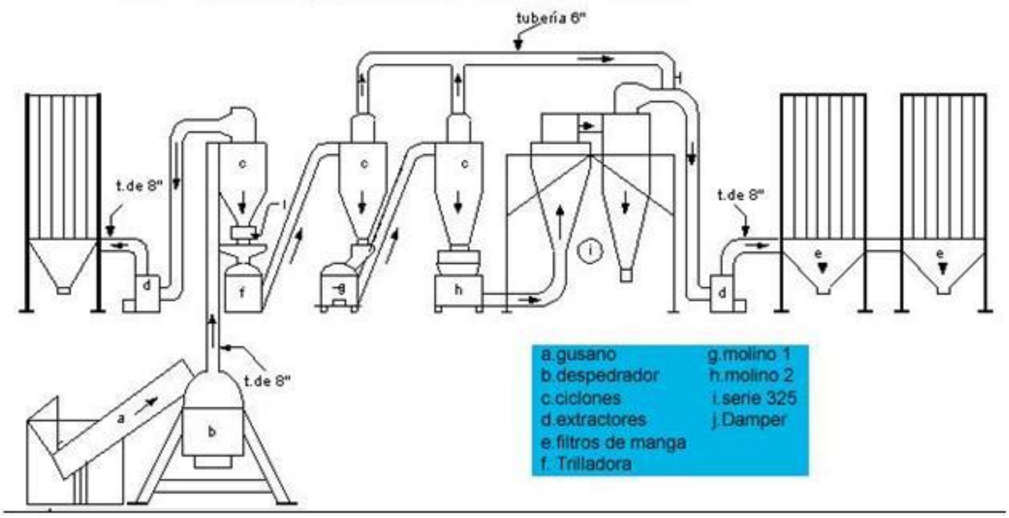


Figure 3: Production chart flow of tara powder

The tara powder is a fine (100 to 200 mesh) yellowish sawdust. Further than the leather industry, it is used, as well, in the chemical industry to obtain tara extract, also used in the leather industry and to other applications. (Annex 2).

The leather industry appreciates the tara powder as a source of vegetable tannins to obtain light colors, with good light fastness, and full and soft leather articles, with a firm and smooth grain. Tara is easily soluble in water and do not contain color substances like other vegetable tannins.

Tara powder can be used to tan all kind of hides and skins and to re-tan chrome tanned leathers to improve the grain-tightening. The main application is in the manufacture of leather for car seats. The general specifications for commercial tara powder for tanning application are[14]:

Tannin content	min. 48%
Water content	max. 13 %
pH (at 6.9ºBè)	3 – 4

Table 3: General specifications for commercial tara powder

Annex 3 shows a typical production recipe to produce car upholstery leather from bovine hides with a wet white process pretanning with glutaraldehyde.

There are, however, some difficulties of the tara tannin when compared with other vegetable tannin extracts:

- High concentration of insoluble solids (tara powder contain high quantities of cellulosic compounds from the tara pods if tannins are not extracted properly)
- Tanning limits when tara tannin is the single compound for tanning. Hydrolyzing vegetable tannins cannot increase the shrinking temperature.
- Easily produces complexes with iron and other metals and form dark spots on the leather when is contaminated. Usually tara mills and several machines used during the leather processing for mechanical operations contain parts made with iron and the risk of such dark spots is quite high.

To obtain tara extract, the tara powder should be treated at 65-70ºC for 30-40 minutes adding to the powder 4 to 5 parts of is weight with water and washing the liquor 5 times. Then the liquor is purified by decantation and filtration, and concentrated from 2-5º Bè to 11-12ºBè. The powder of tara tannin extract is obtained by atomization.

Tara extract is used to produce tannic acid, and founds valuable applications in the food and beverage industries, to clarify and give astringency to wine, tea, coffee, cacao, beer and other food.

14 ORMOTAN© T polvo. SILVATEAM. Silvachimica S.r.l. Via Torre 7. San Michele di Mondovì (CN). Italia. TE: +39.0174.220256. (Date of consultancy September, 15, 2009)
http://www.silvateam.com/index.php?lang=es&id=1,0,2&v2=1

Recent investigations demonstrate that tara tannin and its derivates have excellent properties as antioxidant agents to prevent cardiovascular diseases[15]. Also, they have astringent properties with pharmaceutical capacity to avoid irritation and harm by reducing protein coagulation. The tannic acid is used as hemostatic to cut down hemorrhages and, mostly, for burning treatment.

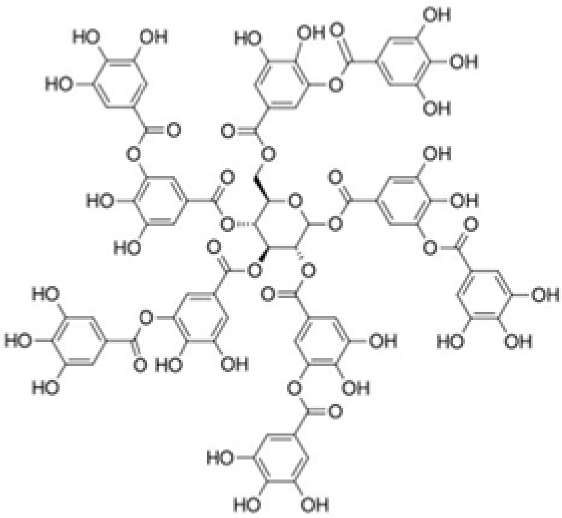


Figure 4: Tannic or Gallotannic acid

The gallic acid can be obtained by hydrolysis of tannic acid with sulfuric acid. Chemical hydrolysis is, however, costly and contains impurities, but enzymes, like tannases from bacteria, can be used. It founds valuable applications in the pharmaceutical industry because has biological properties as antioxidant, biocide (virus and bacteria) and analgesic, but also, is used in other industries, e.g. to clarify vegetable fats, beer, or to obtain inks and as analytical reactive.

The tara gum is obtained by milling the endosperm from the tara seeds, after mechanical separation of the husk and the germ. The high viscosity of the tara gum is well appreciated in the food industry and it is an excellent hydrocolloid with good properties as thickener and stabilizer agent used to prepare ice creams, gelatin, powder and liquid soaps, yogurt, sauces like mustard, mayonnaise, ketchup; cream and soft cheeses, bakery, meat, among others. It is stable at pH higher than 3.5, retains water, soluble at cool temperatures, and do not modifies the savors. Further than the food industry, tara gum has also applications in the pharmaceutical industry, cosmetics, mining, paper, textile, oil, and others.

15 M. Skowyra, M. dávila, C. fabregat, J.C. Castell, M.P Almajano. Actividad Antioxidante de la vaina de tara. VI Congreso Nacional de Ciencia y Tecnología de los Alimentos. Valencia, 8-10 June, 2011.

The germ of tara, obtained from the seed cotyledons, has a high content of proteins and it is sold for animal feed and, also, to the pharmaceutical and cosmetic industry as a source of proteins. The germ of tara is also rich in vegetable oils.

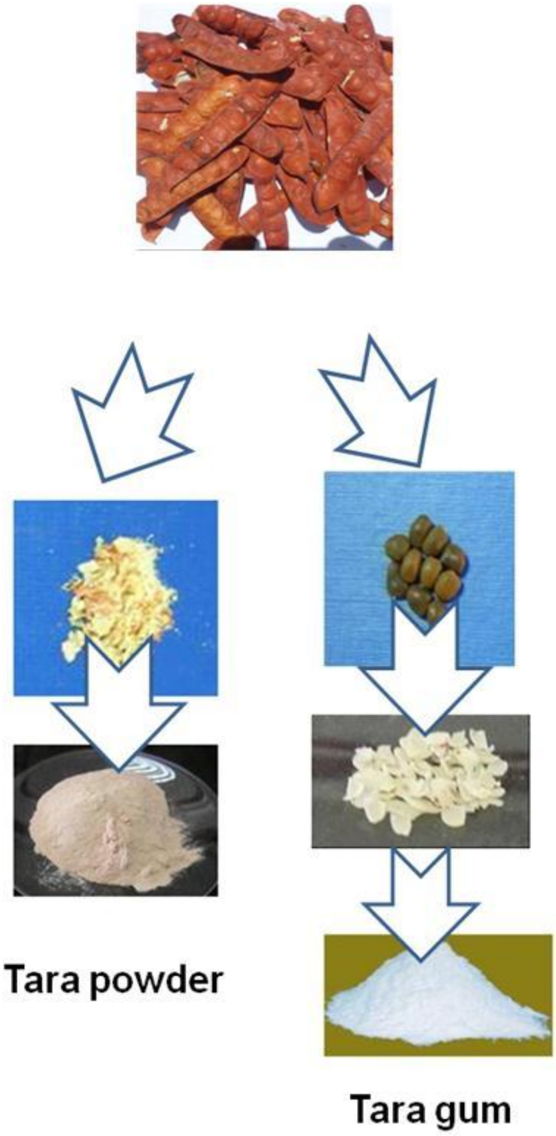


Figure 5: Processes of tara fruit

3. Economical and commercial viability of the tara tanning trading

3.1. Analysis of the supply chain

The current source of tara is mainly natural forests from the Andean region of South America where some agro-forestry exploitations are introduced. Peru is the main area for sourcing tara fruits to obtain tannins followed by far by Bolivia, Chile, Ecuador and Columbia.

The tara supply chain stars from planting the tara tree seeds in agro forestry farms or from harvesting the fruits from wild trees in natural forests. Much of the tara production consists of wild collection, thus, a major problem comes from the quality differences between collected tara and cultivated tara. This thesis compares in Part Two, Experimental, section 6, characterization of commercial tara powder and section 7, characterization of tannins from Bolivian tara fruits, commercial and samples collected in different regions of Bolivia.

The actors of the production and supply chain are those that are involved in the trading process, from farming, harvesting, collecting, transforming and trading the product and the final users. Annex 4 fully describes the tara supply chain and it is summarized in figure 6.

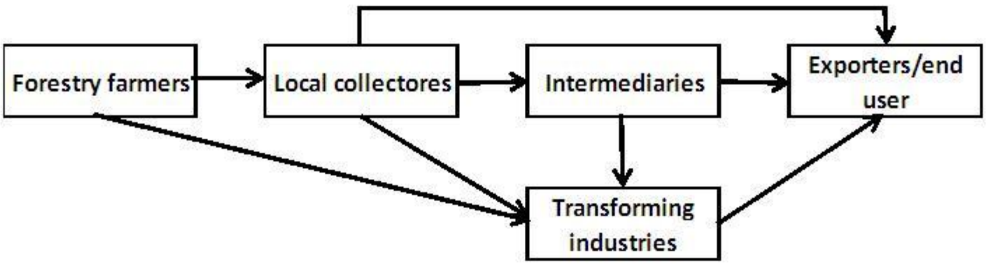


Figure 6: supply chain of tara products

Currently, the major source of tara pods are wild forests and, only in certain areas, tara pods come from forestry farmers.

There is a gap between the production of tara and its demand, thus, there are clear opportunities for forestry farmers to increase production to supply tara powder for the leather industry and tara gum for the food industry. Industry sources are speaking about a monopoly in the market for unprocessed tara with one of a few Italian companies dominating the market. As a result of the undersupply, prices go up. Some processors have, therefore started their own tara production. However, it takes years before the new tara trees start producing.

3.2. Global production

Despite tara tree is native from a wide range of countries according to the World Agroforestry Center[16], approximately 80% of global production takes place in Peru.[17] Sources of tara are also found in Chile, Ecuador and Colombia and other countries like Bolivia, Venezuela, Cuba and cultivated in China, India, Ethiopia, Kenya and Morocco.

According to Schciaffino[18], production of tara in 2004 was between 115,000 and 138,000 tons of tara pods, considering that a tree of *Cæsalpina spinosa* is able to produce 50-150 kg of fruit per year, and 20-40 kg. of pods.

Annex 5 describes production features in Peru, Bolivia and Equator.

It is calculated that 97% of the production was exported as a tara powder or tara gum, therefore, we can make some estimation based on export trade data.

Year	2004	2005	2006	2007	2008	2009
FOB Value USD	13,959,936	16,.705,333	20,956,791	31,756,831	41,326,224	25,317,.943
Delta FOB Value		20%	25%	52%	30%	-39%
Tons	12,878	15,043	15,005	19,918	17,852	17,828
Delta volum		17%	0%	33%	-10%	0%
Price USD/kg	1.08	1.11	1.40	1.59	2.31	1.42

Table 4: Tara exports statistics. Peru.

Table 4 clearly shows how the variability of the market prices has impacted in terms of export value. Since exports in volume (demand) increased from 2004 to 2006, prices rose from an average of USD/kg 1,08 to USD/kg 1,40. During the years 2005 to 2007 the market was consolidated because the highest demand of chrome-free leather for automobile seats.

As production of tara is unable to satisfy the demand, obviously prices go up. This factor is enhanced when the market is dominated by one company, creating a monopoly in the market.

In 2007, tara powder exports achieved the highest values, probably the full availability of production, close to 20,000 tons. Export selling prices also increased to USD/kg 2.31 exceeding

16 Agroforestry Database 4.0. World Agroforestry Center. Nairobe. (Date of consultancy October, 24, 2009) http://www.worldagroforestry.org/treedb2/AFTPDFS/Caesalpinia_spinosa.pdf

17 Tara Casealpina spinosa. Market Survey. Compiled by Swiss Import Promotion Programme (SIPPO) by ProFound – Advisers In Development 2008/2009.

18 Schiaffino, JC. Estudio de mercado de la tara. Perú Programa Desarrollo Rural Sostenible, GTZ, Universidad del Pacífico, GOPA. 2004

expectations of demand. As a consequence, during 2008 the export value increased but volume production was stabilized to 18,000 tons.

During 2009 the automobile industry, and also the leather industry in general, suffered the international financial crises and figures were stabilized to volume production of 18,000 tons/year and average price[19] around USD/kg 1.50.

For better understanding, Figure 7 compares the trends of the export value in Peru during the years 2004 to 2009 compared with the progress of the production volume.

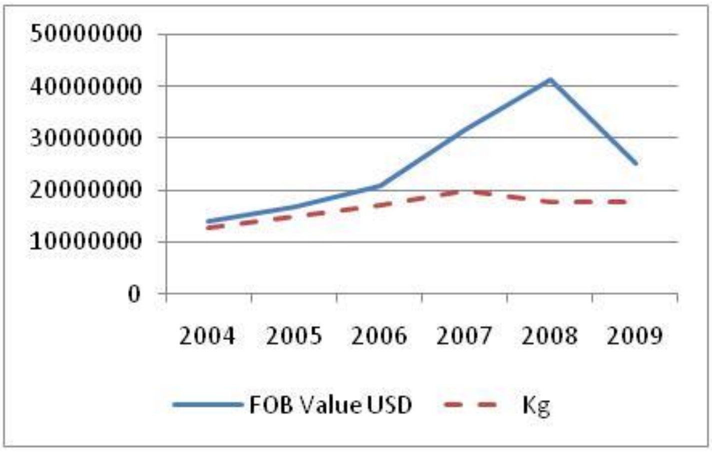


Figure 7: Development of tara exports from Peru comparing value and volume

Figure 8 compares the yearly increase of FOB value of the export trade of tara products and the progress of volume. While the exports in 2007 increased in demand, the market reacted negatively to the price increase. Prices went down in 2009 and production was stabilized.

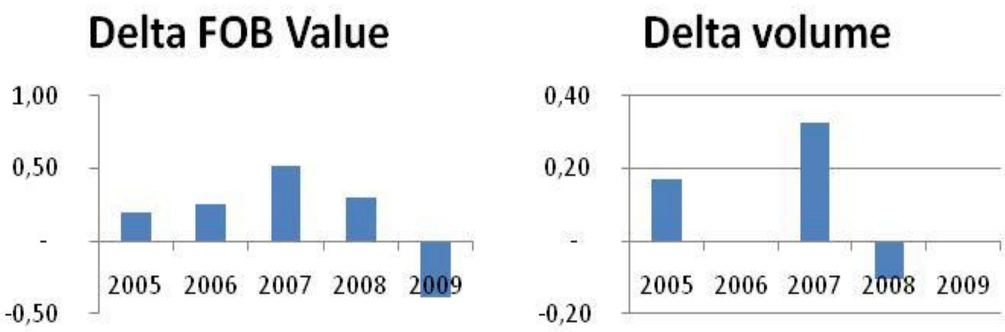


Figure 8: Tara exports in Peru. Increases of FOB value and volume

3.3. Expectations for the tara production during the next years

Currently, administrations from the three Andean countries project new forestry developments of 4,730 ha and future production of tara powder can be estimated according to the table 5[20].

19 Average price is the mix price for tara powder and tara gum.

	Region	**Peru**	**Ecuador**	**Bolivia**
Product ha	7,730	7,500	50	180
t harvested pods	115,950	112,500	750	2,700
t available tara powder	71,889	69,750	465	1,675

Table 5: Estimated tara production. Period 2011-2012

The goals of the development of the tara in the region for 2005 is to double this production figures and exploitation plans are going to be implemented. This is supported with the highest demand of tara products in the leather industry, but also for other products with high potential demand, as the gallic acid and vegetable thickeners.

	Region	Peru	Ecuador	Bolivia
Production ha	14,000	10,000	2,000	2,000
t harvested pods	210,000	150,000	30,000	30,000
t available tara powder	15,960	11,400	2,280	2,280

Table 6: Objective of tara production in 2015

From the production point of view, there is enough experience for forestry technical assistance related to forest and forestry management, plagues control and seed selection and reproduction.

There is a demand for Standardization of the technical quality of the products what is under discussion with International Standardization bodies to coordinate quality requirements according the final application.

There is no doubt that the interest and demand of tara products is growing at international levels. However, alternative products are also available, either from other natural species or by organic synthesis. It is important to develop technologies to improve the present offer of tara products, by customizing or improving the quality, but at the right costs for the market.

There is an opportunity for the leather industry in order to replace chemicals and to obtain sustainable process and articles. Tara tannins offer a wide range of advantages if quality and prices fulfill the expectations of the market.

20 Mancero L., 2008, La Tara (Caesalpinia spinosa) en Perú, Bolivia y Ecuador: Análisis de la Cadena Productiva en la Región. Programa Regional ECOBONA – INTERCOOPERACIÓN, Quito. Quito, febrero 2009. Page 91

3.4. Analysis of tara potential for the leather industry

The production of raw hides and skins depends on animal population and slaughter rate and is related mainly to meet consumption.

The worldwide organization for producers of leather, International Council of Tanners (ICT)[21] estimates a global leather production of 22,930 million square feet:

2007 World leather use by end products		
	million sq. ft	% total
Footwear	11.925	52%
Garments	2.290	10%
Auto	2.340	10%
Furniture	3.210	14%
Gloves	1.010	4%
Other leather products	2.155	9%
Total	**22.930**	

Table 7: 2007 world leather use by end products (Source ICT)

More than half of the world leather production is used for the shoe industry either for upper, sole or lining. While upper leather remains as the most important material for man, women and children footwear and it is strongly appreciate because of its quality, properties and aspect, lining has tendencies to be substituted by textile, natural or synthetic materials, and sole is produced mainly with rubber and other synthetic materials. Sole leather is used for high standard and classic shoes. Sports shoes for high performances also use upper leather technically treated with other materials. The main shoe producers markets are China, India and Brazil with some countries growing during the last years, mainly in South-East Asia, like Vietnam. Italy continues as a reference for fashionable trends in shoe design and also maintains an important market share.

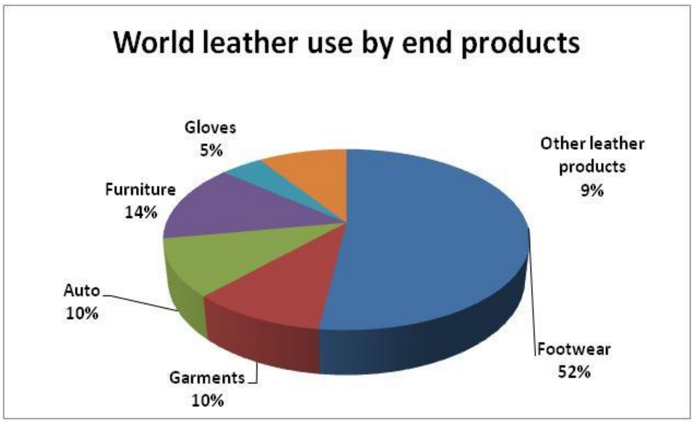


Figure 9: 2007 world leather use by end products

21 ICT, Leather Trade House, Kings Park Road, Moulton Park, Northampton, NN3 6JD, UK, (Date of consultancy May, 15, 2010) www.tannerscouncilict.org

Furniture is the second biggest market for leather where it competes with other materials, mainly textiles and plastics. Elegancy and comfort are the main drivers among design and fashion. Italy, Argentina and Brazil are the biggest markets for upholstery, but China also is growing its production for furniture.

Auto leather has experienced a high increase during the last decades, only interrupted recently due to the automobile industry crisis, especially in North America. Leather is used to personalized high standard auto producers and gives comfort and elegancy. Leather competes in the auto industry with synthetic fabrics.

Auto industry is also very exigent in terms of technical features. Fastness and physical properties are considered by designers and engineers. Also, the substances contained in the leather are strictly analyzed and, in many cases, forbidden. Auto manufacturers are very concerned on social and environmental issues. Comfort and design are key factors for marketing car interiors while sustainability commitment must be considered as prerequisite.

During the last two decades, some auto manufacturers require new tanning processes avoiding the traditional chrome tanning or "wet-blue". Therefore, tanners and the chemical industry have developed alternative processes using organic tannins with the aim to obtain a full degradable material at the end of its cycle life. These organic tanning processes allow obtaining leather to be composted after usage.

This fact is becoming compulsory in Europe. The End-of-Life Vehicle Directive (or ELV Directive 200/53/CE) requires the vehicle manufacturers be responsible for taking back and scrapping cars in the future. Directive specifies that 95% of the vehicle weight must be reused by 2015.

"Wet-white" is the intermediate leather commodity using the tanning properties of aldehydes, mainly, glutaraldehyde[22]. Other "wet-white" systems use metals like Aluminum, Zirconium, Titanium when metals are admitted, vegetable tannins or syntans. Up-today, tara tannin is intensively used to produce automotive "wet-white", as a retanning agent after pre-tanning with glutaraldehyde and the mechanical operations. Annex 3 shows a typical recipe to produce automotive leather, "metal-free", used for supplying of German car manufacturers. Its properties of light fastness and relatively colorless have not been improved with other substances despite the efforts of the chemical industry to find out a "synthetic tara tanning".

Garment and glove industry is a traditional leather consumer. The men of the caverns already used the skins of the animals, hunted for food, to keep worm. Through the tanning techniques, especially with the chrome tanning technology, soft, light and very comfortable leather

22 Glutaraldehyde: $C_5H_8O_2$, CAS number 111-30-8

garments can be manufactured. Garment leather is produced mainly from sheep skins, de-woolen or maintaining its natural wool.

Nowadays, with the development of new textile fabrics adding functionalities in terms of water repellency, lightness, isolation and perspirability, the leather demand for garments is related to fashion trends. However, classical nappa and suede (soft and light skins) and double-face (woolen sheep skins) are very appreciated by luxury trademarks because its elegance and natural feeling.

Luxury companies appreciate leather as a noble and natural material and produce leather goods as complements in prestigious firms and recognized retailers. There is a high quality leather demand for handbags, briefcases, wallets, belts… The natural properties of leather also are related to country ambiances and are used in saddle, golf bags and many other accessories.

Table 8 summarizes market issues and tara consumption opportunities for each leather article. Annex 6 describes the international leather production and it is detailed with figures and statistics.

	Footwear	**Furniture**	**Auto**	**Garment**	**Gloves**	**Other leather goods**
Market trend	Sustainable growing higher than population growth rates	Stable	Growing	Variable	Growing for specific uses	Stable, growing luxury goods.
Main markets	China, Italy, India, Brazil	Italy, China, Argentina	Germany, Argentina, China, Mexico, Brazil	Spain, China, India, Italy, Pakistan	South East countries, Africa	Spain, France, Germany
Main consumers	Worldwide	Central and North Europe, USA	USA, Europe	Europe	USA	USA, Europe, Japan
Drivers	Comfort, fashion, functionalities	Elegancy, design	Elegancy, comfort	Fashion	Compliance to the end uses	Trademark positioning
Leather features	Soft, waterproof, breathable	Surface resistances, light fastness	Very high technical performances	Soft and lightness	Soft and fastness.	High quality, elegance, natural
Competition materials	Textile and plastics	Textile	Textile	Textile	Textile	Plastics
Tara opportunities	Low	Medium	High	Medium	Medium	High

Table 8 : Analysis for tara potential for the leather industry

3.5. European Policy of Chemicals (REACH)

The European REACH Directive is a great opportunity for the trade of tara tannins in Europe[23].

Since 2006 there is a Directive in Europe (CE 1097/2006) concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH).

To point out the most important advantage for tara products, compared with syntans and other vegetable tannins, they are exempted of such Registration as defined in Annex V, #8:

"Substances occurring in nature, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC"

According to Chapter 2, "Definitions and general provision", Article 3, "Definitions", # 39:

"Substances which occur in nature: means a naturally occurring substance as such, unprocessed or processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation, by extraction with water, by steam distillation or by heating solely to remove water, or which is extracted from air by any means"

Trading in Europe with tara powder or tara tannins extracted with water does not need to incurred with tremendous cost required for collecting safety data and register them in REACH.

23 Oficial Journal of the European Union. Regulation (EC) No 1907/2006 of the European Paliament and of the Council of 18 December 2006. L 396/1. 30.12.2006

4. Theoretic fundamentals

4.1. The Tanning science: the collagen chemistry

The process of tannage consists essentially in the production, from raw animal hides and skins, residues of the food industry, of materials, normally referred to as leathers, which have a greater stability to water, bacteria, heat and abrasion and have, as consequence a wide range of domestic and industrial applications[24].

Leather is in downstream sectors of the consumer products industry. For the latter, leather is often the major material input, and is cut and assembled into shoes, clothing, leather goods, furniture and many other items of daily use[25].

The type of leather produced is to a large extent dependent on the origin (calf hides, cow, sheepskin, goatskin, reptiles…) and previous treatment of the hides and skins but some control may also be effected by the use of different tanning materials and by variation of the conditions employed during tannage, e.g. temperature, pH, duration.

In the simplest terms of chemistry of leather manufacture is seen as the interaction of inorganic, natural or synthetic tannins with the collagen fibers of the corium of skin.

Hides and skins contain three layers; the outer is the epidermis and the inner the subcutaneous tissue. However, the intermediate layer, the dermis or *corium*, is the most valuable for the tanners. Its constitution is mostly a protein, the collagen.

The earliest stages of the tanning process, the beamhouse operations, aim to remove the two outer layers among other proteins from dermis, in order to purify, as much as possible, the fibril structure of the collagen.

Currently, 30 different types of collagen have been described according its composition of aminoacids and its sequence and depending on their function in the living organism.

Like keratin, elastin and silk fibroin, Type I collagen is a scleroprotein consisting like all proteins of aminoacids liked by –CO-NH- groups to form peptide chains.[26]

The Type I collagen molecule is distinguished by its unusually high content of glycine, proline and hydroxyproline which together account for over 50% of the amino acid content of the protein. See table 9. This composition is crucial to the structure and reactivity.

24 E. Haslam. Chemistry of vegetable tannins. Department of Chemistry. The University, Sheffield, England, Academic Press, London. 1966.

25 European Commission. Integrated Pollution Prevention and Control (IPPC). Reference document on Best Available Techniques for the Tanning of Hides and Skins. 2003

26 Prof. Dr. rer. Nat. habil. Günter Reich. From Collagen to leather – the theoretical background. BASF Service Center. Media and Communications. Ludwigshafen. Germany. 2007.

Amino acids	Content in %	Number per molecule
Glycine	33.53	1056
Proline	11.97	377
Hydroxyproline	11.18	352
Aspargine	1.19	37
Aspartic acid	3.07	97
Glutamine	2.57	81
Glutamic acid	4.75	150
Lysine	3.17	100
Hydroxilysine	0.40	13
Arginine	5.04	159
Histidine	0.20	6
Serine	3.46	109
Trypophane	0.20	6
-CO-NH-		3147

Table 9: Type I collagen: content of amino acids. Source: Dr. G. Reich

Collagen is composed by three chains of polypeptides in α-helix form, as protofibrils and each one contain approximately 1,000 aminoacids.

A collagen fibril is the union of 7,000 – 8,000 protofibrils and they come together to form fibers of about 5 µm of diameter.

The content of acidic and basic amino acids, amino acids containing OH groups and peptide groups is important and decisive for the reactivity of the collagen, which is a requirement for its transformation into leather.

To understand the chemistry of the tanning processes, it should be taken into account that all the reaction coordination and links with the tanning products is produced in the surface of the collagen molecules formed by fibrils, by means, between the chemicals agents and the lateral chains of aminoacids of collagen[27].

The most important reactive groups in the tanning process are:

- Hydroxilic groups: from aminoacids serine, tyrosine and hydroxyproline

27 Josep Mª Morera. Química Técnica de la Curtición. Escola Universitaria d'Enginyeria Tècnica Industrial d'Igualada. Escola Superior d'Adoberia. ISBN 84-931837-0-9.

- Carboxyl groups: from aminoacids aspartic acid and glutamic acid
- Amide groups: from aminoacids aspargarine and glutamine
- Amine groups: from aminoacids lysine, arginine, histidine, hydroxylysine.

Owning to the comprehensive information available on collagen, the modes of transformation relevant to leather manufacture of the individual functional groups with the help of the chemically widely disparate tanning agents are now known for the greater part[28]. Table 10:

Functionality	Bond type	Typical tanning agents
Carboxyl groups	Complex bonding	Metallic salts, in particular basic chromium (III) sulphates
Basic groups	Covalent bonding	Aldehydes, diisocyanates, etc.
Peptide groups	Hydrogen bonds	Phenolic natural and synthetic tanning agents
Surface overall	Hydrophobic, “van der Waals” bonds	Including polymers, tensides
Pores/capillarites	Fillers	Various substances

Table 10: The potential reactions on collagen during leather making

After flying, hides and skins have a higher number of chemical basic groups than acid groups, thus, the pH value is between 7 and 8.

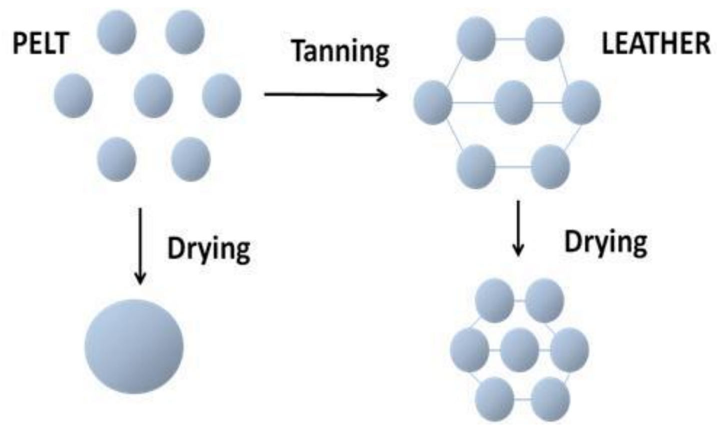


Figure 10: Diagram of the nature of leather formation by which "leatherlike drying out" is ensured by the crosslinking and distance-enhancing action of the tannin agents. Source Dr. G. Reich

28 Prof. Dr. rer. Nat. habil. Günter Reich. From Collagen to Leather – the theoretical background. BASF Service Center. Media and Communications. Ludwigshafen. Germany. 2007.

The tanning operation is the treatment of hides and skins with chemicals in order to stabilize the collagen structure from hydrolysis caused by water or enzymes and increase the heat resistance higher that the natural temperature. Furthermore, tanning reactions have to avoid the union of carboxyl and amino groups inside the collagen structure in order to obtain the required properties of the leather suitable for its final uses or able to react with other chemicals to achieve such features. Otherwise, when hides and skins are dried causes a fragile, hard and translucent material well known as parchment.

The bound quantity of collagen is determined primary by stoichiometric aspects, but also influenced by available surfaces on the fibrils, elementary fibers and fibers, and in the voids between them (capillarities and pores).

The tanning materials exploiting these potential reactions on the collagen and the mechanism by which they do so is now well understood, at least in basic terms[29].

Tanning chemicals must have more than one chemical functionality to be able to react with more than one collagen molecule at the same time and to assure transversal bonds. Also, it is important to consider both, their molecular size to be able to penetrate into the collagen microstructure and its water solubility as tanning is made in water baths. Colloidal dispersion with very small micelles and very disaggregate can have also, good tanning properties.

Furthermore the bonding chemical reactivity of the tanning substances and the protein structure of the collagen net, diffusion and penetration concern the tanning processes. In principle, simple stirring, the movement of a paddle wheels or movement of the drum used in tanneries to achieve these mechanical effects, accelerate the diffusion process. However, the situation is different where substances with an affinity for collagen are concerned. In these cases, the bond types and the functional groups for the affinity are of secondary importance. The most important factor is their accessibility to the collagen structure.

It is generally accepted that the penetration depth is dependent upon a diffusion coefficient k multiplied by the square root of the tanning agent concentration and the duration of tanning, the diffusion coefficient varying according the tanning agent type.

Pelts contain approximately 75% of water, a small part is bounded to the collagen and the greater part is “free”, acting as a solvent and forming the “inner float”. This contrasts with the “outer float” from a pit, paddle or drum in which the reacting substances are initially present molecularly dispersed or in colloid suspension.

29 Prof. Dr. rer. Nat. habil. Günter Reich. From Collagen to Leather – the theoretical background. BASF Service Center. Media and Communications. Ludwigshafen. Germany. 2007. Page 119

As soon as the tanning substances reach the inner float from the outer float, it is taken up by the collagen. This takes place from the outer layers towards the inside of the pelt. Provided the supply of the substance remains below the saturation limit of the collagen, the process will repeatedly restore the concentration gradient between the inner and the outer floats, and diffusion will continue until complete exhaustion.[30]

However, there are facts to constrain the diffusion of the substances in the leather:

- Astringency: happens when large-particle substances of high affinity, bonding of the substance initially on the outer layers of the pelt may lead to blockage of the diffusion paths.
- Formation of aggregates: All tanning agents which owe their affinity for collagen to their ability to form hydrogen bonds, tend to aggregate to form larger particles due to such dipolar or "secondary valence" character.

Currently, the chemical industry provides the chemicals with tanning properties for the leather industry. They offer mineral salts able to stabilize the collagen structure from hides and skins; plant extracts (tannins); synthesized chemicals with tanning properties (syntans) and commercializes tailor-made formulations to achieve products ready to be used in the tanneries.

Vegetable tannins are natural products of relatively high molecular weight which have the ability to complex strongly with carbohydrates and proteins. The most common vegetable extracts come from mimosa, quebracho and chestnut.

Among the mineral salts, the chromium III salts are, by far, the most used in the tanning process.

4.2. Hydrothermal Stability

Hydroxyproline is an amino acid specific to collagen and substantially responsible for the hydrothermal stability of native, fully hydrated collagen.

When collagen is wet, the matrix can be degraded by rising temperature, at the same time hydrogen bonds in the triple helix are broken, observed as shrinking, leading to gelatinization. The hydrothermal stability of collagen can be altered by many different chemical reactions, well known in the fields of histology, leather tanning and other industrial applications of collagen.

30 Prof. Dr. rer. Nat. habil. Günter Reich. FROM COLLAGEN TO LEATHER – THE THEORITICAL BACKGROUND. BASF Service Center. Media and Communications. Ludwigshafen. Germany. 2007. Page 43

The effects of some of these chemical modifications can be summarized in table 11, where the denaturation temperature is typically measured by the perceptible onset of shrinking[31]:

Chemical modification	**Denaturation temperature ºC**
None	60
Metal salts: Al(III), Ti(IV), Zr(IV)	70-85
Plant polyphenol gallotannin or ellagitannin	**75-80**
Plant polyphenols: flavonoid	80-85
Synthetic tanning agent: polymerized phenols	75-85
Aldehyde: formaldehyde or glutaraldehide	80-85
Aldehyde: phosphonium salt or oxazolidine	80-85
Basic chromium (III) sulfate	105-115
Combination: gallotannin + Al(III)	105-115
Combination: flavonoid polyphenols + oxazolidine	105-115

Table 11: Effects of chemical modifications on shrinking temperature

The increase in hydrothermal stability has frequently been regarded as the characteristic indicating completion of tannage crosslinking[32]. It is undisputed that the shrinkage temperature T_s which is based upon it is a quantity of interest in tanning theory. It provides an indication of various types and grades of crosslinking, and its isometric measurement yields considerable information on the modification which the collagen / leather structure has undergone. A.D. Convington has attempted to formulate a new tanning theory encompassing all tanning processes on the basis of detailed thermodynamic discussions[33].

However, it provides little indication of the practical value of the leather, as wet leather is seldom subjected to thermal load during processing and use. Attainment of as high a T_s value as possible is not an objective in the development of new tanning methods.

31 A. Convington, L. Song, O. Suparno, H. Koon, M.J. Collins. Link-Lock: An explanation of the chemical stabilization of collagen. World Leather. October/November 2010

32 Prof. Dr. rer. Nat. habil. Günter Reich. From collagen to leather – The theoretical background. BASF Service Center. Media and Communications. Ludwigshafen. Germany. 2007. Page 115

33 A. Convington, G. Lampard, R. Hancock, I. Ioannidis. Studies on the origien of hydrothermal stability. A theory of tanning. Journal of the American Leather Chemists Association, 93 (1998), 107

4.3 Current tanning practices, processes and techniques for leather

The production process in a tannery can be split into four main categories: hide and skin storage and beamhouse operations, tanning operations, wet-end operations and finishing operations. After the hides and skins are flayed from carcass at the abattoirs, they are delivered to the hide and skin market or directly to the tanneries. Where necessary, hides and skins are cured before transport to prevent them from putrefying. Upon delivery to the site, hides and skins can be sorted, trimmed, cured and stored pending operations in the beamhouse.

Table 12 is a general overview of making leather from raw hides and a short description of them[34] can be found in Annex 7, always, will depend of the raw materials and the desired final articles.

		Chrome tanned leather	**Vegetable tanned leather**	
			Upper leather	**Sole leather**
Beam-house	Raw hides	Soaking	Preliminary soaking Soaking	Soaking
		Liming	Liming	Liming
		Flesing Splitting	Fleshing Splitting	Fleshing
Tanning		Deliming Bating	Deliming, bating Washing, Drippping	Deliming Bating
		Pickling Chorme tanning	Vagetable pit tanning	Vegetable pit tanning
		Samming	Dripping, washing Samming	Washing Samming
	Wet-blue	Shaving	Shaving	
		Washing	Fatliquoring (drum)	Fatliquoring
		Neutralization	Dryeing	Dryeing
Wet-end		Washing	Retanning	
		Retanning Dyeing, fatliquoring	Dyeing Fatliquoring (drum)	
		Washing	Samming, washing	
		Drying	Drying	
	Crust	Buffing	Staking	
Finishing		Lacquering	Buffing	
		Mechanical finishing	Toggling Ironing	Staking (Rolling)
	Leather article			

Table 12: Process steps for the production of leather from raw hides. Source: BREF

34 Reference Document on Best Available Techniques for the Tanning of Hides and Skins. 2003. Pag. 17.

4.4. Environmental considerations for the leather industry

The tanning industry is a potentially pollution-intensive industry. The environment effects that have to be taken into account comprise not merely the load and concentration of the classic pollutants, but also the use of certain chemicals. Of world tanneries, 80 – 90 % use chromium (III) salts in their tanning processes. The degree of toxicity of chrome is perhaps one of the most debated issues between the tanning industry and authorities. Annex 8 describes the main environmental concerns in the tannery operations.

4.5. The vegetable tanning principles

It has been known since prehistoric times that raw skin is colored and rendered imputrescible with aqueous solutions of materials obtained from many forms of plant life. Primitive peoples in all parts of the globe and from all the ages of the past have developed vegetable tanning systems based on materials available locally[35]. Records exist relating to its operation in Mediterranean regions around 1500 B.C. The active principle, which is widely distributed throughout the vegetable kingdom, is a class of complex organic compounds, capable of combining with skin protein, and known as tannin. By vegetable tanning is meant the combination of tannin with the protein matter of skin to form leather.[36]

The plants have a particular ability to synthesize aromatic compounds[37], fundamental for their metabolism. These aromatic compounds include aromatic amino acid (phenylalanine, tyrosine, tryptophan) and aromatic phenolic and phenylpropenic acids. Tannins are the results of condensation reaction of substances containing phenolic and carboxylic groups and are widely distributed in the vegetal kingdom but very low concentrations. Gallic acid ($C_6H_2(OH)_3COOH$) participates in many of these condensation reactions (Figure 11).

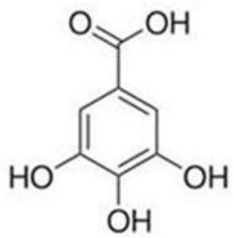


Figure 11: Gallic acid

35 Thomas C. Thorstensen. Practical Leather Technology. Robert E. Krieger Publishing Company. Malabar, Florida. USA. 1985

36 John Arthur Wilson. The Chemistry of Leather Manufacture. The Chemical Catalog Company Inc. New York. U.S.A. 1928. Page 391

37 Krysztof Bienkiewicz. Physical Chemistry of Leather Making. Rober E. Krieger Publishing Company. Malabar, Florida, USA. 1983. Page 385

Certain plant cells are very rich in tannin. In the living cell, the tannin occurs dissolved in the cell sap and associated with other substances, including carbohydrates and salts. Carbohydrates are able to link up with the tannin in some way so as to prevent its attack upon living protoplasm. The tannin appears to be useful in some way in the metabolism of the plant but their physiological function remains a mystery. It seems they have a certain effect controlling enzyme reaction and act as inhibitors.

The vegetable tannins are polyphenols with a molecular weight in the range of 500 – 3000. Among the materials which have assumed commercial importance as a source of tannins for leather manufacture are barks, woods, leaves, twigs, fruits, pods and roots. Aqueous solutions of tannins have an astringent taste; give dark blue or green colorations with iron salts, and precipitate gelatin, other soluble proteins, and alkaloids from solution.

Attempts to isolate the pure tannins and to study their organic structures have proved exceeding difficult. Tanning extracts obtained from different sources show very different properties, which are due in a large measure to the foreign matter extracted with the tannin, such starches, gums and other materials. Therefore, the extract is not a true solution but will contain suspended insoluble materials that contribute to the leather producing building into the fiber of skins certain characteristics of fullness of feel and resiliency which are features of the tanning materials and methods used.

The application of vegetable tanning has been based on empirical skills and experiences but has become a major field of work by leather chemists and scientists to understand the structure of the vegetable tannins and the estimation of the tannin content of grinded parts of the plants or its extracts.

Freudenberg (1938) classified plant tannins in two major groups according to their chemical nature and structural characteristics. The hydrolysable tannins are readily hydrolyzed by mineral acids or enzymes (tannase and emulsion) into sugar or a related polyhydric alcohol and a phenolic carboxylic acid.

Depending on the nature of the phenolic carboxylic acid the hydrolysable tannins are usually subdivided into gallotannins and ellagitannins (Figure 12). Hydrolysis of gallotannins yields gallic acid while ellagitannins, hexahydroxydephenic acid.

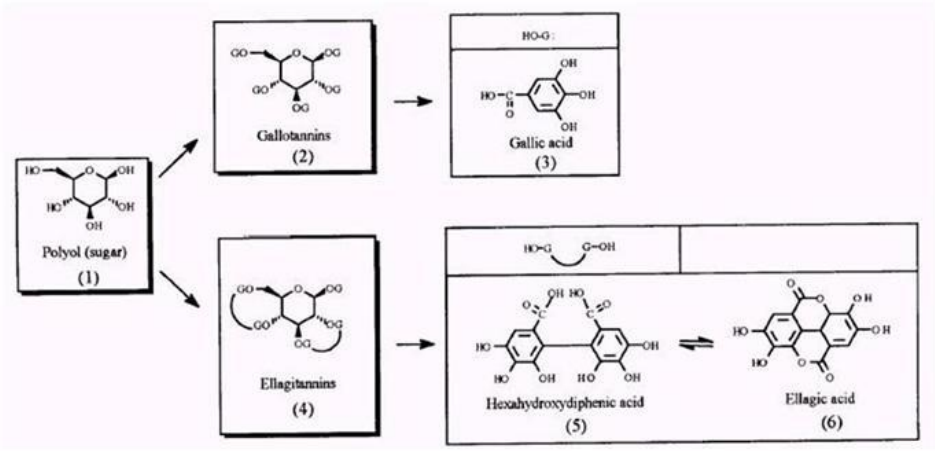


Figure 12: Hydrolysable gallotannins and ellagitannins

The condensed tannins are polyflavonoids in nature, consisting of chains of lavan-3-ol units. The most common class of condensed tannins or proanthocyanidins are the procyanidins which consist of chains of catechin or epicatechin. In contrast to hydrolyzed tannins, condensed tannins undergo polymerization to the amorphous phlobaphens or tannins reds, under action of acids[38].

There is not a clear theory of the vegetable tannin fixation yet despite this practice has been investigated for decades.

The vegetable tannins are, thus, complicated mixtures of chemical components and it is difficult to obtain their structure. Furthermore, the colloidal behavior[39] and the hide protein condition the chemical reactions. According to Thortensen, all factors are important: degree of opening of the fibers, the availability of reactive groups for vegetable tanning, the degree of hydration, the presence of salts, the extent of swelling of the skin… All the relationship between all these factors includes synergies between them or, contrary, working against one to another. This makes impossible to establish a structured mechanism for practical and controlled tanning process. Tanner’s forums still discuss whether vegetable tanning process is an organic chemical action or strictly a physical absorption. The explanation of these discussions is the number of relatively simple principles of physical facts that seem to apply to the tanning process.

38 J.M. Garro Galvez, B. Riedls and A.H. Conner. Analyutical studies on tara tannins. Departement des Sciences du bois et de la Forêt, Centre de Recherche en Sciences et Ingénierie des Macromolécules, Université de Laval, Quebec. Canada. USDA-Forest Service, Forest Products Latoratories, Madison USA. Holzforschung. Vol 51.1997. Pag. 235-243. Walter de Gruyter. Berlin. Germany.

39 The stability of a colloidal dispersion is determined by the electrical difference of potential between the film of solution wetting the particles and the bulk of the surrounding solution. According to Procter and Wilson theory, the astringency of a tan liquor in practice is assumed to be a function of the potential difference between the solution immediately in contact with the tannin particles and the bulk of the tan liquor as well as the potential difference between the tan liquor and the collagen jelly. J.A. Wilson. The Chemistry of the Leather Manufacture. Chemistry of the tannins. Page. 467.

The most acceptable reaction is the bonding to the CO-NH linkage of the protein through the phenolic hydroxyl group of the vegetable tannin, among other side reactions.

The curve of the fixation of vegetable tannin materials as a function of pH indicates a slope downward from the strong acid range to a minimum near the isoelectric point, a rise to a minor peak, and a fall.

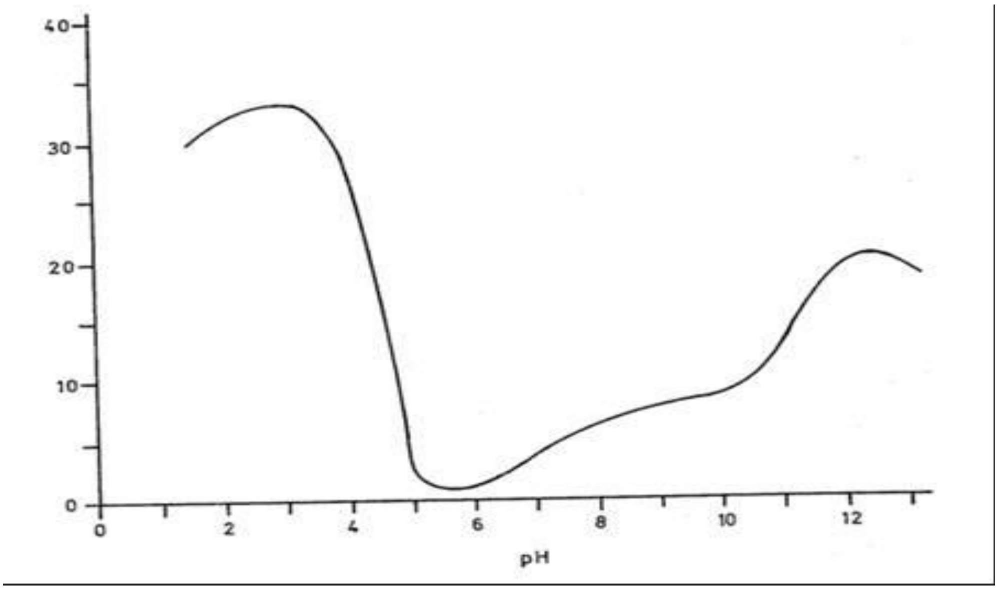


Figure 13: Fixation curve of the vegetable tannins

The explanation of this behavior can be a function of the availability of hydrogen bonds or hydrogen atoms on the protein and on the vegetable tanning material. pH values for the vegetable tannins are from 5 to 7. The vegetable tannins are, therefore, un-ionized through the range of the vegetable tanning. The protein increases its hydrogen ion fixation with the lowering pH. This explains, at this point, that fixation is a reaction of the hydrogen ion with the protein.

The S curve, however, demonstrate that this reaction cannot be strictly explained as a chemist phenomena. Increase of pH after the isoelectric point causes an increase in hydration of the protein and the fixation of the tannin just at pH values just above the isoelectric point.

As vegetable tannage proceeds, the fiber is no longer dominated by water of hydration and changes its ionic character as a result of the fixation of the vegetable tannins. The hydration factor becomes less significant, and the eventual fixation curve is a smoother sweep from the neutral pH range to a high fixation at the strong acid range.

Other considerations to take into account during the vegetable tanning process is the size of the tannin molecules, often relatively large and chemical reactions can be blocked resulting in eventual coating of the fibers and filling the voids of the hide with vegetable tanning materials.

For an effective vegetable tanning these stoichiometric constraints oblige to follow a certain sort of steps, starting with the chemical reaction between the vegetable tanning material and the hide protein, the coating of the fibers and isolation of the reactive groups and, finally, the filling of the physical voids in the leather. Therefore, the technicians accurately control the penetration of the vegetable tannin materials into the hide or the skin. According the final leather article, they will give more or less value to the dispersion of the tannins, the degree of penetration and the degree of the filling properties. For heavy leather, where filling action and weight are important, the colloidal character of the tannins will be considered more than the chemical nature, and hides and skins are processed mainly in rockers. Light articles, aiming to achieve a full but soft tannage with a minimum amount of material, the chemical aspects are more important and process is carried out in drums.

Vegetable tannins, also contain other substances with influence in the tanning process. So called non-tannins, they are tannins with low molecular size and weight, and with limited reactivity with the collagen protein.

Annex 9 briefly describes the vegetable sources of tannins most widely use for tanning leather.

4.6. Analytical characterization of tara tannins

In general, to determine the quality of the vegetable tannins the following parameters are examined:

- Tannin content: To characterize the content of tannins in the tara powder, there is no yet an approved standard method but a proposal has being submitted based on the filter method[40]. It determines tanning agents through filtration of all vegetable and synthetic tanning products. It is based on indirect gravimetric analysis through fixing of the absorbent compounds on low-chromed hide powder.
- Non tannin content: They are organic compounds with low molecular weight and, therefore, they do not have tanning capacity. Free gallic acid and other organic acids content in the powder are non tannins compounds, as well as carbohydrates. They are determined by gravimetry.
- Insolubles: Are particles or aggregates, non soluble, but are component of the powder as lignin and cellulose. The gravimetric method is used after filtering the sample with a membrane of 0.45 microns.

[40] ISO/IULTCS International Standard. Reference number ISO/FDIS 14088:2011; IULTCS/IUC 32:2011. “Leather – Chemical tests – Quantitative analysis of tanning agents by filter mothod”.

- Total solids: is the quantity of non-volatile substances at 100ºC. They are calculated by gravimetry.

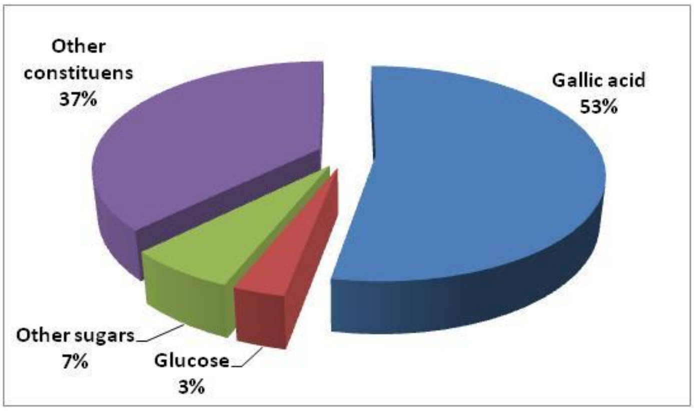


Figure 14: Constituents of tara tannins

Garro Galvez, Rields and A.H. Conner[41] evaluated the tannin content extracted from tara for its utilization in wood adhesives. Spectrophotometric and chromatographic analyses were performed before and after hydrolysis to quantify amounts of free and combined components. The results obtained in this study show that gallic acid is the main constituent (53%) and it was easily isolated by alkaline hydrolysis of the plant extract. In the total sugars present in the extract (9.6%) glucose had the biggest concentration (3.1%). Other constituents were present to a less important extent. Figure 14.

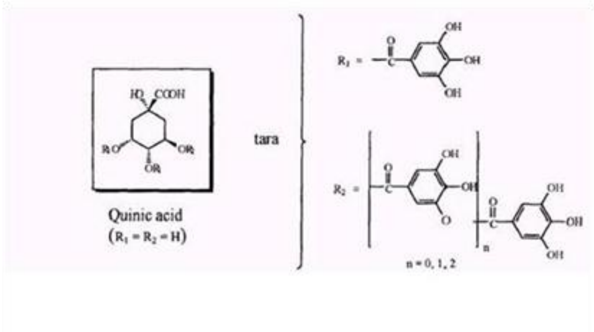


Figure 15: Galloylated quinic acid and structure of tara tannin

According to Horler and Nursten (1961) the principal components of tara tannins are based on a galloylated quinic acid structure:

Thus, they differ from other members of the hydrolysable tanning group which are based upon galloylated or ellagoylated hexose.

41 J.M. Garro Galvez, B. Riedls and A.H. Conner. ANALYTICAL STUDIES ON TARA TANNINS. Departement des Sciences du bois et de la Forêt, Centre de Recherche en Sciences et Ingénierie des Macromolécules, Université de Laval, Quebec. Canada. USDA-Forest Service, Forest Products Latoratories, Madison USA. Holzforschung. Vol 51.1997. Pag. 235-243. Walter de Gruyter. Berlin. Germany.

For this reason, tara tannins are notable for their high acidity and on mild acid hydrolysis, the tannin gives gallic acid, and instead of the usual carbohydrate fragment, the alicyclic quinic acid. The acidity of the tannin is directly related to the presence in its structure of the free carboxyl group of quinic acid[42].

4.7. The chemistry of the syntans

The modern operations of vegetable tanning, requires the use of auxiliaries to better control the behavior of the tannins during the process, or to give or improve the final physical and fastness properties and the quality of the final leather articles. With the aid of the chemical industry during the 20th century and the knowledge of the organic synthesis, it is possible to obtain molecules similar to the tannins or with special features to combine with them.

The syntans available to the leather industry are in constant evolution. The product ranges from the chemical suppliers change very often to maintain their competitiveness as a result of inversions in research programs. Nowadays, products and formulations are launched to the market and the nature of the products is seldom revealed and they are kept confidential for competitive reasons.

Stiasny observed the properties of the Gallic acid and concluded that products of phenol sulphonic acid were able to condensate and react with the protein to produce leather. He was first patenting a synthetic tannin or syntan.

The phenol is first sulphonated with sulfuric acid, to obtain a sulphonic acid that will be either the alpha or beta position depending upon the temperature of the sulphonation. Figure 16.

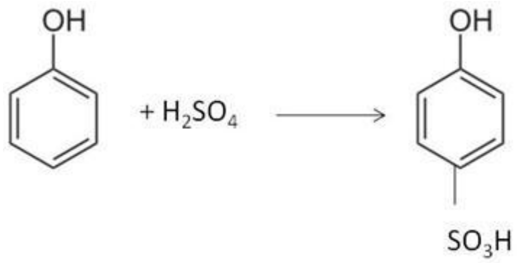


Figure 16: Phenol sulphonation

The phenol sulphonic acid is condensed with formaldehyde. Figure 17.

[42] E. Haslam. *Chemistry of vegetable tannins*. Academic Press. London and New York. 1966. Pag. 113.

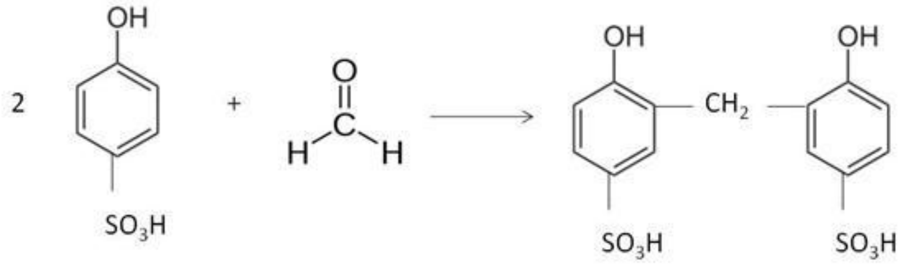


Figure 17: Condensation of phenol sulphonic acid

The tanning properties increase with the molecular size until certain limit. This happens because they are not able to penetrate in the collagen structure. The sulphonic groups should be kept as lower as possible, just to assure that the molecule is soluble.

The syntans based on phenol condensation are classified as "replacement" syntans. This is due to those tanning properties, thus they are able to replace vegetable tannins.

In another hand, and with the same principles of condensation and sulphonation, naphthalene syntans are the simplest and easiest to make. Naphthalene is a solid, aromatic compound with a melting point of 80ºC[43]. The material is melted and sulphuric acid is added for the formation of the naphthalene sulphonic acid. The sulphonic acid is diluted with water and condensed with formaldehyde. The condensation of formaldehyde binds some of the unreacted naphthalene, and a completely water soluble product is obtained.

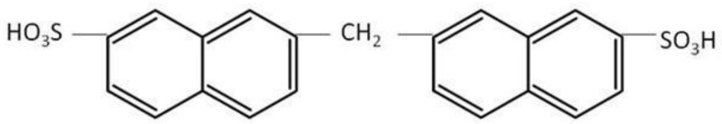


Figure 18: Naphthalene sulphonic acid

The material is strongly acid. The product may be marketed as an acid liquid to be applied in formulations for whitening chrome leathers or bleaching vegetable tannins. It may also be neutralized to form a neutral salt of the syntan which may be marketed as a liquid or often, dried and as a solid syntan.

Naphthalene syntan is an example of a material capable of being absorbed by the hide protein through hydrogen bonding. As the pH is lowered, the syntan is bound according to the curve of the figure 11. The naphthalene syntan is a large organic molecule containing hydrophilic sulphonic acid groups. It is, therefore, somewhat related to the detergents. The sulphonic acid group pulls the molecule toward the water, whereas the aromatic naphthalene rings will be

43 Thomas C. Thortensen. Practical Leather Technology. Robert E. Krieger Publishing Company. Malabar. Florida. 1985. Third edition. Page 172.

attracted to other less soluble materials dispersed in the solution. When dissolved with the vegetable tanning materials, the syntan adds negative charges to form a more negatively colloid charges. The addition of negative charges to the vegetable tannin will aid in dispersing the tanning particles and help in the penetration of the hide.

The naphthalene syntan will also compete with the vegetable tanning for the absorption positions on the hide protein, and consequently, it will aid in the brightening of the color and the penetration of vegetable tannins.

Since the fixation of the naphthalene syntan is based on the acid absorption phenomenon, the reaction is not permanent and the syntan can be removed. It does not have leather-forming properties in that the leather will not dry soft but will continue to dry hard and bony. There is no real permanent stabilization of the hide fiber and only a slight raising of the shrink temperature. For this reason, naphthalene sulphonic syntans are classified as "auxiliary" syntans and are used mainly to confer supplementary properties to the main tanning agents, either vegetable tannins or chromium salts.

A large number of different synthetic tannins are presently being offered in the leather industry. As the molecules become more complicated, more specific tanning properties can be built into them. Examples of the types of materials of various syntans are protected with patents by various manufacturers.

PART TWO: EXPERIMENTAL

5. Objectives of the experimental part

The experimental part of the research is intended to prove the hypothesis that the application of tara tannins, known since remote eras, can respond as newest technologies of tanning leather that comply quality article standards at the time to meet the highest exigencies of chemical auxiliaries used in goods supply chains.

Section 6, consisting on chemical analysis carried out according the parameters described by the chemistry industry detailed in section 4.6, aims to compare commercial samples of tara powder from different suppliers of leather chemical auxiliaries and determine statistical significant differences among them. Also the purpose is to have a range of parameters to validate the results for all other experiments of carried out during this research.

A expedition to Bolivia was planned to identify areas where tara is found either wildly or cultivated in forestry farms. During the trip, samples of tara fruits were collected and its components characterized to determine the feasibility of its commercialization. Therefore, section 7 aims to compare the samples of tara fruits among them and with the range of the analytical values obtained in the section 6.

The market analysis described in section 3 pointed out the needs of standardization to improve international requirements by offering a range of quality products. As a natural source, many conditions, such a climatic, soil, altitude and many others may cause differences in the chemical composition of the fruits.

Section 7 includes the determination of the gallic acid content. This will give an idea of the hydrolysis of the tara tannins and whether this characterization can be used to test the quality of the tara products. Also, the hydrolysis of the tara tannin will be tested to confirm the classification of tara tannin as hydrolysable vegetable tannin as described in section 4.5.

Section 8, 9 and 10 statistically analyze the results of the experiments designed with the support of the Statgraphics Plus software, version 5.0 from Statpoint Technologies, Inc (Warrenton, VA, USA)[44]. In all cases, the considered dependent variables will be the hydrothermal stability calculated with the shrinkage temperature according section 4.2, the measurement of the tensile strength and elongation and the measurement of the tear load. All these physical properties are common required for most of the leather article quality specifications.

44 Bacardit A., L. Ollé. Diseño de experimentos en ingeniería del cuero. Escola d'Enginyeria d'Igualada. escola Superior d'Adoberia d'Igualada. ISBN: 84-931837-8-4

Blends of tara powder with a naphthalene sulphonic syntan and a phenol condensate syntan as auxiliaries for the pretanning process, section 8, experimental design 1, were calculated with a Simplex with centroids method.

Section 9 will optimized the blend composition ratios of tara powder and the syntan. Design II is based on quadratic, orthogonal, centralized and rotatable model to analyze best fitted variable response surface.

This composition will be afterward applied under certain conditions, by means pH measurement previous and after pretanning operation, Section 10. Design III will be also based on quadratic orthogonal, centralized and rotatable model to analyze best fitted variable response.

Section 11 will consist in the manufacturing of an automobile-interior leather article from wet-white processed with tara, at pilot scale and according the results of the experiments. The leather will be treated later a regular recipe of retanning, fatliquoring, dyeing, mechanical operations and finished by coating, as described in section 4.3. The leather article will be tested for physical properties according the ISO standards of article specification.

6. Characterization of commercial tara powder

Four commercial samples were collected from four specialty leather chemicals suppliers. as common practice, there were no indication of the origin of the tara pods where they were harvested or processed. All of them, however, indicate that the commercial products were imported from Peru and they were not been chemically treated. Therefore, it must be assumed that the tara powder was processed as described in section 2.4.

Physical appearance of samples were similar, a fine yellowish-light brown powder.

Tests of characterization were carried out in the laboratory according to descriptions in section 4.6 with the following results:

Determination	Sample 1	Sample 2	Sample 3	Sample 4
pH analytical solution	3.4	3.5	3.3	3.5
Soluble solids (%)	74.5	67.9	59.8	59.70
Total solids (%)	89.0	92.2	93.6	92.90
Non tannins(%)	15.0	17.9	10.9	14.70
Tannins(%)	59.5	50.1	49.0	45.0
Insoluble(%)	14.5	24.2	33.8	33.20
Water(%)	11.0	7.8	6.4	7.10

Table 13: Characterization of 4 commercial samples of tara powder

6.1. Analysis summary of commercial tara commercial samples

The analysis method was based on creating individual charts for each determination or variable. It allowed confirming whether the data came from a process which is in a state of statistical control. The control charts were constructed under the assumption that the data came from a normal distribution.

6.1.1. Data variable: pH analytical solution

<u>Analysis Summary</u>: 4 values ranging from 3.3 to 3.5

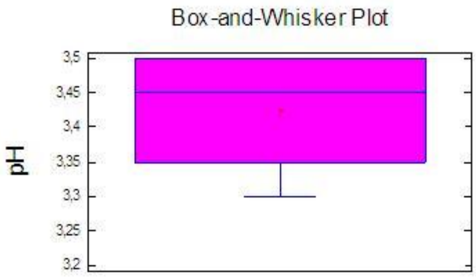
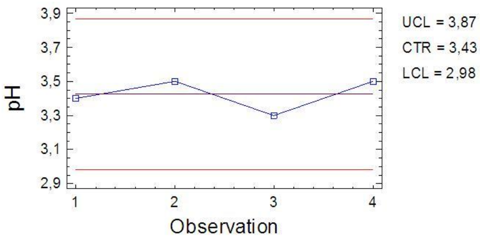
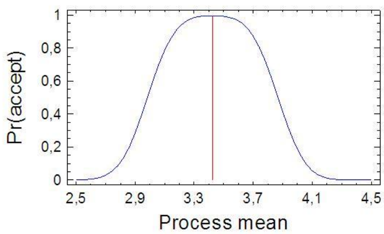


Table 14: Analysis summary for pH (commercial samples)

Average	= 3.42	Maximum	= 3.50
Variance	= 0.10	Range	= 0.20
Standard deviation	= 0.10	Stnd. skewness	= -0.70
Minimum	= 3.30	Stnd. kurtosis	= -0.53

Table 14 shows summary statistics for pH. It includes measures of central tendency, measures of variability, and measures of shape. Of particular interest here are the standardized skewness and standardized kurtosis, which can be used to determine whether the sample comes from a normal distribution. Values of these statistics outside the range of -2 to +2 indicate significant departures from normality, which would tend to invalidate any statistical test regarding the standard deviation. In this case, the standardized skewness value is within the range expected for data from a normal distribution. The standardized kurtosis value is within the range expected for data from a normal distribution.





Number of observations = 4	0 beyond limits
0 observations excluded	
X Chart	Estimates
UCL : +3,0 sigma = 3.87	Process mean = 3.42
Centerline = 3.42	Process sigma = 0.15
LCL : -3,0 sigma = 2.98	Mean MR(2) = 0.17

Table 15: Normal distribution for pH

The mean is equal to 3.42 and the standard deviation equal to 0.15. Since the probability of seeing 0 or more points beyond the limits just if the data comes from the assumed distribution, we cannot reject the hypothesis that the process is in a state of statistical control at the 90% confidence level.

6.1.2. Data variable: Tannins (%)

Analysis Summary: 4 values ranging from 45.0 to 59.5

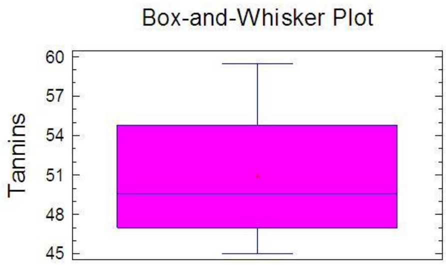
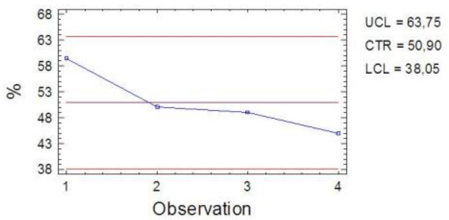
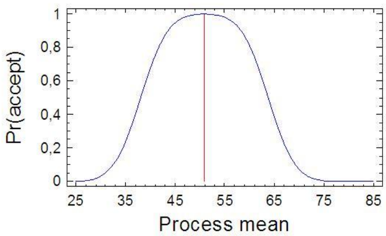


Table 16: Analysis summary for tannins (%)

Average	= 50.90	Maximum	= 59.50
Variance	= 37.67	Range	= 14.50
Standard deviation	= 6.14	Stnd. skewness	= 1.00
Minimum	= 45.00	Stnd. kurtosis	= 0.91

Table 16 shows summary statistics for Tannins. In this case, the standardized skewness value is within the range expected for data from a normal distribution. The standardized kurtosis value is within the range expected for data from a normal distribution.





Number of observations = 4
0 observations excluded
X Chart
UCL : +3.0 sigma = 63.75
Centerline = 50.90
LCL : -3.0 sigma = 38.05

0 beyond limits
Process mean = 50.9
Process sigma = 4.28
Mean MR(2) = 4.83

Table 17: Normal distribution for tannins (%)

The mean is equal to 50.90 and a standard deviation equal to 4.28. Since the probability of seeing 0 or more points beyond the limits if the data comes from the assumed distribution, we cannot reject the hypothesis that the process is in a state of statistical control at the 90% confidence level.

6.1.3. Data variable: Non-Tannins (%)

Analysis Summary: 4 values ranging from 4 values ranging from 10.9 to 17.9

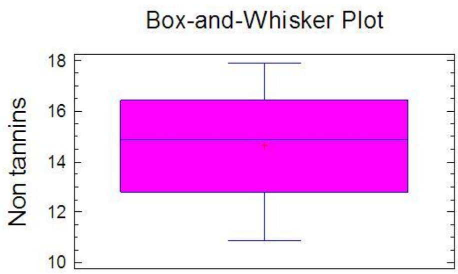
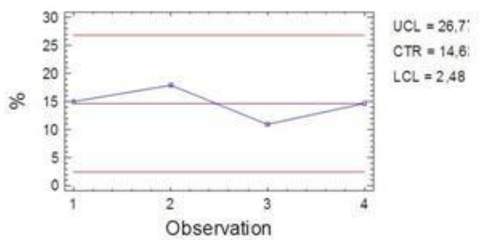
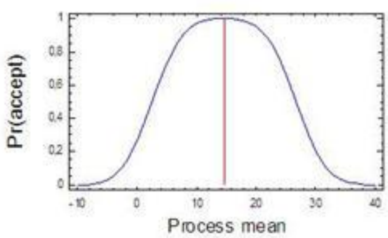


Table 18: Analysis summary for Non-tannins (%) (commercial samples)

Average	= 14.62	Maximum	= 17.90
Variance	= 8.25	Range	= 7.00
Standard deviation	= 2.87	Stnd. skewness	= -0.38
Minimum	= 10.90	Stnd. kurtosis	= 0.64

Table 18 shows summary statistics for Non tannins. In this case, the standardized skewness value is within the range expected for data from a normal distribution. The standardized kurtosis value is within the range expected for data from a normal distribution.





Number of observations = 4	LCL : -3,0 sigma = 2,48
0 observations excluded	0 beyond limits
X Chart	Process mean = 14.62
UCL : +3,0 sigma = 26.77	Process sigma = 4.05
Centerline = 14.62	Mean MR(2) = 4.57

Table 19: Normal distribution for Non-tannins (%)

The mean is equal to 14.62 and a standard deviation equal to 4.05. Since the probability of seeing 0 or more points beyond the limits if the data comes from the assumed distribution, we cannot reject the hypothesis that the process is in a state of statistical control at the 90% confidence level.

6.1.4. Data variable: Insolubles (%)

Analysis Summary: 4 values ranging from 4 values ranging from 14.5 to 33.8:

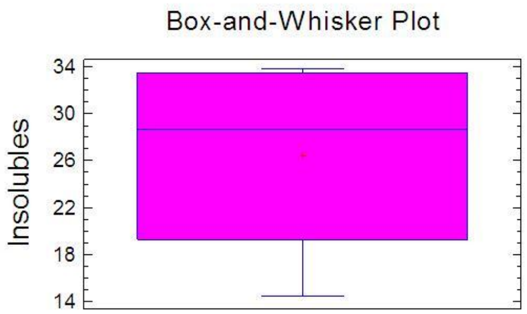
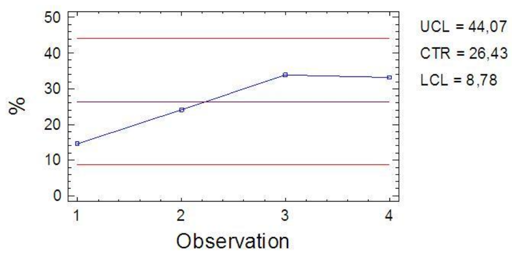
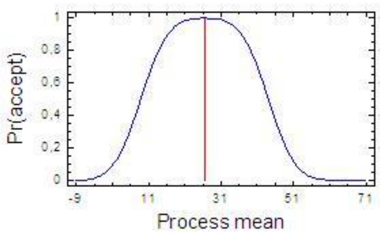


Table 20: Analysis symmary for Non-tannins (%) (commercial samples)

Average	= 26.42	Maximum	= 33.80
Variance	= 82.48	Range	= 19.30
Standard deviation	= 9.08	Stnd. skewness	= -0.72
Minimum	= 14.50	Stnd. kurtosis	= -0.45

Table 20 shows summary statistics for Insolubles. In this case, the standardized skewness value is within the range expected for data from a normal distribution. The standardized kurtosis value is within the range expected for data from a normal distribution.





Number of observations = 4	LCL : -3.0 sigma = 8.78
0 observations excluded	0 beyond limits
X Chart	Process mean = 26.42
UCL : +3,0 sigma = 44.07	Process sigma = 5.88
Centerline = 26.42	Mean MR(2) = 6.63

Table 21: Normal distribution for insolubles (%)

The mean is equal to 26.42 and a standard deviation equal to 5.88. Since the probability of seeing 0 or more points beyond the limits if the data comes from the assumed distribution, we cannot reject the hypothesis that the process is in a state of statistical control at the 90% confidence level.

6.2. Conclusion characterization of commercial tara powder

Considering the normal distribution, all the variable results of the chemical tests carried out to consider the quality consistence of the four commercial tara powder analyzed, do not show significant statistic differences. Therefore, Table 22 indicates reference values for tara characterization that will be used for the next experimental parts of this research. The higher value corresponds to the mean value plus standard deviation and the lower the mean value minus the standard deviation:

Determination	Values	Higher	Lower
pH analytical	3.42	3.57	3.27
Soluble solids (%)	65.53		
Total solids (%)	91.95		
Non tannins(%)	14.63	18.67	10.58
Tannins(%)	50.90	55.18	46.62
Insoluble(%)	26.43	32.31	20.54
Water(%)	8.05		

Table 22: Reference values of tara characterization

To carry out the trials in the following experimental part, any of the samples can be validated as deviations on results remain under a normal distribution.

7. Characterization of tannins from Bolivian tara fruits

7.1. Description of samples

Samples of tara fruit were collected from five different Departments in Bolivia, La Paz, Santa Cruz, Potosí, Cochabamba and Chiquisata in August 2009.

The samples were prepared at the origin with a mixture of fruits coming from, at least, 5 different trees. Each sample was weighted to 1.1 kg, packed in plastic sacks and properly labeled.

Photo 2: Samples of tara fruit collected in Bolivia

The tara fruits were constituted with a brownish-orange pod and, internally, dark brown seeds. Pods sized between 8 to 10 cm long and 2 cm wide. Each pod contained between 4 and 7 round seeds of 0.6-0.7 mm diameter.

Samples were very dry and there were no differences on humidity content after drying the samples at 30ºC during 4 o 7 days:

Origin	**Humidity % (drying 4 days)**	**Humidity % (drying 7 days)**
La Paz	1.4	1.4
Santa Cruz	3.2	3.2
Potosí	1.8	1.9
Cochabamba	1.2	1.2
Chiquisata	2.6	2.6

Table 23: Humidity content of tara fruits

7.2. Preparation of the samples:

Samples were manually prepared by splitting the pods and the seeds.

Once the seed were separated, the pods were grounded and sieved to 250 µm. The fibers of the cellulosic material remained in the thicker fraction, and the powder was sieved to 150 µm. In this case, the thicker fraction was milled again until the particle size was homogenized.

Photo 3: Components of the tara fruit samples from Bolivia (seeds, fibers and powder).

7.3. Composition of the fruits:

The fractions obtained during the preparation of the samples were weighted with an analytical balance:

Origin	% Seed	% Fiber	% Powder
La Paz	44.3	9.0	46.6
Santa Cruz	47.5	6.7	45.8
Potosí	35.4	8.1	56.5
Cochabamba	46.7	6.9	46.4
Chiquisata	49.5	9.0	41.5

Table 24: Composition of the fruits

The sample coming from Potosí was the poorest in seed content, but richest in powder. Chiquisata’s sample was the richest in seed and fiber, but the poorest in powder.

7.4. Characterization of the tara powder

Tannins were determined by filter method, indirect gravimetric analysis with fixing of the absorbent compounds in a low-chromed hide powder[45]. Results were compared with the values of commercial tara obtained in Section 6.

	La Paz	Santa Cruz	Potosi	Cochabamba	Chiquisata	Reference
Non tannin	11.30	17.60	11.70	13.40	17.20	14.63
Tannin	60.30	50.90	59.40	55.70	50.70	50.90
Soluble solids	71.60	68.50	71.10	69.10	67.90	65.53
Insoluble	21.00	22.00	20.10	22.90	23.70	26.43
Total solids	92.60	90.50	91.20	92.00	91.60	91.95
Water	7.40	9.50	8.80	8.00	8.40	8.05

Table 25: Chemical characterization of tara powder from Bolivian samples

By comparing the values of table 25 with the table 22 where the higher and lower values were determined by the standard deviations, there is a clear consistency. Only two values are above the values of the normal distribution with higher tannin content, La Paz and Potosí.

Therefore, the tara fruit collected in Bolivia during this work has a good quality to be valorized in the market of the tara powder and can be considered as a consistence sustainable source of tannins for the leather industry. To point out that the sample coming from Potosí was the richest in powder and tannin concentration with the lower content of insolubles.

Theoretically, we calculated soluble and insoluble solids in dry conditions with the aim to obtain more quality data.

	La Paz	Santa Cruz	Potosi	Cochabamba	Chiquisata	Reference
Soluble solids	77.32	75.69	77.96	75.11	74.13	71.26
Insoluble	22.68	24.31	22.04	24.89	25.87	28.74

Table 26: soluble / insoluble matter content in dry conditions

45 Hide powder with certificate for analysis of substances released by hide powder in contact with distilled water (blank value) was purchased from FILK, Meissner Ring 1-5, 09599 Freiberg, Germany. www.filkfreiberg.de

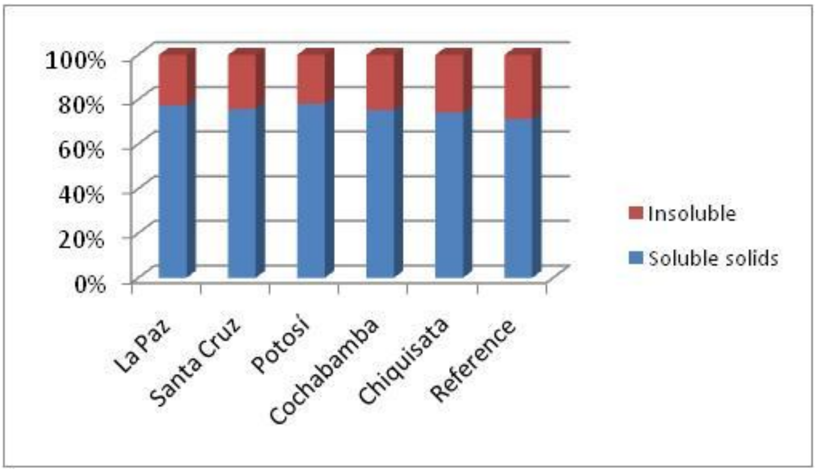


Figure 19: Bar chart of soluble and insoluble matter of tara powder

The highest insoluble matter in the commercial reference means that production factories do no separate properly the cellulosic fibers during the milling process. This is a potential action to improve the quality of the tara powder. A certain contamination from the mills to the product is also plausible.

The relationship between the tannin and the non-tannin content in the tara powder could be used also as a reference of the quality of the powder and it can be correlated to the degree of hydrolysis.

This relation is calculated without the effects of humidity and insoluble matter content in the tara powder:

	La Paz	Santa Cruz	Potosi	Cochabamba	Chiquisata	Reference
Non tannin	15.78	25.69	16.46	19.39	26.33	22.32
Tannin	84.22	74.31	83.54	80.61	74.67	77.68

Table 27: Tannin / non tannin content of tara powder

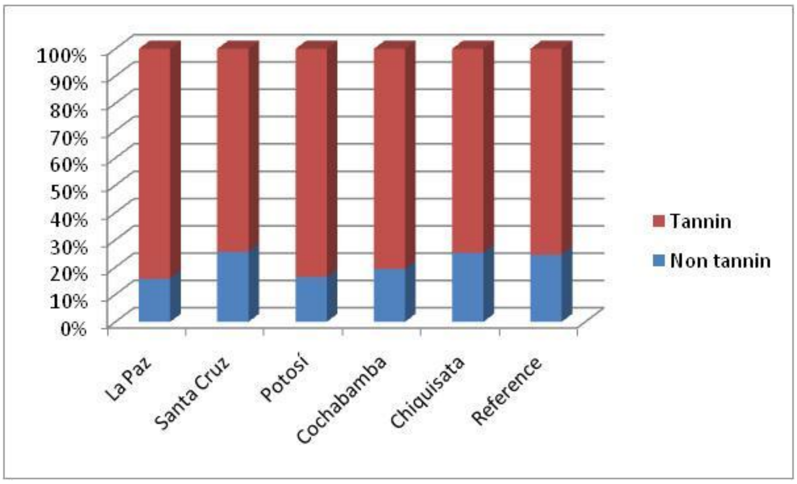


Figure 20: Tannin /non tannin content of tara powder

The tanning content of the commercial tara powder reference is similar to the samples of the tara powder of trees from Santa Cruz, Cochabamba and Chiquisata. La Paz contains the higher amount of tannin followed by the sample from Potosí.

The highest content of non tannin could be compared with the content of free gallic acid as a result of a certain hydrolysis. It was described in Section 4.6, Figure 14, the chemist composition of the tara tannin by 53% of gallic acid and 10% sugar.

As tara tannin is hydrolysable, the content of free acid gallic can be determined and quantified by high-performance liquid chromatography (HPLC) chromatographic technique.

To optimize this method, several tests were carried out with different elusion gradients.

The following conditions were considered to obtain the best results:

- Instrument : Agilent 1200 chromatograph
- Column : Zorbax eclipse XBC C-18 (Agilent)
- Gradient: A=80% H_2O / HCOOH (999 / 1 v/v) + B=20% Methanol / HCOOH (999 / 1 v/v), in 15 min 100% B
- Injection volume : 10 µL
- Flux : 1 mL/min
- Temperature: 25ºC

Calibration curve of gallic acid (Panreac) is calculated to proceed with analytic determination of tara powder samples.

For the calibration curve, 5 watery analytical solutions are acidified with 1% formic acid to the following concentrations: 0.5, 1, 2.5, 5, and 10 mg/L. Samples are analyzed by HPLC and calibration was calculated through the area graphic of the obtained pick of gallic acid against the concentration.

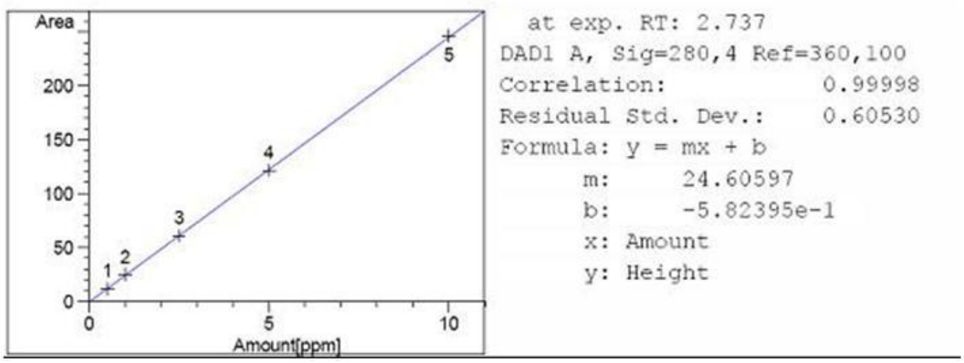


Figure 21: Calibration curve of Gallic acid for HPLC

To quantify the gallic acid content for each sample, a 2% of tara solution was prepared and the analytical solution was diluted 1/20. The analysis was carried out according the described conditions:

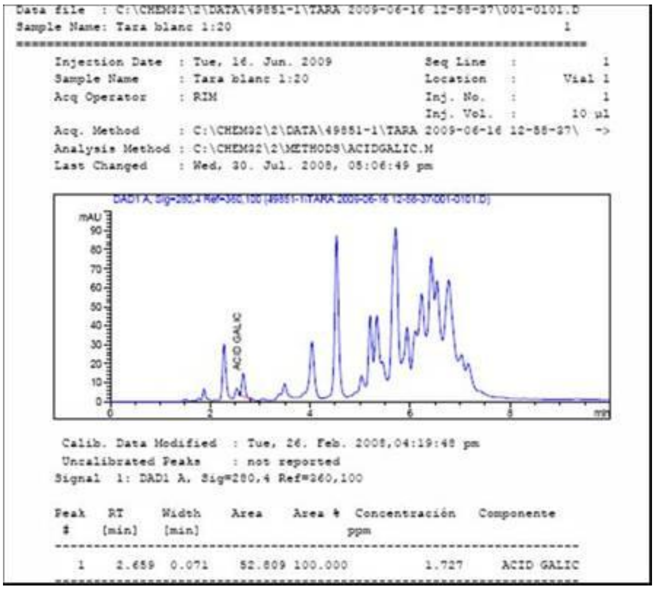


Figure 22: Determination of free Gallic acid of a commercial tara powder by HPLC

Figure 23 compares the HPLC chromatographic curves for the tara powder obtained from the samples of tara fruits collected in different departments in Bolivia.

The resulting values of free gallic acid content are shown in table 28:

Sample	Gallic acid content (mg/kg)
La Paz	759
Santa Cruz	2704
Potosí	738
Cochabamba	684
Chuquisata	790
Commercial reference	1727

Table 28: Content of Gallic acid in tara powder samples

We can analyze the results of gallic acid coming from the HPLC and the non-tannin content:

Regression Analysis – Linear model: Y = a + b*X

Dependent variable: Gallic acid

Independent variable: Non Tannin

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	1.19077E6	1	1.19077E6	1.89	0.2632
Residual	1.89348E6	3	631161.0		

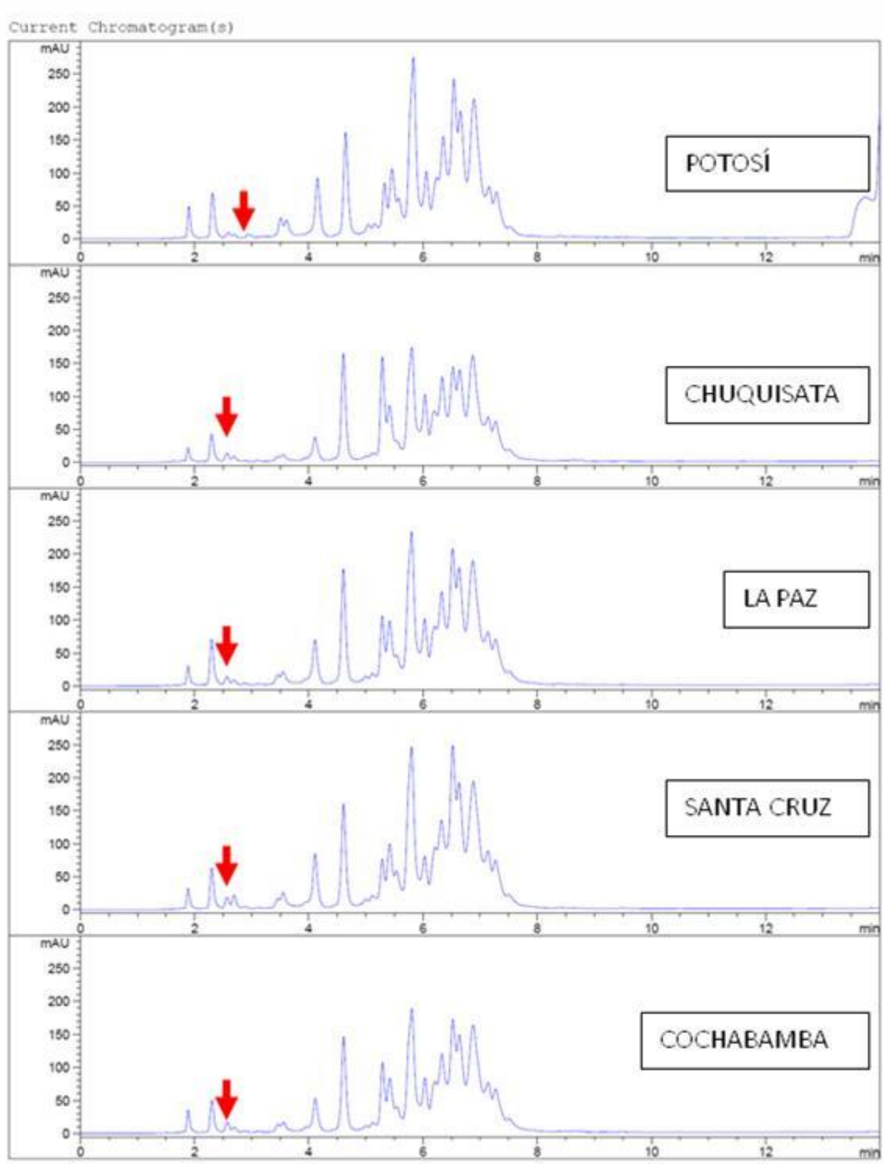


Figure 23: Chromatography of tara powder from Bolivian fruits. Red arrow indicates the content of gallic acid.

The output shows the results of fitting a linear model to describe the relationship between Gallic acid and Non Tannin. The equation of the fitted model is

Gallic acid = -1225.03 + 114.97*Non Tannin

Since the P-value in the ANOVA table is greater or equal to 0.10, there is not a statistically significant relationship between Gallic acid and Non Tannin at the 90% confidence level:

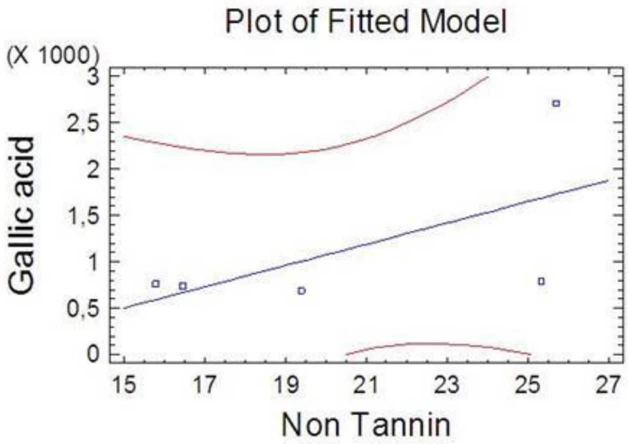


Figure 24: Plot of fitted model for gallic acid and Non Tannin

Therefore, the statistic values of the current analysis are not able to precise a correlation between the non-tannin content and the hydrolyzed gallic acid and other molecules, such sugars and primary condensation, as the null hypothesis cannot be rejected. The content of gallic acid cannot be considered as analytical method for test tara powder quality.

However, as described in 2.4, gallic acid has a high demand in other markets as a worth polyphenol. Despite “other applications” are not in the scope of this work, the degree of hydrolysis with the temperature will validate that tara tannin is a hydrolysable tannin.

A 2% solution of a commercial tara powder was exposed to different temperatures (30º, 100 and 136ºC) during 1 hour and is analyzed by HPLC according the method described above.

Hydrolysis conditions	Free Gallic Acid (mg/kg)
Hydrolysis at 30ºC during 1 hour	1725
Hydrolysis at 100ºC during 1 hour	2743
Hydrolysis at 136ºC during 1 hour	3439

Table 29: Results of hydrolysis test of commercial tara powder

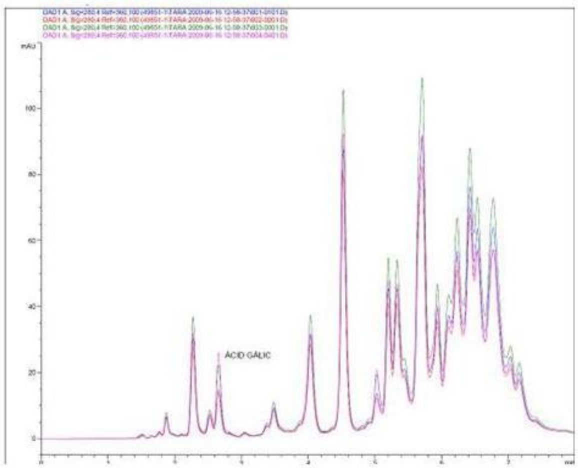


Figure 25: Chromatogram of hydrolyzed tara powder

Figure 25 remarks the pick of Gallic Acid in the chromatograph and, by visual comparing with Figure 22, the difference is quite evident:

Despite the simplicity of this experiment it gives an idea that there exists a relation between the temperature of hydrolysis and the content of free gallic acid.

Data can be statistically analyzed considering that the content of free gallic acid (variable) is the result of the effect of every level considered in the temperature and a residual effect. The mathematical model is:

$$x_{ij} = G_i + z_{ij} \qquad G_i = A + B_j$$

$$i = 1, 2, \dots r \text{ (levels)} \rightarrow 30, 100, 136$$

$j = 1, 2, \dots c$ (replicates) $\rightarrow 0$ (there is only on test for the commercial tara powder)

A = Constant

B_j is a parameter depending of the level i and represents a deviation of G_i with regards to the reference constant A

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	1.47E6	1	1.47E6	174.2	0.0481
Residual	8460.12	1	8460.12		

Multiple Regression Analysis

Dependent variable: Gallic Acid

Parameter	Estimate	Error	Statistic	P. Value
CONSTANT	1224.10	119.44	10.25	0.0619
Temperature	15.93	1.21	13.20	0.0481

The output shows the results of fitting a multiple linear regression model to describe the relationship between Gallic Acid and temperature. The equation of the fitted model is

Gallic Acid = 1224.1 + 15.9*T

Since the P-value in the ANOVA table is less than 0.05, there is a statistically significant relationship between the variables at the 95% confidence level

The R-Squared statistic indicates that the model as fitted explains 99.43% of the variability in Gallic Acid. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 98.86%. The standard error of the estimate shows the standard deviation of the residuals to be 91.98. The mean absolute error (MAE) of 49.23 is the average value of the residuals.

In determining whether the model can be simplified, notice that the highest P-value on the independent variables is 0.0481, belonging to temperature. Since the P-value is less than 0.05, that term is statistically significant at the 95% confidence level.

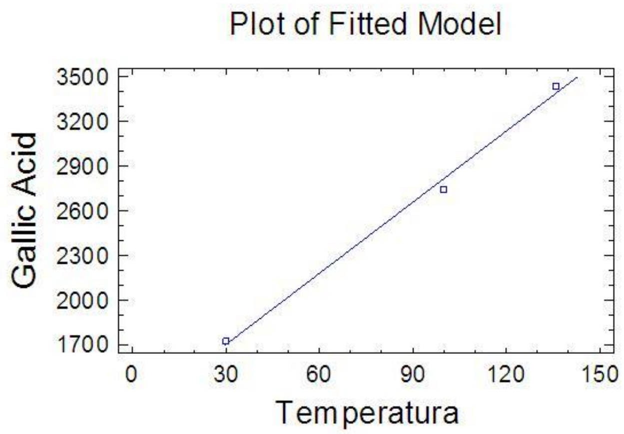


Figure 26: Plot of fitted model for free Gallic acid and temperature

8. Pretanning process. Design I: blending with syntans

In order to propose an innovative wet-white solution for a sustainable pretanning process using tara tannins, the work will be split in three experimental designs:

The first experimental design will focus on finding the best combination of tara with syntans, by means, blending the tara powder with a condensation phenol syntan or a naphthalene sulphonic syntan, or the three of them.

For this selection, the shrinkage temperature, the measurement of tensile strength and percentage elongation (EN ISO 3376 – IUP6[46,47]) and the Measurement of tear load (EN ISO 3377-2, IUP8[48]) were evaluated[49].

As discussed in section 2.4, tara is well appreciated in the leather industry as vegetable tanning agent because its light fastness compared with other vegetable tannins. Therefore, influences of the components of the different mixtures on this feature will be also assesed.

According to the results of the first experimental design, and evaluating the same parameters, further tests are carried out to obtain the best recipe for a pre-tanning wet-white.

8.1. Products, materials and equipment. Design I

To carry out the experimental tests, the following commercial products were selected:

Synthetic tanning of phenol condensation:

Fine powder, white, soluble in water. 95% of tanning content, pH 4 (+/-0.2) solution 1:10

46 J. FONT. Análisis y ensayos en la industria de curtidos. Escola Universitària d'Enginyeria Tècnica d'Igualada. Escola Superior d'Adoberia d'Igualada. ISBN: 84-931837-5-X

47 Normas IUP. Ensayos Físicos de Curtidos. Asociación Química Española de la Industria del Cuero. AQEIC. Octubre 2001. Pag. 20

48 Normas IUP. Ensayos Físicos de Curtidos. Asociación Química Española de la Industria del Cuero. AQEIC. Octubre 2001. Pag. 29.

49 The physical tests on leather determine the capacity of finished leather to resist loads and actions that will be submitted by consumers according the manufactured leather goods. Such tests measure the properties that depend on the whole leather structure, considering all its thickness. The results will depend on factors like the parts of the hides or skins where samples are taken and its dimensions, the technical characteristics of the apparatus, the atmospheric conditions and the procedures. Therefore, the standard ISO methods have to be strictly followed to assure the maximum repetitiveness and reproducibility.

Synthetic tanning of naphthalene sulphonic:

Yellowish liquid. Miscible in water. 40 % of tannin content. pH 3.3 – 3.7 (solution 1:10)

Tara Powder: Origen: Peru

Quality Control	pH	3.5	Insolubles	32 %
	Tannin content	47 %	Soluble solids	60 %
	Non tannin content	13 %	Total solids	92 %
	Water	8 %	Iron	388.9 mg/kg (ppm) by atomic absorbance

Trials were carried out using the following drums:

Deliming, bating and pickling:

Simplex DF drum, stainless steel, 1000 x 500 mm (DxL). Annex 10

Pretanning process:

2 – Fave drums, stainless steel, 500 x 200 mm (DxL). Annex 11

Comparative tests were carried out on Russian bovine hides, green split. They were divided in 8 pieces and marked. The eight pieces were weight and their thicknesses were calibrated.

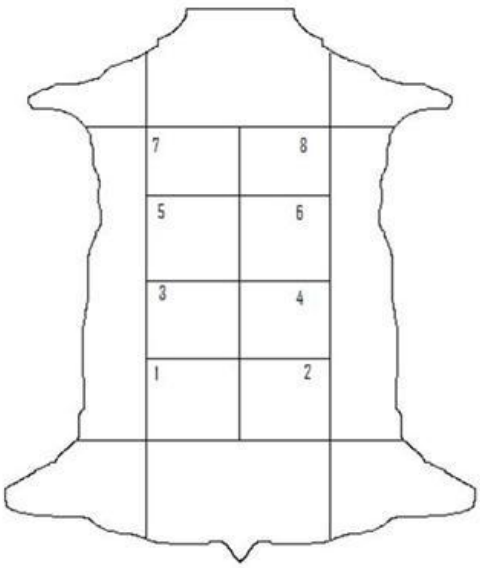


Figure 27: Sampling hides for testing

Deliming, bating and pickling treatment were carried out according the recipe in table 30:

Operation	ºC	%	Product	Time	Comments
Washing	30	150 0.2	Water Lactic acid	 20 min.	 Drain
Deliming Bating	35	100 2.5 0.3 0.8 1	Water Ammonium sulfate Sodium bisulfite Lactic acid Enzyme	 90 min 60 min	6 rpm pH = 8.1 Cut through Check bating pH 7.9 Drain
Washing I	20	200	Water	15 min	Drain
Washing II	20	200	Water	15 min	Drain
Pickling	20	50 10 0.5 1.0 0.1	Water Sodium chloride Formic acid (1:10) Sulfuric acid (1:10) Preservative	 15 min 20 min 120 min Run overnight 15 min	8 rpm pH 3.5 Cut through Drain Horse up

Table 30: Deliming, bating and pickling

8.2. Process and tests. Design I.

The experimental design to evaluate ingredient blends, for the first step, is the Simplex method. It is applied when the sum of the percentages of the two or more factors or ingredients of a blend must be 100%. Therefore, the levels of the factors are not independent and the variation of them can determine the properties of the final product.

If x_1, x_2, …, x_n are the variables representing the percentages of k ingredients or components of a blend, the values of x_i are restricted as follows:

$$0 \leq x_i \leq 1 \qquad I = 1, 2, ..., k$$

and the sum of the percentages of the k ingredients is 1:

$$\Sigma_{(i=1\ldots k)}\, x_i = x_1 + x_2 + \ldots + x_k = 1$$

If the percentage of a component is $x_i = 1$, than there are no other components in the mixture.

To design a blend with three components, the coordinated values are defined as:

$$x_1 + x_2 + x_3 = 1$$

The geometric description of the space of the factors for k components is a Simplex of (k-1) dimensions. Therefore, for three component blend, it will be a triangle which vertex represents one single component and the sides are the designed coordinates for mixtures of two components and a $x_i=0$. The coordinates inside the triangle represent the mixtures of two components where $x_1 > 0$, $x_2 < 0$ and $x_3 < 0$. Any proportional combination of components for the mixture experiment must be placed either in the frontier or inside the triangle of coordinates. The axes of the variables x_i in the Simplex system of three variables are drawn in the figure 25. The axis of the ingredient i is the straight line that goes from the point base $x_i=0$ and $x_j=1/(k-1)$ for the ingredients, $j\neq i$ in the vertex, where $x_i=1$ and $x_j=0$ for $j\neq i$.

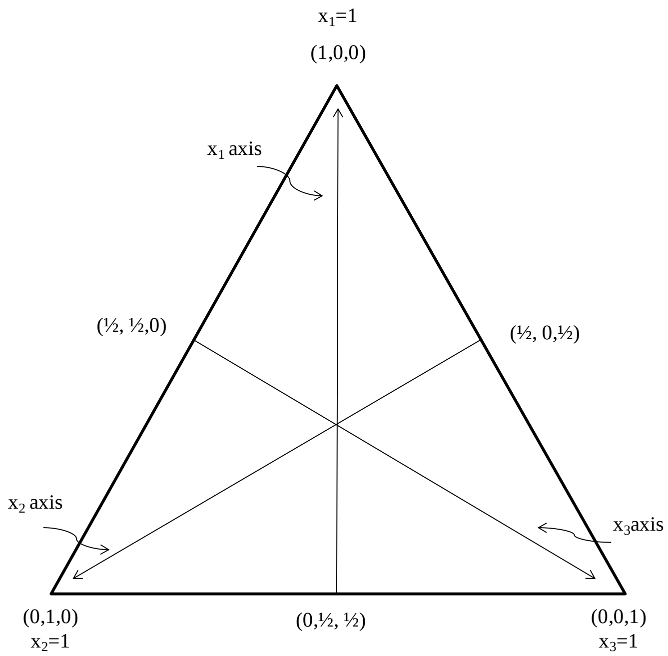


Figure 28: Coordinate axis for a mixture of three ingredients

As an example, for the mixture of three ingredients, the axis x_1 goes from the base of coordinates (0, ½, ½) to the vertex (1, 0, 0):

The Simplex design with centroids is based in the Simplex system coordinates when mixtures containing 1, 2, 3… or k ingredients with identical proportions. This means that there are k mixtures for each ingredient: all possible mixtures for two components is ½, for three 1/3 for k, 1/k. The trials are designed according to Simplex with centroids coordinates, and the percentages are adjusted to the tannin content of each ingredient according table 31:

Test	**X_1**	**X_2**	**X_3**	Tara	Phenol syntan	Naphtalen sulphonic syntan
1	1	0	0	12	0	0
2	0	1	0	0	6	0
3	0	0	1	0	0	14
4	1/2	1/2	0	6	3	0
5	1/2	0	1/2	6	0	7
6	0	1/2	1/2	0	3	7
7	1/3	1/3	1/3	4	2	4.7

Table 31: Simplex with centroids design

The pretanning trials are carried out according to the following general process:

Operation	**ºC**	**%**	**Product**	**Time**	**Comments**
Pre-tanning	20	50	Water		
		4	Sodium chloride	15 min	ºBè: 7
					pH 3.5
		1/2	Tanning agent		
		2	Sulphitated fatliquor	120 min	*Note 1*
		1/2	Tanning agent	Overnight	*Note 2*
		0.5	Formic acid	90 min	pH 3.2
					Drain
Horse up. Samming. Pasting 12 hours at 30ºC. Conditioning and stake.					

Notes:

Test 1:Tara powder

- *Note 1:* pH=4 (paper indicator). Through tanning ½ in the flesh side with ferric chloride. Insolubles are quite visible.
- *Note 2*: pH=4 (paper indicator). Checked with ferric chloride, a thin inside layer remains untanned. The bath is exhausted and insolubles are visible. Grain is shrunk, grey color. Leather is full and round. Thickness 3.5/3.7 mm (2 mm before pretanning).

Test 2: Phenol syntan

- *Note 1:* pH=3.8 (paper indicator). Through tanned (checked with brome-cresol green indicator). Leather is clean and white.
- *Note 2:* pH=4. Through tanned (checked with brome-cresol green indicator). Bath is exhausted. Smooth grain, white and clean.

Test 3: Naphthalene sulphonic syntan

- *Note 1:* pH=3.8. Through tanned (checked with brome-cresol green indicator). Leather is clean in both sides, flesh and grain.
- *Note 2:* pH=4. Through tanned (checked with brome-cresol green indicator). Bath is exhausted. Smooth grain. Leather is clean in both sides, flesh and grain.

Test 4: Tara + phenolic

- *Note 1:* pH=3.7. Through tanned (checked with brome-cresol green indicator), but ferric chloride indicates 1/3 tara penetration. Insolubles are visible.
- *Note 2:* pH4. Through tanned (checked with brome-cresol green indicator and ferric chloride). Insolubles are visible.

Test 5: Tara + naphthalene sulphonic

- *Note 1:* pH = 3.5 (paper indicator). 85%through tanned with syntan and 50 with vegetable tannin. Insolubles are visible.
- *Note 2:* pH=4 (paper indicator). An untanned thin layer is visible and checked with ferric chloride. Some insolubles are still visible.

Test 6: Phenolic + naphthalene sulphonic

- *Note 1:* pH=4. 2/3 through tanned, mainly in flesh side. Bath exhausted.
- *Note 2:* pH=4. Through tanned. Bath exhausted. Smooth white grain, less compact and hardest that test 1. Thickness 3 mm.

Test 7: Tara powder + phenolic + naphthalene sulphonic

- *Note 1:* pH=3.7. 1/3 through tanned (checked with ferric chloride). Some insolubles are visible.
- *Note 2:* pH=3.8. Through tanned. Some insolubles are visible.

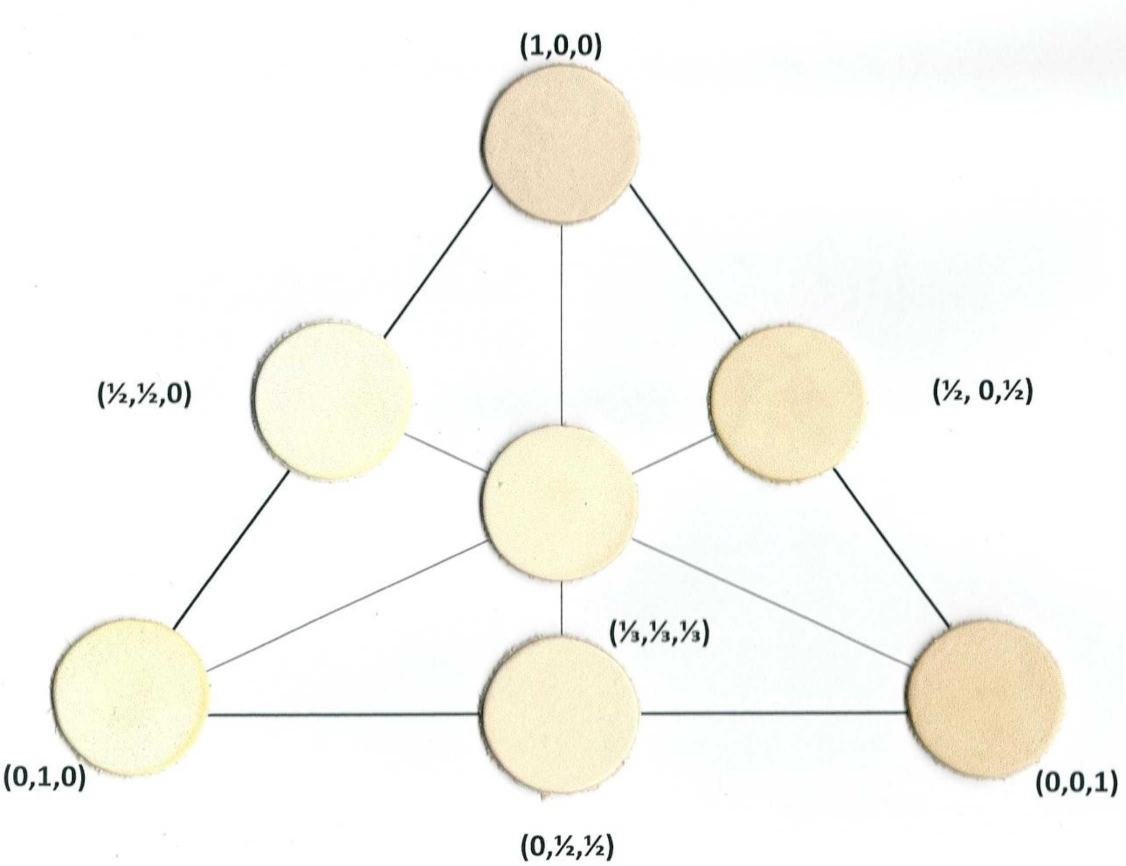


Photo 4: Design of a pretanning process with tara. Experimental Design I

Photo 5. Light fastness tests. Experimental Design I.

8.3. Table of tests results and discussions. Design I.

#	Description	TCºC	Tensile Strength (N) *EN ISO 3376 – IUP6*	% Elongation *EN ISO 3376 – IUP6*	Tear load (N/mm) *EN ISO 3377-2, IUP8*	Light fastness [50]
1	Tara powder	61.5	551.8	51.6	61.4	4
2	Phenol syntan	68.5	360.0	53.8	57.2	1
3	Naphthalene sulphonic	60.5	461.7	47.7	68.6	2
4	Tara + phenol	63.5	427.3	46.7	58.5	2
5	Tara + naphthalene	68.0	463.7	54.0	53.2	3
6	Phenol + naphthalene	65.5	495.2	48.7	89.0	2
7	Tara+phenol+naphthalene	67.5	477.7	51.8	56.3	2

Table 32: Table o test results. Simplex design with centroids. Experimental design I

With the created experimental design, we have defined 5 statistics variables (TC, Tensile, Elongation, Tear and Light) for three factors or components (tara, phenol syntan and naphthalene sulphonic), in a simplex-centroid model, special cubic.

Results are analyzed for each variable in order to obtain the optimal response and the equation of the fitted model (Statgraphics Plus software).

<u>Shrinking temperature </u>(S_T):

Estimated Full Model Effects for S_T:

Source	P-Value
Mean	-
Linear	0.0909
Quadratic	0.0004
Special Cubic	-

This table shows the results of fitting different models to the data in S_T. The mean model consists of only a constant. The linear model consists of first-order terms for each of the components. The quadratic model adds crossproducts between pairs of components. The special cubic model adds terms involving products of three components. Each model is shown with a P-value which tests whether that model is statistically significant when compared to the mean square for the term below. It is selected the most complicated model with a P-value less than 0.05, assuming operating at the 95% confidence level.

50 For the mathematic model, de values of light fastness have been adjusted and the standard criteria have not been considered. The aim is to have a comparison between the trials carried out and not the value of light fastness.

According to this criterion, it appears that the quadratic model is adequate for the data. The currently selected model is the quadratic model.

Analysis of variance for S_T:

Source	Sume of squares	Df	Mean Square	F-Ratio	p-Value
Quadratic Model	104.46	5	20.89	109.04	0.0002
Total Error	0.77	4	0.19		
Total (corr.	105.22	9			

R-squared = 99.27 percent
R-squared (adjusted for d.f.) = 98.36 percent
Standard Error of Est. = 0.44
Mean absolute error = 0.18392
Durbin-Watson statistic = 2.31
Lag 1 residual autocorrelation = -0.16

Since the P-value for this model is less than 0.01, there is a statistically significant relationship between S_T and the components at the 99% confidence level and there is an indication of possible serial correlation.

Quadratic Model Fitting Results for S_T:

Parameter	Estimate	P-Value
A: Tara	61.5	
B: Phenol syntan	68.5	
C: Naphthalene sulphonic acid	60.5	
AB	-4.6	0.0652
AC	29.38	0.0001
BC	5.38	0.0425

The equation of the fitted model, excluding cross-product AB is:

TC = 61.5*Tara + 68.5*Phenol syntan + 60.5*Naphth sulfonic + 29.38*Tara*Naphth sulfonic + 5.38*Phenol syntan*Naphth sulfonic

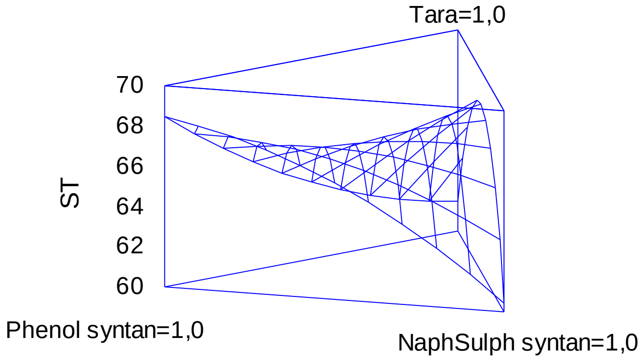


Figure 29: Estimated response surface for shrinking temperature. Experimental design I

Optimize Response:
Goal: maximize S_T
Optimum value = 68.5ºC

Factor	Low	High	Optimum
Tara	0	1	0
Phenol syntan	0	1	1
Naphthalene sulphonic acid	0	1	0

It is confirmed that phenol condensation tannins increase the shrinking temperatures more than plan polyphenol gallotannins (Table 11, section 4.2). However, observing the response surface, similar range of shrinking temperature is obtained with the combination of tara-naphthalene sulphonic syntan. The synergy can be explained because, despite the low influence on shrinking temperature of the naphthalene sulphonic syntan, it allows to penetrate tara in the inner layer of the leather, as is appreciate the SEM in photos 6, 7, 8, and 9.

Tensile strength

Estimated Full Model Effects for Tensile:

Source	P-Value
Mean	-
Linear	0.0048
Quadratic	0.0006
Special Cubic	-

Under the criteria of the estimated Full Model Effects for tensile, it appears that the quadratic Model Fitting Results is adequate for the data.

Analysis of variance for tensile:

Source	Sume of squares	Df	Mean Square	F-Ratio	p-Value
Quadratic Model	39,136.9	5	7,827.39	208.45	0.0001
Total Error	150.20	4	37.55		
Total (corr.	39,287.1				

R-squared = 99.67 percent
R-squared (adjusted for d.f.) = 99.14 percent
Standard Error of Est. = 6.13
Mean absolute error = 2.57
Durbin-Watson statistic = 2.31
Lag 1 residual autocorrelation = -0.16

Since the P-value for this model is less than 0.01, there is a statistically significant relationship between Tensile and the components at the 99% confidence level and there is an indication of possible serial correlation.

Quadratic Model Fitting Results for Tensile:

Parameter	Estimate	P-Value
A: Tara	551.26	
B: Phenol syntan	359.46	
C: Naphthalene sulphonic acid	461.16	
AB	-95.09	0.0207
AC	-152.89	0.0040
BC	344.71	0.0002

The equation of the fitted model is:

Tensile = 551.26*Tara + 359.46*Phenol syntan + 461.16*Naphth sulfonic – 95.09*Tara*Phenol syntan – 152.89*Tara*Naphth sulfonic + 344.71*Phenol syntan*Naphth sulfonic

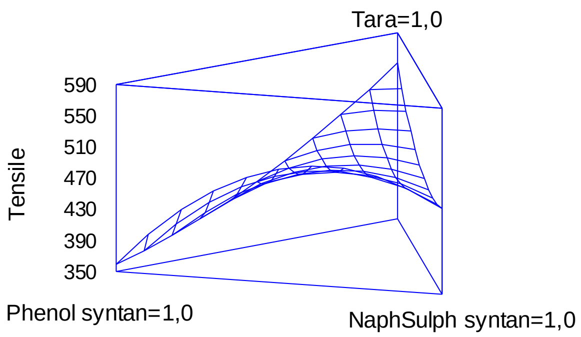


Figure 30: Estimated response surface for tensile strength. Experimental design I

Optimize Response:
Goal: maximize Tensile
Optimum value = 551.26 N

Factor	Low	High	Optimum
Tara	0	1	1
Phenol syntan	0	1	0
Naphthalene sulphonic acid	0	1	0

Pretanning with tara optimizes the values of tensile strength, while the phenolic syntan do not help to increase this resistance. Combinations of tara and naphthalene sulphonic syntans, as observed in the estimated response surface, have a range of the highest values. This is confirmed observing SEM in photos 6, 7, 8 and 9 as fibers keep compacted all through the leather than the other combinations.

Tensile strength elongation:

Estimated Full Model Effects for Elongation:

Source	P-Value
Mean	-
Linear	0.3558
Quadratic	0.0086
Special Cubic	-

Under the criteria of the estimated Full Model Effects for elongation, it appears that the quadratic Model Fitting Results is adequate for the data.

Analysis of variance for elongation:

Source	Sume of squares	Df	Mean Square	F-Ratio	p-Value
Quadratic Model	67.32	5	13.46	14.92	0.0108
Total Error	3.61	4	0.90		
Total (corr.	70.62	3			

R-squared = 94.91 percent
R-squared (adjusted for d.f.) = 88.55 percent
Standard Error of Est. = 0.95
Mean absolute error = 0.40
Durbin-Watson statistic = 2.31
Lag 1 residual autocorrelation = -0.16

Since the P-value for this model is near to 0.01, there is a statistically significant relationship between Tensile and the components at the 95% confidence level and there is an indication of possible serial correlation.

Quadratic Model Fitting Results for Elongation:

Parameter	Estimate	P-Value
A: Tara	50.52	
B: Phenol syntan	53.72	
C: Naphthalene sulphonic acid	47.62	
AB	-21.01	0.0062
AC	20.39	0.0068
BC	-5.51	0.2604

The equation of the fitted model is after excluding cross-product BC:

Elongation = 50.52*Tara + 53.72*Phenol syntan + 47.626*Naphth sulfonic – 21.01*Tara*Phenol syntan + 20.39*Tara*Naphth sulfonic

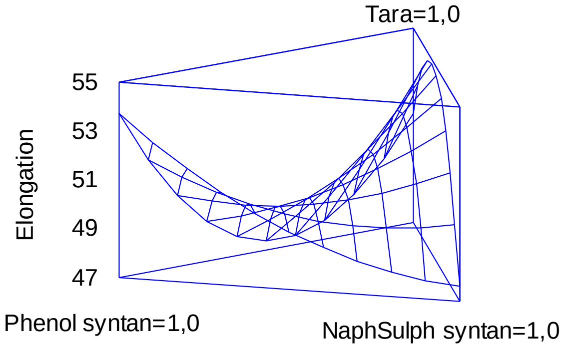


Figure 31: Estimated response surface for tensile elongation. Experimental design I

Optimize Response:
Goal: maximize Elongation
Optimum value = 54.85 %

Factor	Low	High	Optimum
Tara	0	1	0.60
Phenol syntan	0	1	0
Naphthalene sulphonic acid	0	1	0.40

Optimal is the combination of tara and naphthalene sulphonic tannin and similar elongation is obtained with phenol tannin.

<u>Tear load:</u>

Estimated Full Model Effects for Tear:

Source	P-Value
Mean	-
Linear	0.4390
Quadratic	0.0252
Special Cubic	-

Under the criteria of the estimated Full Model Effects for tear, it appears that the quadratic Model Fitting Results is adequate for the data.

Analysis of variance for tear:

Source	Sume of squares	Df	Mean Square	F-Ratio	p-Value
Quadratic Model	881.23	5	176.25	7.76	0.0347
Total Error	90.87	4	22.72		
Total (corr.	972.10	9			

R-squared = 90.65 percent
R-squared (adjusted for d.f.) = 79 percent
Standard Error of Est. = 4.77
Mean absolute error = 2.00
Durbin-Watson statistic = 2.31
Lag 1 residual autocorrelation = -0.16

Since the P-value for this model is less than 0.05, there is a statistically significant relationship between Tear and the components at the 95% confidence level and there is an indication of possible serial correlation.

Quadratic Model Fitting Results for tear:

Parameter	Estimate	P-Value
A: Tara	61.82	
B: Phenol syntan	57.61	
C: Naphthalene sulphonic acid	69.02	
AB	-18.22	0.4127
AC	-62.22	0.0356
BC	89.38	0.0110

The equation of the fitted model is after excluding cross-product AB:

Tear = 61.82*Tara + 57.61*Phenol syntan + 69.02*Naphth sulfonic – 62.22*Tara*Naphth sulfonic + 89.38 Phenol syntan*Naphth sulfonic

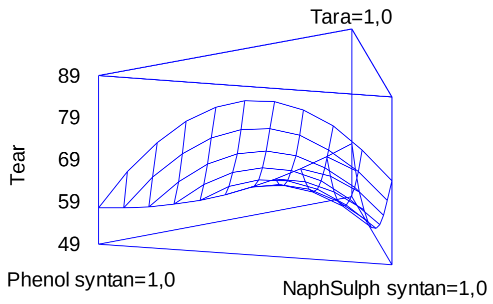


Figure 32: Estimated response surface for tensile elongation. Experimental design I

Optimize Response:
Goal: maximize Tear
Optimum value = 86.03 N/mm

Factor	Low	High	Optimum
Tara	0	1	0
Phenol syntan	0	1	0.40
Naphthalene sulphonic acid	0	1	0.60

Light fastness

Estimated Full Model Effects for lightfastness:

Source	P-Value
Mean	-
Linear	-
Quadratic	0.0288
Special Cubic	-

Under the criteria of the estimated Full Model Effects for tear, it appears that the quadratic Model Fitting Results is adequate for the data.

Analysis of variance for tear:

Source	Sume of squares	Df	Mean Square	F-Ratio	p-Value
Quadratic Model	10.03	5	2.01	116.36	0.0002
Total Error	0.67	4	0.02		
Total (corr.	10.10				

R-squared = 99.32 percent
R-squared (adjusted for d.f.) = 98.46 percent
Standard Error of Est. = 0.13
Mean absolute error = 0.06
Durbin-Watson statistic = 2.31
Lag 1 residual autocorrelation = -0.16

Since the P-value for this model is less than 0.01, there is a statistically significant relationship between Lightfastness and the components at the 99% confidence level and there is an indication of possible serial correlation.

Quadratic Model Fitting Results for lightfastness:

Parameter	Estimate	P-Value
A: Tara	4.01	
B: Phenol syntan	1.01	
C: Naphthalene sulphonic acid	2.01	
AB	-2.41	0.0118
AC	-0.41	0.4934
BC	1.59	0.0447

The equation of the fitted model is after excluding cross-product AC:

Lightfastness = 4.012*Tara + 1.01*Phenol syntan + 2.01*Naphth sulfonic –0.41*Tara*Phenol syntan + Phenol syntan*Naphth sulfonic

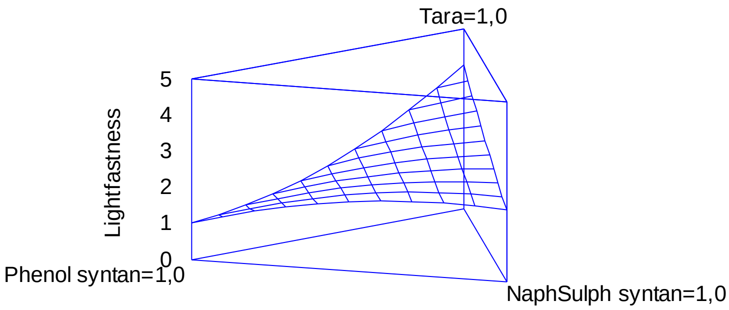


Figure 33: Estimated response surface for lightfastness. Experimental design I

Optimize Response:
Goal: maximize lightfastness
Optimum value = 4.01

Factor	Low	High	Optimum
Tara	0	1	1
Phenol syntan	0	1	0
Naphthalene sulphonic acid	0	1	0

Tara itself has gives good light fastness to the leather, as we have already commented in section 2.4. It is well know the use of tara in the automobile industry. It is required in interior materials able to maintain its properties under extreme expositions. Combinations with naphthalene sulphonic syntan have a lower negative influence in the light fastness values than the phenol condensation syntan.

8.4. Conclusions of the Experimental Design I

There is a variety of results and the optimization of the mixtures will depend of the variables we analyze:

a) Shrinking temperature is optimized when using a phenolic syntan but similar result is obtained blending tara powder and naphthalene sulphonic syntan.
b) Tensile strength is optimized when using tara powder and its combinations with syntans has a negative effect. Naphthalene sulphonic syntan lower effect in tensile strength blending tara powder is less than the blend of tara powder with phenolic syntan.
c) Elongation is optimized when using a phenolic syntan but similar result is obtained blending tara powder and naphthalene sulphonic syntan.

d) Tear load is optimized by combining phenolic and naphthalene sulphonic syntans. Blends with tara do not improve tear load.
e) Lightfastness is optimized when using tara powder and its combinations with syntans has a negative effect. Naphthalene sulphonic syntan lower effect in lightfastness blending tara powder is less than the blend of tara powder with phenolic syntan.

It can be observed that tara powder has, in general, good properties because its tanning effect, but in most of the cases, it is not optimal because, due to its astringency, it has certain limits to penetrate inside the leather.

With the help of an auxiliary syntan, naphthalene sulphonic type, penetration is improved considerably and the behavior of their combinations are able to obtain similar or even better values than a replacement syntan, phenol condensation type. This thesis is supported also, with the following SEM photographs:

Photo 6: SEM photo. Tara. 24x & 202x

The leather is well tanned on surface, while the inner layer fibers are open and well differentiated. The rapid superficial tanning effect of tara, due to its astringency, does not allows the unreacted tannins to penetrate inside the leather.

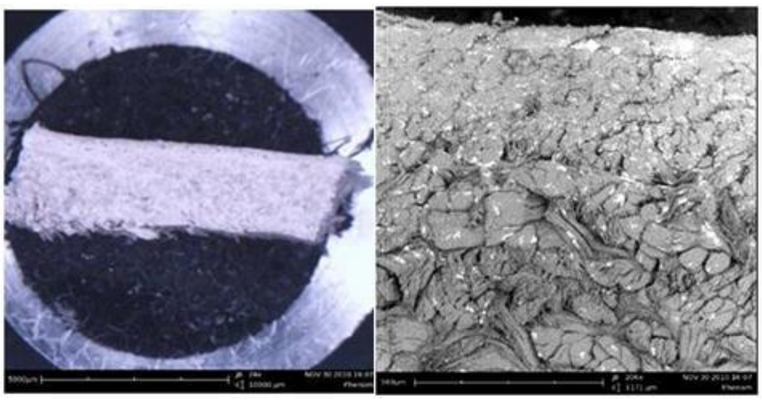


Photo 7: SEM photo. Tara + Naphthalene sulphonic syntan. 24x & 202x

The fibers are very compacted and they are not differentiated due to the crosslinking effect of the tannins.

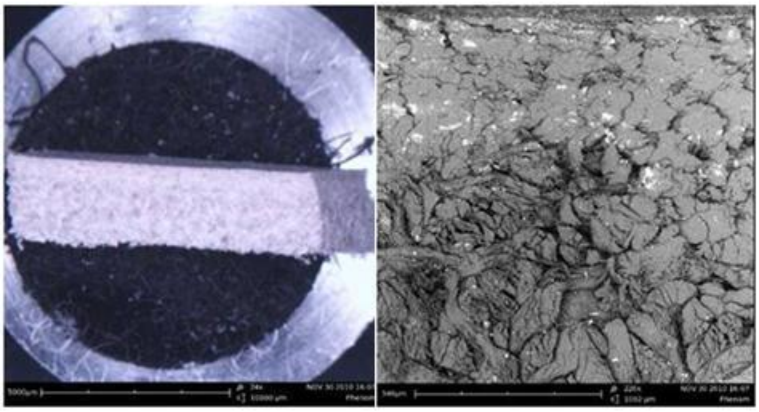


Photo 8: SEM photo. Tara + phenol condensation syntan. 24x & 202x

Fibbers are very compacted and tanning is obtained all through the leather. Especially in the grain layer, fibbers have disappeared and material is tight and homogeneous.

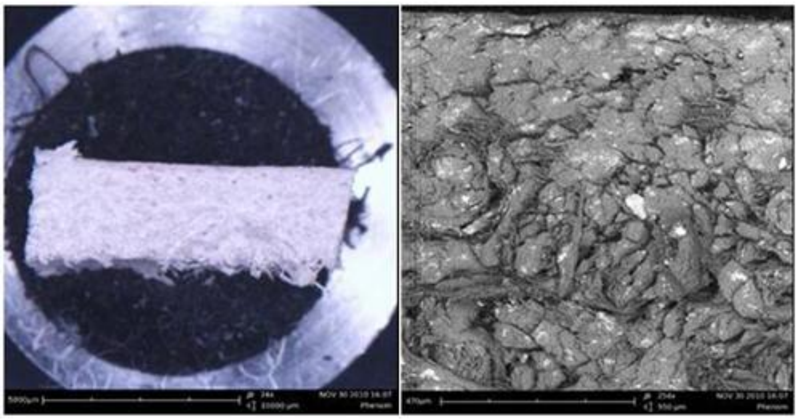


Photo 9: SEM photo. Tara + Naphth. sulphonic syntan + phenol condensation syntan. 24x & 202x

Fibers are visible and there is certain uniformity among the grain and the inner layers.

Differences between the tests are remarkable and the behavior of the leather depends much more of the variables than the combination of products.

Considering the goals of the work, using tara as sustainable tanning agent, we observe that, further the test where tara alone has the best results (light fastness and tensile strength), good results and comparable to the ones achieved with the phenol condensation syntan, are the combinations of tara tannin and the naphthalene sulphonic syntan acting as tanning auxiliary. In these cases, a certain synergy is observed (Tensile elongation).

We assume that this combination (tara + naphthalene sulphonic syntan) will enhance the performance of the tara tannins what is the aim of this resaerch.

The chosen experimental design has only determined a mixture of equal proportions of the ingredients, calculated on the tanning content.

The second experimental design will analyzed different percentages of the two products to define the most appropriate recipe for a sustainable wet white formulation.

9. Pretanning process with tara. Experimental design II: Optimizing with naphthalene sulphonic syntan.

Pretanning process with tara, part I, aims obtaining the components of a mixture that better fits tara by improving its performance for a sustainable wet white pretanning process. Combining tara powder with a naphthalene sulphonic syntan was selected. This part 2 optimizes the best blend composition of the two ingredients to maximize the values of shrinking temperature, tensile strength, tensile elongation and tear resistance.

9.1. Products, materials and equipment. Experimental design II.

To carry out the experimental tests, the following commercial products were selected:

Synthetic tanning of naphthalene sulphonic:

Yellowish liquid. Miscible in water. 40 % of tannin content. pH 3.3 – 3.7 (solution 1:10)

Tara Powder: Origen: Peru

Quality Control	pH	3.5	Insolubles	32 %
	Tannin content	47 %	Soluble solids	60 %
	Non tannin content	13 %	Total solids	92 %
	Water	8 %	Iron	388.9 mg/kg (ppm) by atomic absorbance

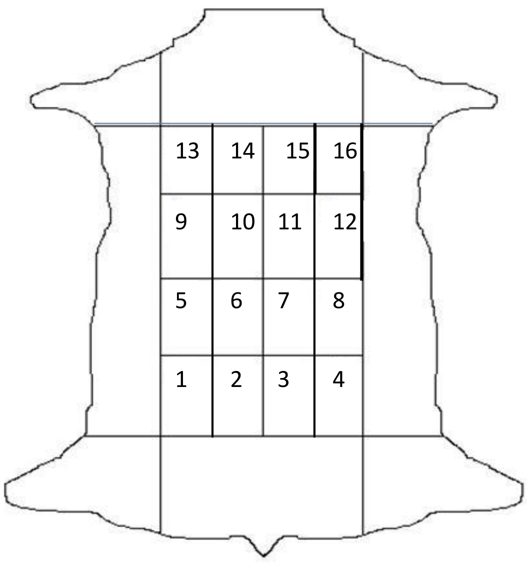


Figure 34: Sampling hides for testing. Experimental design II

The trials were carried out using the following drums:

Pretanning process:

2 – Simplex drums, stainless steel, 4 T.D.F. Annex 10.

9.2. Tests to optimize ratios with naphthalene sulphonic syntan. Experimental design II.

To obtain comparative tests, it was used Russian bovine hides, green split. They were divided in 16 pieces and marked (Figure 34). The sixteen pieces were weight and their thicknesses were calibrated.

Deliming, bating and pickling treatment were carried out according the recipe of table 30.

Trials were carried out according to the recipe of table 33. The percentages of the pretanning commercial agents were adjusted to their tannin content according to the same calculation as in design I.

Operation	%	Product	T ºC	Running time	Control
Conditioning	50	Water	20		
	4	Sodium chloride			
				10 min.	ºBè=6
Add hides to drum				10 min.	
Pretanning	50	Water	20		
	A	**Tara powder**			
	B	**Naphthalene sulphonic syntan liquid**		Overnight	
	2,0	**Fatliquor**		2 hours	
	0,5	**Formic acid 85%**		120 min.	
Drain					
Washing	300	Water	20	20 min.	
Drain					
Horse up. Samming. Pasting 12 hours at 30ºC. Conditioning and stake.					

Table 33: Recipe for pretanning. Experimental design II

To optimize a magnitude that depends from one o more variables X = (x, y, …z), it is necessary to determine the values of the parameters which the function obtains the absolute optimal, maximal or minimal values.

There exists several techniques to optimize a function, but to simplify and better understand the behavior of the blend, the experiments will be based on a design with a response surface. Visually, best fitted response can be analyzed in a certain area of interest factor levels and the sensibility to the factors can be evaluated.

The response surface and the analysis strategy will assume that the average of the response variable μ_y is a function of the quantitative factor levels represented by the variables x_1, x_2, …, x_k. The polynomials models are used in the practice to estimate the real function. Normally, the real function is unknown and polynomial function often gives a good loom in areas relatively small of the quantitative factor levels.

The polynomial models used to analyze variable response surfaces are normally lineal:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2$$

or quadratic:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2$$

When the optimal surface region is identified, a new design is necessary to characterize the variable response surface. 2^k factorial models are useful designs to identify significant factors and optimal response regions but require a big number of tests.

Box and Wilson (1951) proposed decentralized designs reducing the number of combinations, based on 2^n factorials with 2n additional combinations, or axial points, through the coordinated axis of codified factor levels: $(\pm\alpha,0,0,\dots,0),(0,\pm\alpha,0,\dots0),\dots(0,0,0\dots\pm\alpha)$ and m replications in the designed center of the coordinates.

In order to obtain the same accuracy for all the mean estimations, it is necessary a rotatable design. In this case, the accuracy of the estimated surface is independent of the design orientation with regard to the real response.

Centralized design becomes rotatable establishing axial points values a $\alpha = (2^n)^{1/4}$.

The α value for a 2 factor design is:

$$\alpha = (4)^{1/4} = \sqrt{2} = 1{,}414$$

The surface graphic for a quadratic, centralized, orthogonal and rotatable design is in Figure 35.

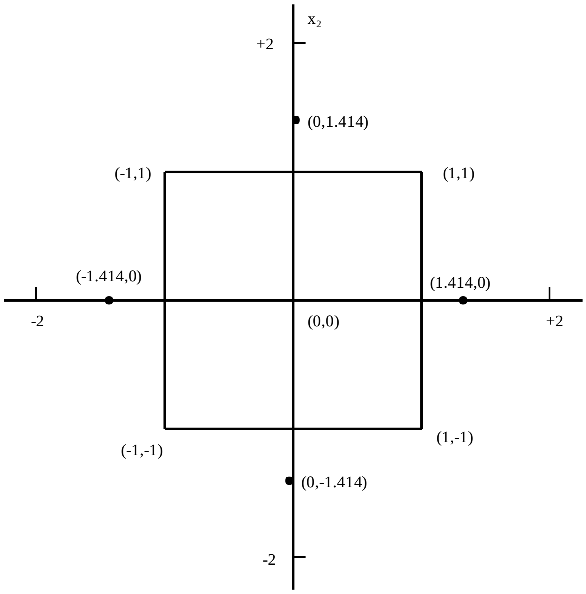


Figure 35: Quadratic, centralized, orthogonal and rotatable design

Limits ($V_{1,414}$, $V_{-1,414}$) of independent variable % tara powder and % naphthalene sulphonic syntan are based on previous experiences and technical information from chemical suppliers. % tara powder shall range between 0 and 12% while % Naphthalene sulphonic syntan between 0 and 14%. The values on coordinates 1 and -1, V_1 and V_{-1} are calculated proportionally.

If V_0 is the value of the variable to the origin and $V_{1,414}$ and $V_{-1,414}$ the performance limits of the ranges of the variables:

$$V_0 = (V_{1,414}+V_{-1.414})/2$$

$$(x+1.414)/1.414= (V_x-V_{-1.414})/(V_0-V_{-1.414}) \rightarrow V_x = (V_0-V_{-1.414})(x+1.414)/1.414+V_{-1.414}$$

Replacing the values for tara powder:

$V_{1,414}$= 12 % tara powder i $V_{-1.414}$=0% tara powder

V_0= (12 + 0)/2= 6 % tara powder

V_1= (6-0) (1+1.414)/1.414+0 = 10,2 %

V_{-1} = (6-0) (-1+1.414)/1.414+0 = 1,76 %

Replacing the values for naphthalene sulphonic syntan:

V_0 = (14+0)/2=7% naphthalene sulphonic syntan

V_1= (7-0) (1+1.414)/1.414+0 = 12 %

V_{-1} = (7-0) (-1+1.414)/1.414+0 = 2 %

Experimental independent variables: % of tara powder and % Naphthalene sulphonic syntan added to the pre-tanning process according application recipe of table 34.

Test	**x_1**	**x_2**	**% Tara powder**	**% Naphthalene sulphonic syntan**
1	-1	-1	1.8	2
2	-1	1	1.8	12
3	1	-1	10.2	2
4	1	1	10.2	12
5	0	-1.414	6	0
6	0	1.414	6	14
7	-1.414	0	0	7
8	1.414	0	12	7
9	0	0	6	7
10	0	0	6	7
11	0	0	6	7
12	0	0	6	7
13	0	0	6	7

Table 34: Quadratic, centralized, rotatable and orthogonal design for tara and naphthalene sulphonic syntan. Codification table. Experimental design II.

Photo 10 shows the leather pieces test results in the coordinates according the described experimental design:

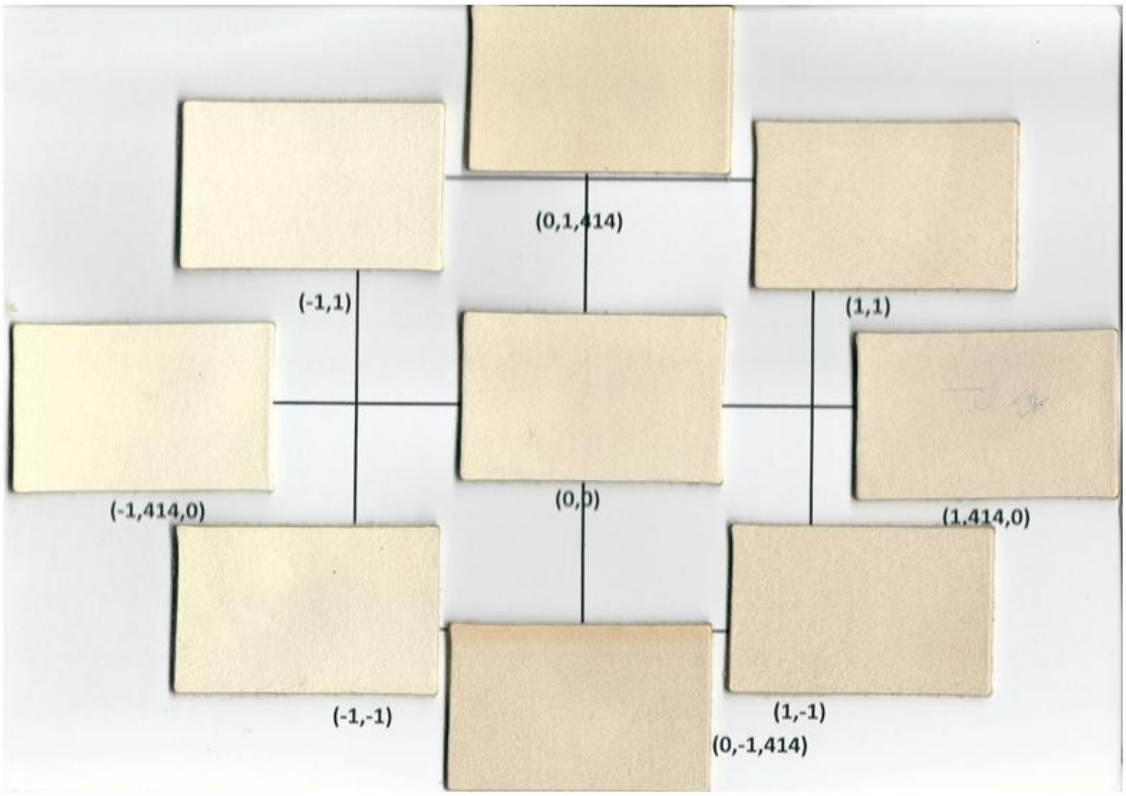


Photo 10: Optimization for a pretanning process with tara. Experimental design II.

Table 35: includes the physical test results to be statistically analyzed:

Test	Coordinates	TCºC	Tensile Strength (N) *EN ISO 3376-IUP6*	% Elongation *EN ISO 3376-IUP6*	Tear load (N/mm) *EN ISO 3377-2 IUP8*	Lightfastness
1	(-1, -1)	61	743.0	49.0	76.9	2
2	(-1, 1)	69	725.3	44.1	79.5	2
3	(1, -1)	59	777.3	38.1	65.5	3
4	(1, 1)	71	709.5	39.5	64.3	3
5	(0, -1.414)	63	848.0	38.9	68.1	3
6	(0, 1.414)	74	900.5	37.0	72.3	1
7	(-1.414, 0)	63	875.0	52.8	81.9	1
8	(1.414, 0)	70	1022.0	48.4	82.8	4
9	(0, 0)	65	903.0	44.7	82.3	2
10	(0, 0)	65	903.0	44.7	82.3	2
11	(0, 0)	65	903.0	44.7	82.3	2
12	(0, 0)	65	903.0	44.7	82.3	2
13	(0, 0)	65	903.0	44.7	82.3	2

Table 35: Test results from experimental design II

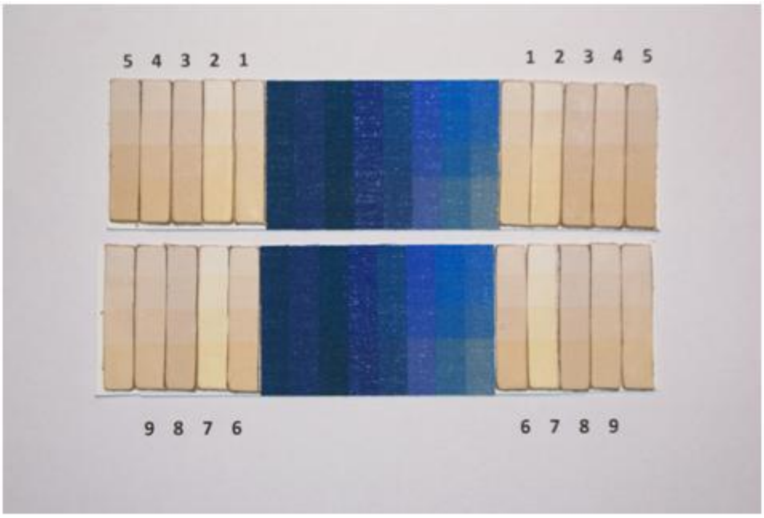


Photo 11: Light fastness test. Experimental design II

9.3. Test results and discussion. Experimental design II:

Results are analyzed for each variable in order to obtain the optimal response for each variable:

<u>Shrinking temperature</u> (S_T °C):

Estimated effects for S_T

average	65.00	+/- 0.88
A:Tara	2.47	+/- 1.39
B:Syntan	8.89	+/- 1.39
AA	0.25	+/- 1.50
AB	2.00	+/- 2.00
BB	2.25	+/- 1.50

Analysis of Variance for S_T

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	12.25	1	12.25	3.15	0.1192
B:Syntan	158.03	1	158.03	40.64	0.0004
AA	0.11	1	0.11	0.03	0.8719
AB	4.00	1	4.00	1.03	0.3442
BB	8.80	1	8.80	2.26	0.1761
Total error	27.22	7	3.89		

The ANOVA table partitions the variability in S_T into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, % syntan has P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

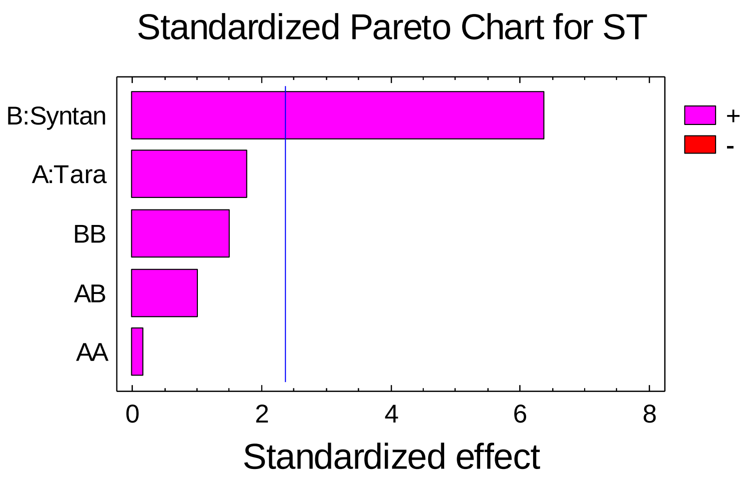


Figure 36: Pareto chart for shrinking temperature. Experimental design II

Since the effect of the % of syntan has statistical significance to the variable shrinking temperature at 95% confidence, we conclude that there is a correlation between the shrinking temperature and the % of syntan according the following lineal equation:

$$S_T = 65.77 + 4.44*\text{Syntan}$$

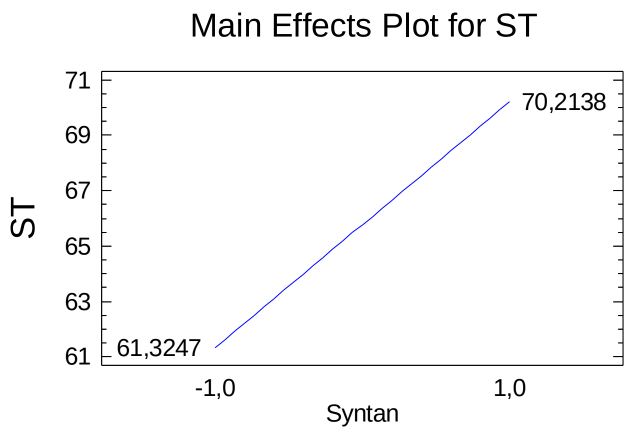


Figure 37: Lineal correlation ST and % syntan. Experimental design II.

Despite the variable responses tara cannot be statistically proved within the mathematical at 95% confidence, figure 38 illustrates tendencies of shrinking temperature responses for effects % tara and % syntan, excluding the other cross-products.

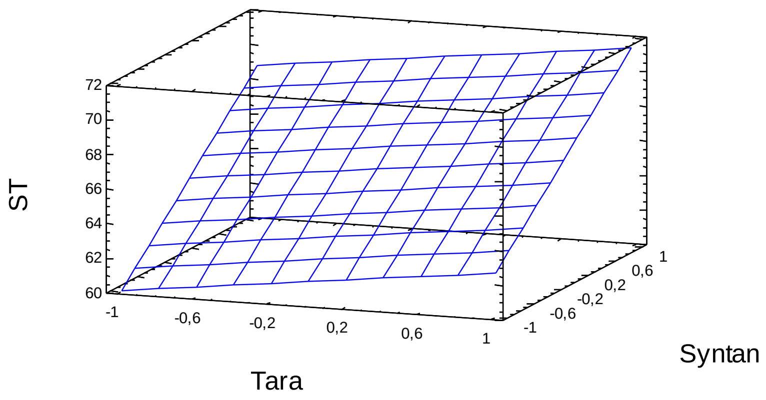


Figure 38: Estimated Response Surface for shrinking temperature. Experimental design II

Optimize Response:
Goal: maximize Shrinking temperature
Optimum value: 73.80ºC

Factor	Low	High	Optimum
Tara	-1.414	1.414	1.414
Syntan	-1.414	1.414	1.414

<u>Tensile strength (N)</u>

Estimated effects for Tensile		
average	903.00	+/- 43.84
A:Tara	56.60	+/- 69.31
B:Syntan	-2.81	+/- 69.31
AA	-40.80	+/- 74.33
AB	-25.05	+/- 98.02
BB	-115.05	+/- 74.33

Analysis of Variance for ST

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	6406.51	1	6406.51	0.67	0.4411
B:Syntan	15.83	1	15.83	0.00	0.9688
AA	2895.09	1	2895.09	0.30	0.6001
AB	627.50	1	627.50	0.07	0.8056
BB	23020.20	1	23020.20	2.40	0.1650
Total error	67254.70	7	9607.81		
Total (corr.)	98501.90	12			

None of the effects have P-values less than 0.05, indicating that they are not statically significant at the 95.0% confidence level.

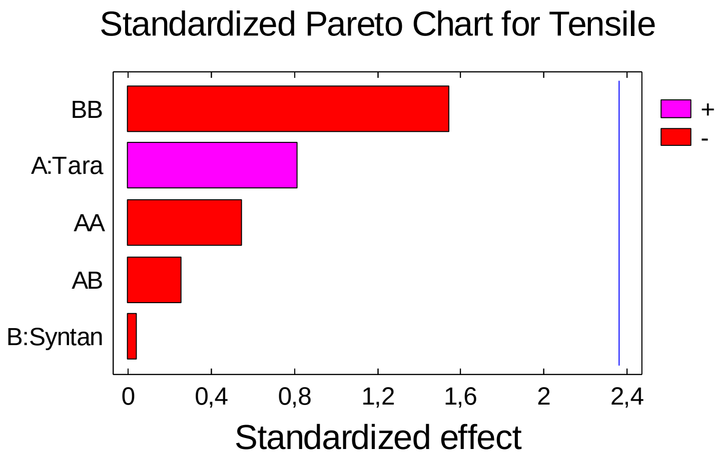


Figure 39: Pareto chart for tensile strength. Experimental desing II

Despite statistically significant effects have not been found, estimated response surface considers interaction of syntan (BB) and % of tara to have an idea of a tendency and to draw a conclusion about.

$$\text{Tensile} = 903 + 28.30*\text{Tara} - 1.41*\text{Syntan} - 20.40 * (\text{Tara})^2 - 12.53 * \text{Syntan} - 57.53*(\text{Syntan})^2$$

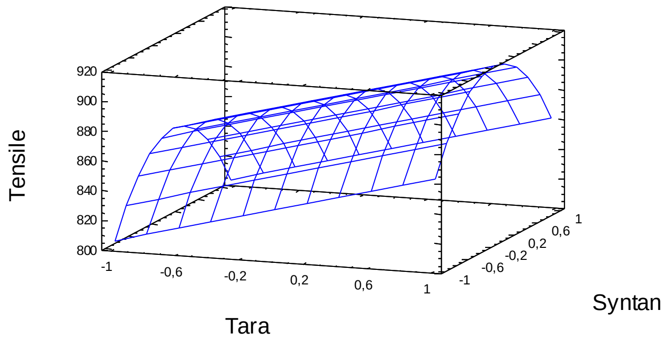


Figure 40: Estimated response surface for Tensile. Experimental design II

Optimize Response:
Goal: maximize Tensile
Optimum value: 913.27 N

Factor	Low	High	Optimum
Tara	-1.414	1.414	1.414
Syntan	-1.414	1.414	0.000

Tensile elongation (%)

Estimated effects for Tensile

average	44.70	+/- 0.89
A:Tara	-6.66	+/- 1.40
B:Syntan	-0.32	+/- 1.40
AA	5.71	+/- 1.50
AB	0.70	+/- 1.98
BB	-6.94	+/- 1.50

Analysis of Variance for Elongation

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	88.60	1	88.60	22.56	0.0021
B:Syntan	0.21	1	0.21	0.05	0.8250
AA	56.75	1	56.75	14.45	0.0067
AB	0.49	1	0.49	0.12	0.7343
BB	83.70	1	83.70	21.31	0.0024
Total error	27.49	7	3.93		
Total (corr.)	277.96	12			

For % elongation, 3 effects, % of tara and the quadratic effects of % tara and % of tannin have P-values less than 0.05, indicating that they are significant at the 95.0% confidence level.

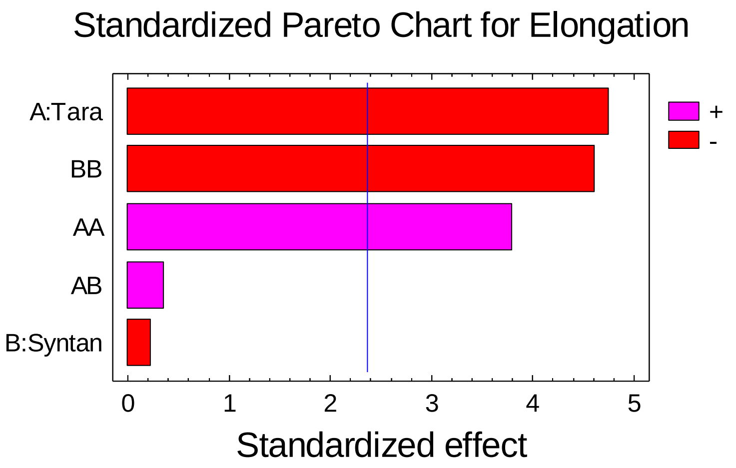


Figure 41: Pareto chart for tensile elongation. Experimental design II

After excluding the effects AB and B with no statistic significance, we drew the estimated response surface and optimize response.

$$Elongation = 44.7 - 3.33*Tara + 2.86*(Tara)^2 - 3.47\,(Syntan)^2$$

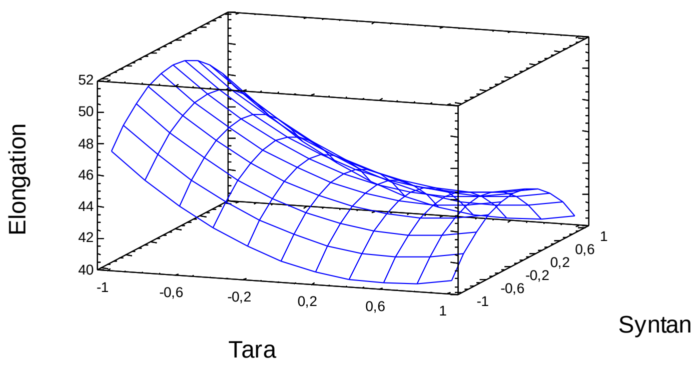


Figure 42: Estimated response surface for tensile elongation. Experimental design II

Optimize Response:
Goal: maximize Elongation
Optimum value: 55.12%

Factor	Low	High	Optimum
Tara	-1.414	1.414	-1.414
Syntan	-1.414	1.414	0

Tear load (N/mm)

Estimated effects for tear load		
average	82.30	+/- 2.03
A:Tara	-5.68	+/- 3.21
B:Syntan	1.18	+/- 3.21
AA	-2.64	+/- 3.44
AB	-0.60	+/- 4.54
BB	-14.7+	+/- 3.44

Analysis of Variance for Tear

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	64.57	1	64.57	3.14	0.1197
B:Syntan	2.81	1	2.81	0.14	0.7227
AA	12.10	1	12.10	0.59	0.4682
AB	0.63	1	063	0.02	0.8985
BB	380.30	1	380.30	18.49	0.0038
Total error	143.99	7	20.57		
Total (corr.)	592.91	12			

For tear load, the quadratic effec of syntan has P-values less than 0.05, indicating that they are significant at the 95.0% confidence level.

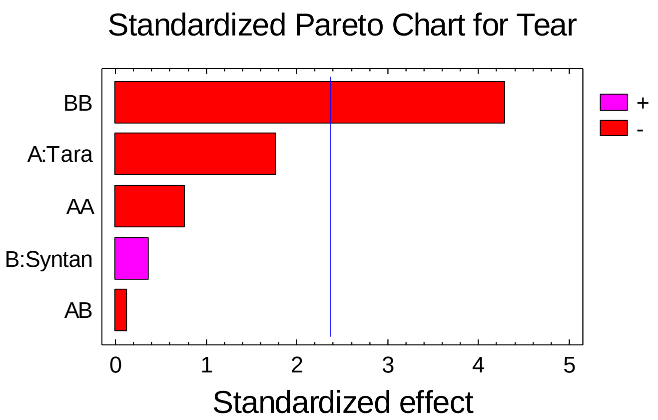


Figure 43: Pareto chart for tear load. Experimental design II

After excluding the effects with no statistic significance, AA, B and AB, we drew the estimated response surface and optimize response.

$$Tear = 81.38 - 2.84*Tara - 7.22\ (Syntan)^2$$

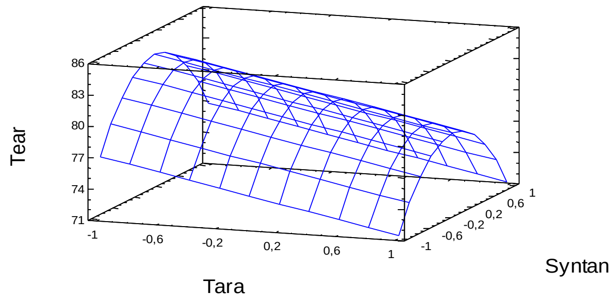


Figure 44: Estimated response surface for tear load. Experimental design II

Optimize Response:
Goal: maximize Tear load
Optimum value: 81.38 N/mm

Factor	Low	High	Optimum
Tara	-1.414	1.414	0.0
Syntan	-1.414	1.414	0.0

Lightfastness

Estimated effects for lightfastness

average	3,20	+/- 0,43
A:Tara	1,56	+/- 0,68
B:Syntan	-0,71	+/- 0,68
AA	-0,58	+/- 0,73
AB	-0,00	+/- 0,97
BB	-1,07+	+/- 0,73

Analysis of Variance for Lightfastness

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	4.87	1	4.87	5.20	0.0566
B:Syntan	1.00	1	1.00	1.07	0.3358
AA	0.57	1	0.57	0.61	0.4589
AB	0.00	1	0.00	0.00	1.0000
BB	2.00	1	2.00	2.15	0.1863
Total error	6.55	7	0.94		
Total (corr.)	14.77	12			

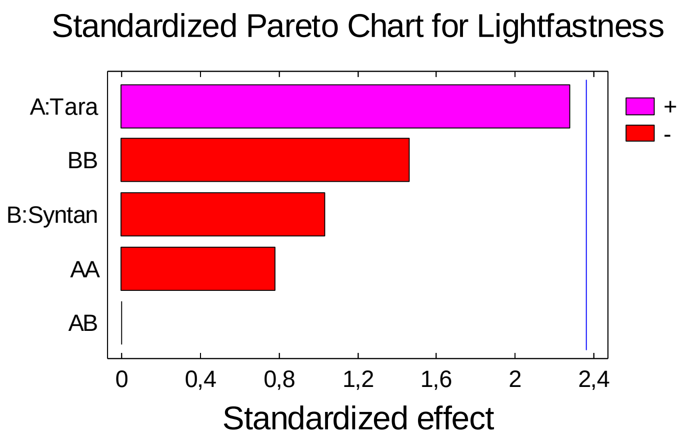


Figure 45: Pareto chart for lightfastness. Experimental design II

When excluding all effects except % of tara, the following analysis of variance is obtained:

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Tara	4.87	1	4.87	5.41	0.0401
Total error	9.90	11	0.90		
Total (corr.)	14.75	12			

Effect tara has P-value less than 0.05, indicating that it is significant at the 95.0% confidence level.

In this case, regression coefficients were calculated to obtain the equation of the fitted model:

Lightfastness = 2,69 + 0,78*Tara

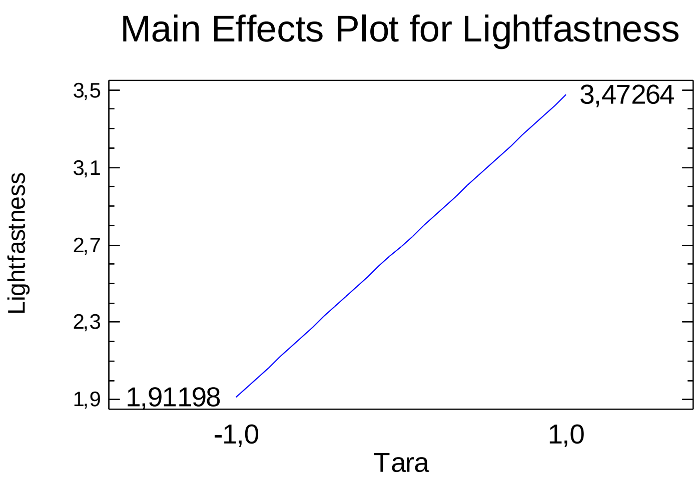


Figure 46: Linea correlation lightfastness and % tara. Experimental design II

Optimize Response:
Goal: maximize lightfastness
Optimum value: 3.80

Factor	Low	High	Optimum
Tara	-1,414	1,414	1,414
Syntan	-1,414	1,414	0,0

9.4 Conclusions of the Experimental Design II

The values of the statistic results indicate the influence of the effects of % naphthalene sulphonic syntan with % tara powder to the response variables of shrinking temperature, tensile strength, tensile elongation, tear load and lightfastness.

The amount of tara in the recipe has very little influence on the shrinking temperature but this can be considerably improved with the help of the auxiliary syntan and confirming, at the same time, the results of the experimental design I. This can be checked with the SEM microscopy photos (photos 6 and 7) and can be implicit to the improvement of the penetration of the tara powder allowing the cross linking with the inner fiber of the collagen structure. The correlation is calculated and expressed with a lineal equation valid for the area of the analysis.

Optimization for tensile strength cannot be proposed as the tests do not prove a significance correlation between this response variable and the effects of the factors % of tara and % of syntan. By observing the estimated response surface the naphthalene sulphonic has an irrelevant negative effect on this variable from the statistical analysis.

With regard to the tensile elongation, the % of tara has a negative effect what is a general characteristic of vegetable tannins when compare with chrome tanning. Improvement with naphthalene sulphonic syntan has not been statistically validated. Observing estimated response surface, the graphic shows that % of tara and % of syntan is optimized when concentrations are similar.

Similar results are obtained for variable response tear load. % of tara has a negative effect and the naphthalene sulphonic syntan optimal responses are observed along the coordinate axis.

Tests on lightfastness also confirm that tara tannins are appreciated because this property. Naphthalene sulphonic syntan may have a negative effect but results do not demonstrate a statistical significance effect. Table 36 summarizes these general tendencies:

Variable responses	Effect of the factor		Influence of the syntan to the effect of the tara powder
	% Tara poder	% Naphthalene sulphonic syntan	
Shrinking temperatura	+	++	++
Tensile strength	+	()	()
Tensile elongation	--	()	+
Tear load	-	+	+
Lightfastness	++	-	-

Table 36: Conclusions effects of tara and syntan on wet-white properties

Legend: ++ Very positive

+ Positive

() No influence

- Very negative
- Negative

Optimal values for	Syntan	Tara
Shrinking temperature	1,41	1,41
Tensile strength	1.41	0.00
Tensile elongation	-1.41	0.00
Tear loan	0.00	0.00
Light fastness	1.41	0.00
Mean	1.41	0.00
Average	0.57	0,28

Table 37: Optimal values syntan and tara

The values in table 37 values will be considered according to the requirements of the final article to be manufactured with the subsequent processes of retanning, fatliquoring, dyeing and finishing.

Shrinking temperature needs to be maximized to ensure heat resistance to the mechanical treatments after pretanning, mainly shaving, to obtain appropriate and regular thickness among the different parts of the hides or skins.

The physical properties will depend on the quality requirements of the goods manufactured with the leather article. While tear load is an important property for apparel, elongation is fundamental for the manufacture of shoes where leather is exposed to high tensile forces.

In general, however, all these physical properties considered in this research are common for most of the leather articles produced for the shoe, apparel, upholstery and leather good markets, thus the mean of all these coordinate values is considered as the most balanced value.

Considering the means of the values for optimize response of table 37, the summary from table 36 and proposing to maximize the use of tara tannins as a main component for a sustainable pre-tanning agent, we conclude that optimal values for the ingredients of a mixture of tara powder and a naphthalene sulphonic syntan as:

1.41 tara powder + 0 Naphthalene sulphonic syntan

According to the formulas for Codification Table, Design II, table 34:

Coordinate value tara tannin $[x_1]$ = Me $[S_T$, Tens, Elon, Tear$]$ = 1.41

% tara powder = 12 %

Coordinate value naphthalene sulphonic syntan $[x_2]$ = Me $[S_T$, Tens, Elon, Tear$]$ = 0.00

% naphthalene sulphonic syntan = 7 %

12 % Tara powder **7 % Naphthalene sulphonic syntan**

When comparing the concentration of tannins of the commercial samples of tara powder and the naphthalene sulphonic syntan used for the experiments, the calculated ratios are:

12 x 0.47 % of tara tannins = 5.64 → 67%

7 x 0.40 % of naphthalene sulphonic tannins = 2.80 → 33%

10. Pretanning process with tara. Experimental design III: Optimizing pre-tanning pelt and final pH conditions.

10.1. Tests to optimize pretanning process. Design III.

Design of a pretanning process with tara, design III, aims to identify the most appropriate conditions, by means, optimal pH before and after the wet white pretanning process that better enhance selected physical properties. This design III optimizes the best working conditions of pH for the application of the blend of tara tannin and naphthalene sulphonic syntan obtained in design II maximizing the values of shrinking temperature, tensile strength, tensile elongation and tear resistance.

The tests were carried out according to the application formula in table 38:

Operation	%	Product	T °C	Running time	Control
Conditioning	50	Water	20		
	4	Sodium chloride			
				10 min.	°Bè=6
Add hides to drum				10 min.	pH= 3.3
Depickling	**A**	**Sodium formate**			
	A/2	Sodium bicarbonate		120 min.	**pH=**
Drain					
Pretanning	50	Water	20		
	12	Tara powder			
	7	Naphthalene sulphonic syntan liquid		Overnight	
	2	Fatliquor			
	B	**Formic acid 85%**		120 min.	**pH=**
Drain					
Washing	300	Water	20	20 min.	
Drain					
Horse up. Samming. Pasting 12 hours at 30ºC. Conditioning and stake.					

Table 38: Application formula for wet-white. Experimental design III

To optimize the magnitude that depends from the variables X=(Ts, Tens, Elon, Tear, Light), according to Table 39, it is necessary to determine the values of the parameters, **% of sodium formate and % of formic acid 85%**, which the function obtains the absolute optimal, maximal or minimal values.

Ts	Temperature of shrinkage	ºC	
Tens	Tensile strength	N	EN ISO 3376-IUP6
Elon	Elongation	%	EN ISO 3376-IUP6
Tear	Tear load	N/mm	EN ISO 3377-2 IUP8

Table 39: Variables for Experimental design III

The experiments were based on a design with a response surface. The mathematic model has been described in 9.2.

Visually, best fitted response can be analyzed in a certain area of interest factor levels and the sensibility to the factors can be evaluated. The % of sodium formate and % of formic acid 85% were calculated according to a quadratic, centralized, orthogonal and rotatable design as summarized in table 40.

Limits of % sodium formate and % of formic acid 85% are based on previous experiences. Depickling shall range between the pickling pH (no addition of neutralizing salts) to pH of approximately 5-5.5, approximately the isoelectric point of the collagen. See figure 1.3.

In order to fix the anionic tannins on the collagen substrate it is necessary to reduce pH, lower than its isoelectric point. Range is fixed between 0.2 to 1%.

The values on coordinates 1 and -1, V_1 and V_{-1} are calculated proportionally.

If V_0 is the value of the variable to the origin and $V_{1.414}$ and $V_{-1.414}$ the performance limits of the ranges of the variables:

$$V_0 = (V_{1.414}+V_{-1.414})/2$$

$$(x+1.414)/1.414= (V_x-V_{-1.414})/(V_0-V_{-1.414}) \rightarrow V_x = (V_0-V_{-1.414})(x+1.414)/1.414+V_{-1.414}$$

Replacing the values:

Depickling:

$$V_{1.414}= 1\% \text{ de NaCOOH i } V_{-1.414}=0\% \text{ de NaCOOH}$$

$$V_0= (1 + 0)/2= 0.5\% \text{ de NaCOOH}$$

$$V_1= (0.5-0)\ (1+1.414)/1.414+0 = 0{,}85\ \%$$

$$V_{-1} = (0.5-0)\ (-1+1.414)/1.414+0 = 0{,}15\%$$

Fixing:

$$V_0=(1+0.2)/2=0.6\% \text{ de HCOOH}$$

$$V_1= (0.6-0.2)\ (1+1.414)/1.414+0{,}2 = 0.88\ \%$$

$$V_{-1} = (0.6-0.2)\ (-1+1.414)/1.414+0{,}2 = 0.32\%$$

Test	x_1	x_2	% Sodium formate	% Formic acid 85%
1	-1	-1	0.15	0.32
2	-1	1	0.15	0.88
3	1	-1	0.85	0.32
4	1	1	0.85	0.88
5	0	-1.414	0.5	0.2
6	0	1.414	0.5	1
7	-1.414	0	0	0.6
8	1.414	0	1	0.6
9	0	0	0.5	0.6
10	0	0	0.5	0.6
11	0	0	0.5	0.6
12	0	0	0.5	0.6
13	0	0	0.5	0.6

Table 40 Quadratic, centralized, rotatable and orthogonal design for % sodium formate and % formic acid 85%. Codification table. Experimental design III

10.2. Test results and discussions. Experimental design III:

Photo 12 shows the leather pieces test results in the coordinates according the described experimental design:

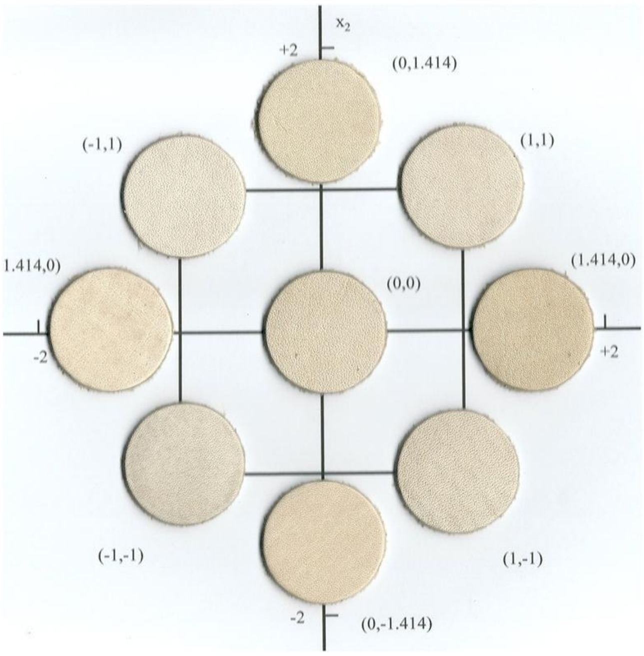


Photo 12: Optimizing for a pretanning process with tara. Experimental design III.

10.2.1 % NaCOOH vs. initial wet-white process pH

Since conditioning of pre-tanning depends of the pH of the pelts, the pH obtained after the treatment with sodium formate and sodium bicarbonate were recorded in table 41:

% NaCOOH	0	0	0.15	0.15	0.5	0.5	0.85	0.85	1	1
pH	3.3	3.3	3.53	3.55	4.4	4.5	4.87	4.91	6.5	6.5

Table 41: pH vs % NaCOOH. Experimental design III.

<u>Analysis of Variance</u>

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	13.0194	4	3.25486	2712.38	0.0000
Within groups	0.006	5	0.0012		
Total (Corr.)	13.0254	9			

The ANOVA table decomposes the variance of pH into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 2712.38, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the mean pH from one level of NaCOOH to another at the 95,0% confidence level.

<u>Multiple Regression Analysis</u>

Dependent variable: pH

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	3.1451	0.,2237	14.0613	0.0000
NaCOOH	2.7819	0.3541	7.85635	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	11.5309	1	11.5309	61.72	0.0000
Residual	1.4945	8	0.1868		
Total (Corr.)	13.0254	9			

R-squared = 88.5259 percent
R-squared (adjusted for d.f.) = 87.0916 percent
Standard Error of Est. = 0.4322
Mean absolute error = 0.2912
Durbin-Watson statistic = 1.2057 (P=0.0315)
Lag 1 residual autocorrelation = 0.2792

The output shows the results of fitting a multiple linear regression model to describe the relationship between pH and 1independent variables. The equation of the fitted model is

$$pH = 3.15 + 2.78*NaCOOH$$

Since the P-value in the ANOVA table is less than 0.01, there is a statistically significant relationship between the variables at the 99% confidence level.

The R-Squared statistic indicates that the model as fitted explains 88.53% of the variability in pH. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 87.09%. The standard error of the estimate shows the standard deviation of the residuals to be 0.43. This value can be used to construct prediction limits for new observations.

The mean absolute error (MAE) of 0.29 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in the data file. Since the P-value is less than 0.05, there is an indication of possible serial correlation. Plot the residuals versus row order to see if there is any pattern which can be seen.

In determining whether the model can be simplified, notice that the highest P-value on the independent variables is 0.0000, belonging to NaCOOH. Since the P-value is less than 0.01, the highest order term is statistically significant at the 99% confidence level.

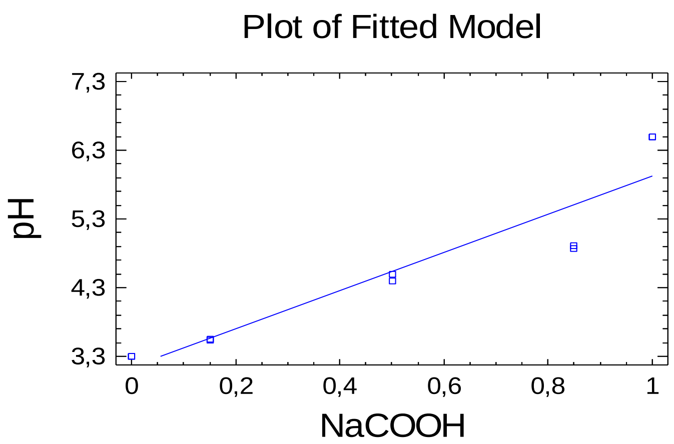


Table 42: Fitted model for pH vs. NaCOOH. Experimental design III

10.2.2 % NaCOOH and % HCOOH vs. final wet-white process pH

This second statistic analysis determines the influence of %NaCOOH and %HCOOH to the final pH. The aim is to ensure the quality of the data and validate the factors prior to final analysis and conclusions.

The results obtained in the experimental design were recorded in Table 43:

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
%NaCOOH	0.15	0.15	0.85	0.85	0.5	0.5	0	1	0.5
%HCOOH	0.32	0.88	0.32	0.88	0.2	1	0.6	0.6	0.6
Final pH	3.4	3.1	4	3.6	3.9	3.5	3	4	3.6

Table 43: % NaCOOH and %HCOOH vs. final pH. Experimental design III.

<u>Analysis of Variance for Final pH</u>

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:% NaCOOH	0.7902	1	0.7902	47.64	0.0000
B:% HCOOH	0.2002	1	0.2002	12.07	0.0060
AA	0.0703	1	0.0703	4.24	0.0665
AB	0.0025	1	0.0025	0.15	0.7060
BB	0.0003	1	0.0003	0.02	0.8935
Total error	0.1658	10	0.0166		
Total (corr.)	1.,2294	15			

R-squared = 86.5097 percent
R-squared (adjusted for d.f.) = 79.7645 percent
Standard Error of Est. = 0.1288
Mean absolute error = 0.0671
Durbin-Watson statistic = 1.9775 (P=0.4439)
Lag 1 residual autocorrelation = -0.0158

The ANOVA table partitions the variability in Final pH into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significant at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 86.5097% of the variability in Final pH. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 79.7645%. The standard error of the estimate shows the standard deviation of the residuals to be 0.1288. The mean absolute error (MAE) of 0.0671 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

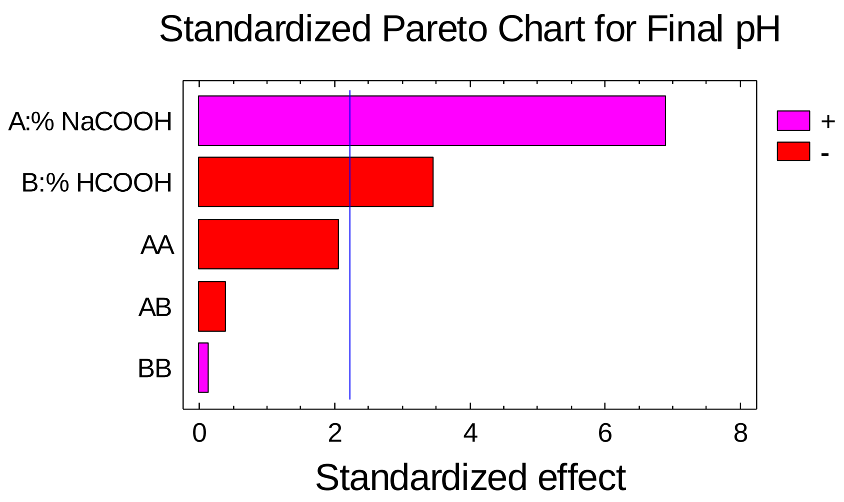


Figure 47: Standardized Pareto Chart for Final pH. Experimental design III

Considereing the significant effects, % HCOOH and % NaCOOH, as well as the quadratic effect of % NaCOOH (P-value higher that 0.05 when excluding other effects), estimated surfacer response is drawn in figure 48.

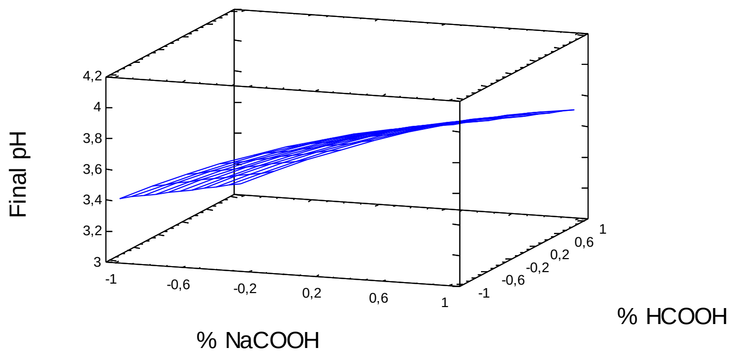


Figure 48: Estimated response surface Final pH vs. %NaCOOH and HCOOH

Regression coeffs. for Final pH

constant = 3.65

A:% NaCOOH = 0.31

B:% HCOOH = -0.16

AA = -0.19

This pane displays the regression equation which has been fitted to the data. The equation of the fitted model is

$$\text{Final pH} = 3.65 + 0.31*\%\ NaCOOH - 0.16*\%\ HCOOH - 0.19*(\%NaCOOH)^2$$

where the values of the variables are specified in their original units.

Photos 13 and 14 show the exhaustion baths after pretanning operation for each of the tests carried out according to design II.

The lowest part demonstrate the fraction of insolubles that were not introduced into the protein structure during the pretanning operation, while the top is a cleaner liquor which intensity of color demonstrate the portion of tannins that bond with the reactive groups of the collagen. See table 10 from section 4.1.

Photo 13: Exhaustion baths I. Experimental design III.

Photo 14: Exhaustion baths II. Experimental design III.

10.3 Results and discussions. Experimental design III

Table 44: includes the physical test results to be statistically analyzed:

Test	Coordinates	S_T (^oC)	Tensile Strength (N) *EN ISO 3376-IUP6*	Elongation (mm) *EN ISO 3376-IUP6*	Tear load (N/mm) *EN ISO 3377-2 IUP8*
1	(-1, -1)	67	626.0	36	127
2	(-1, 1)	69	543.0	46	141
3	(1, -1)	67	549.0	48	144
4	(1, 1)	71	574.0	48	118
5	(0, -1.414)	67	468.0	43	98
6	(0, 1.414)	69	499.0	39	116
7	(-1.414, 0)	63	507.0	42	140
8	(1.414, 0)	68	370.0	52	129
9	(0, 0)	63	601.0	43	89

Table 44: Test results from experimental design III

Results for shrinking temperature (S_T)

Analysis of Variance for S_T

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:NaCOH	10.2855	1	10.2850	9.71	0.0110
B:HCOOH	9.74265	1	9.7426	9.19	0.0126
AA	22.7812	1	22.7812	21.50	0.0009
AB	1.0000	1	1.0000	0.94	0.3542
BB	69.0313	1	69.0313	65.14	0.0000
Total error	10.5967	10	1.05967		
Total (corr.)	123.438	15			

R-squared = 91.4154 percent
R-squared (adjusted for d.f.) = 87.123 percent
Standard Error of Est. = 1.0294
Mean absolute error = 0.,459596
Durbin-Watson statistic = 2.67484 (P=0.0868)
Lag 1 residual autocorrelation = -0.337422

The ANOVA table partitions the variability in St into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 4 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 91,4154% of the variability in St. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 87,123%. The standard error of the estimate shows the standard deviation of the residuals to be 1,0294. The mean absolute error (MAE) of 0,4596 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals. Excluding cross-product AB

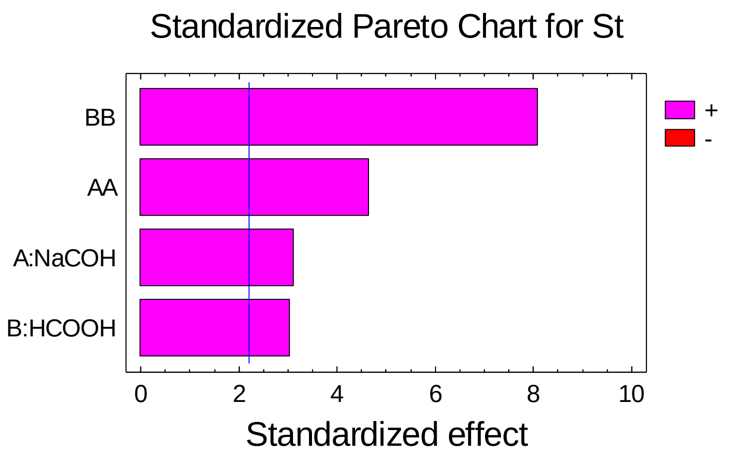


Figure 49: Pareto Chart for shrinking temperature. Experimental design III.

$$S_T = 63.00 + 1.13\ NaCOOH + 1.10\ HCOOH + 1.69\ (NaCOOH)^2 + 2.94\ (HCOOH)^2$$

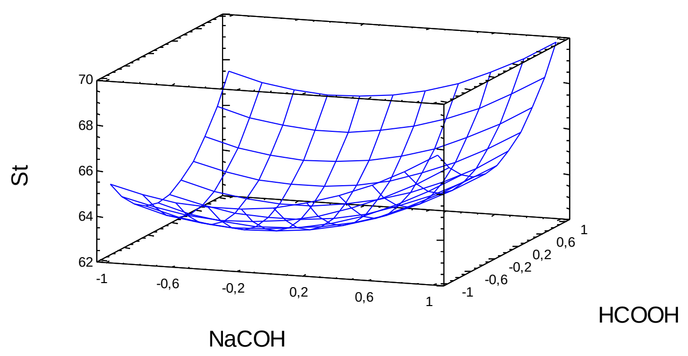


Figure 50: Estimated response surface for ST. Experimental design III

Optimize Response

Goal: maximize shrinking temperature

Optimum value = 75ºC

Optimum value for factor NaCOOH= 1.414
Optimum value for factor HCOOH= 1.414

<u>Results for tensile strength (Tens)</u>

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-Ratio**	**P-Value**
A:NaCOH	7184.83	1	7184.83	2.47	0.1473
B:HCOOH	25.06	1	25.06	0.01	0.9279
AA	22684.30	1	22684.30	7.79	0.0191
AB	2916.00	1	2916.00	1.00	0.3405
BB	7564.40	1	7564.40	2.60	0.1381
Total error	29113.30	10	29113.30		
Total (corr.)	69488.00	15			

R-squared = 58.1031 percent
R-squared (adjusted for d.f.) = 37.1547 percent
Standard Error of Est. = 53.9567
Mean absolute error = 28.0002
Durbin-Watson statistic = 2.36478 (P=0.2714)
Lag 1 residual autocorrelation = -0.18239

The ANOVA table partitions the variability in Tensile into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 58.1031% of the variability in Tensile. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 37.1547%. The standard error of the estimate shows the standard deviation of the residuals to be 53.9567. The mean absolute error (MAE) of 28.0002 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

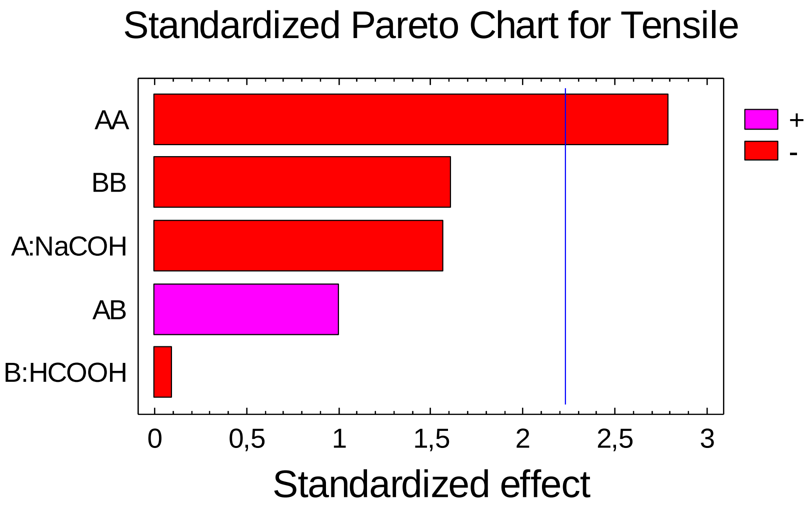


Figure 51: Standardized Pareto Chart for Tensile. Experimental design III.

When excluding all effects at p-value lower than 0.05, estimated response surface is calculated as in figure 52.

$$\text{Tensile} = 585.62 - 53.25\ (\text{NaCOOH})^2$$

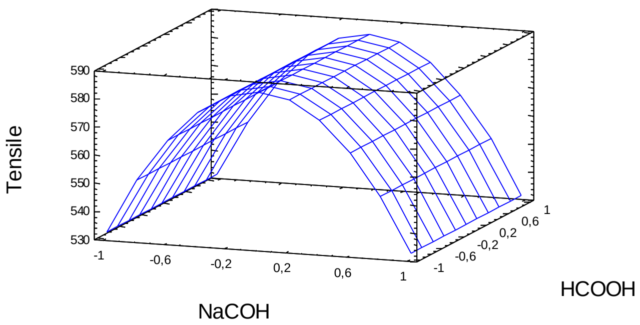


Figure 52: Tensile strength estimated response surface. Experimental design III.

Optimize Response

Goal: maximize Tensile

Optimum value = 585.62 N

Optimum value for factor NaCOOH= 0.0
Optimum value for factor HCOOH= 0.0

Results for elongation (Elon)

Analysis of Variance for Elongation

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:NaCOH	98.9975	1	98.9975	31.79	0.0002
B:HCOOH	2.3579	1	2.3579	0.76	0.4046
AA	36.1251	1	36.1251	11.60	0.0067
AB	25.0000	1	25.0000	8.03	0.0178
BB	6.1250	1	6.1250	1.97	0.1911
Total error	31.1446	10	3.1144		
Total (corr.)	199.7500	15			

R-squared = 84.4082 percent
R-squared (adjusted for d.f.) = 76.6123 percent
Standard Error of Est. = 1.76478
Mean absolute error = 0.866497
Durbin-Watson statistic = 1.68533 (P=0.3117)
Lag 1 residual autocorrelation = 0.157334

The ANOVA table partitions the variability in Elongation into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 3 effects have P-values less than 0.05, indicating that they are significant the 95.0% confidence level. These effects are % NaCOOH and its quadratic effect and the interaction with % HCOOH.

The R-Squared statistic indicates that the model as fitted explains 84.4082% of the variability in Elongation. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 76.6123%. The standard error of the estimate shows the standard deviation of the residuals to be 1.7648. The mean absolute error (MAE) of 0.8665 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

Excluding B and BB effects with P-value less that 0.05, we obtain the Pareto chart in figure 53:

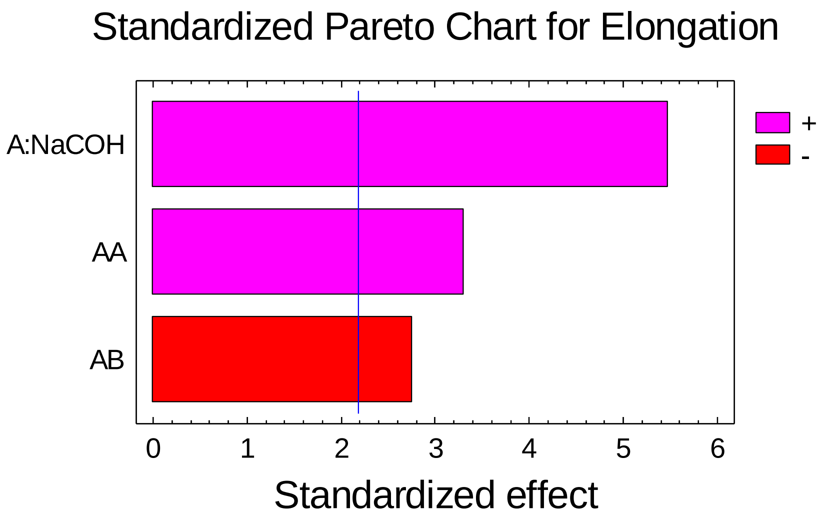


Figure 53: Standardized Pareto chart for Elongation. Experimental design III

$$Elon = 42.56 + 3.52\ NaCOOH + 2.13\ (NaCOOH)^2 - 2.5\ NaCOOH{*}HCOOH$$

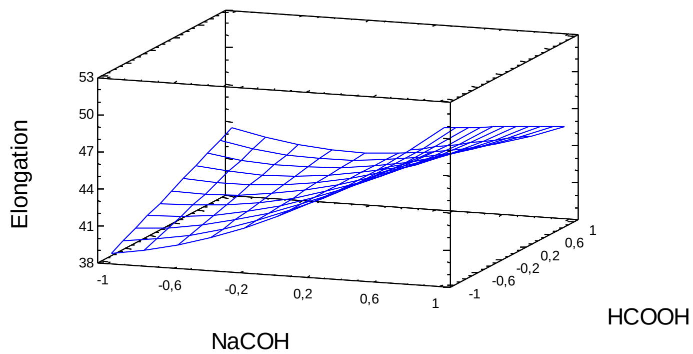


Figure 54: Elongation response surface. Experimental design III

Optimize Response

Goal: maximize Elongation

Optimum value = 56.79 mm

Optimum value for factor NaCOOH= 1.414
Optimum value for factor HCOOH= -1.414

Results for tear load (tear)

Analysis of Variance for Tear

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:NaCOH	58.0845	1	58.0845	1.25	0.2888
B:HCOOH	22.6323	1	22.6323	0.49	0.5003
AA	5278.7800	1	5278.7800	114.04	0.0000
AB	400.0000	1	400.0000	8.64	0.0148
BB	1140.0300	1	1140.0300	24.63	0.0006
Total error	462.8990	10	46.2899		
Total (corr.)	7362.440	15			

R-squared = 93.7127 percent
R-squared (adjusted for d.f.) = 90.569 percent
Standard Error of Est. = 6.80367
Mean absolute error = 3.03097
Durbin-Watson statistic = 2.12887 (P=0.4763)
Lag 1 residual autocorrelation = -0.0644357

The ANOVA table partitions the variability in Tear into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, the quadratic effects of % NaCOOH and % HCOOH and the interaction effect among them have P-values less than 0.05, indicating that they are significant at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 93.7127% of the variability in Tear. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 90.569%. The standard error of the estimate shows the standard deviation of the residuals to be 6.80367. The mean absolute error (MAE) of 3.03097 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

Excluding A and B effects with P-value less that 0.05, we obtain the Pareto chart in figure 55:

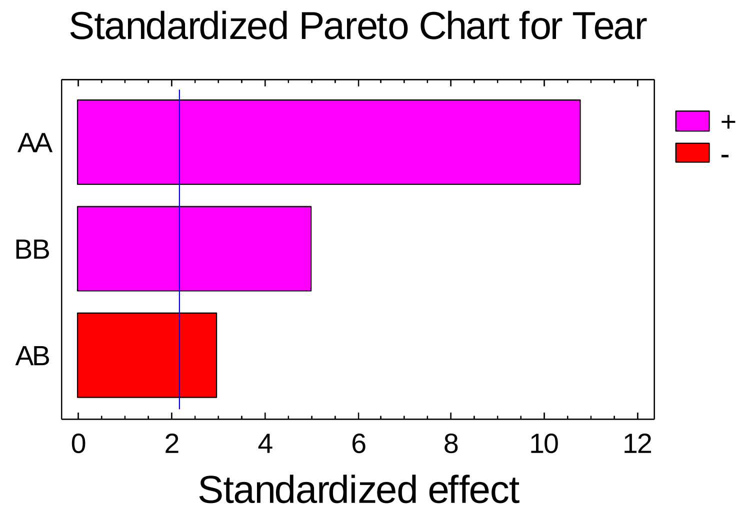


Figure 55: Standardized Pareto chart for tear load. Experimental design III

$$Tear = 89.00 + 26.69*(NaCOOH)^2 – 10.0*NaCOOH*HCOOH + 11.94*(HCOOH)^2$$

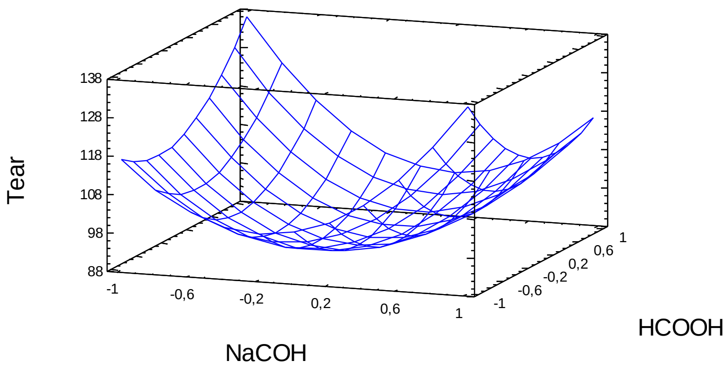


Figure 56: Tear load estimated response surface. Experimental design III

Optimize Response

Goal: maximize Tear

Optimum value = 184.25 N/mm

Optimum value for factor NaCOOH= -1,414
Optimum value for factor HCOOH= 1,414

10.4 Conclusions of the Experimental Design III:

- Shrinking temperature increases with the amount of sodium formate and formic acid that means at the highest pH conditions before the pretanning process and the lowest pH to fix the tannins at the end, previous to the mechanical operations.
- The amount of formic acid and sodium formate has not statistically significance on tensile strength, but the effect of the quadratic % NaCOOH. Optimal values for the application are in central points.
- The amount of sodium formate, it quadratic effect and interaction with % HCOOH have statistically significance. The increase of sodium formate increases elongation.
- The quadratic effects of percentage of formic acid and sodium formate have statistical significance on the results of tear load among the interaction. Values are optimized when amount of sodium formate is lowered and formic acid is increased.
- The amount of sodium formate or the highest pH for conditioning the pelts before the pre-tanning process has a positive effect on the results of shrinking temperature and tensile elongation at 95% of statistic confidence level.
- The amount of formic acid or the lowest pH at the end of the pre-tanning process in order to fix non-exhausted tannins on the collagenic structure, has a positive effect on the results of shrinking temperature at 95% of statistic confidence level.

The calculated optimal values obtained from the mathematic models for each of the variables considered in this Experimental Design III are summarized on table 45:

	NaCOOH	**HCOOH**
Shrinking Temperature	1.414	1.414
Tensile Strength	0.0	0.0
Elongation	1.414	-1.414
Tear load	-1.414	1.414

Table 45: Optimal values for each variable. Experimental Design III

These values will be considered according to the requirements of the final article to be manufactured with the subsequent processes of retanning, fatliquoring, dyeing and finishing.

Shrinking temperature needs to be maximized for ensure heat resistance to the mechanical treatments after Pretanning, mainly in shaving to obtain appropriate and regular thickness among the different parts of the hides or skins.

The physical properties will depend on the performance of the goods manufactured with the leather article. While tear load is an important property for apparel, elongation is fundamental for the manufacture of shoes where leather is exposed to high tensile forces.

In general, however, all these physical properties considered in this thesis are common for most of the leather articles produce for the shoe, apparel, upholstery and leather good markets, thus the mean of all these coordinate values is considered as the most balanced value:

$$\text{Coordinate value NaCOOH} = \text{Me}\ [S_T, \text{Tens, Elon, Tear}] = 0.707$$

$$\text{Coordinate value HCOOH} = \text{Me}\ [S_T, \text{Tens, Elon, Tear}] = 0.707$$

According to the formulas for Codification Table, Design III, Table 40, for sodium formate:

$$V_x = (V_0-V_{-1.414})(x+1.414)/1.414+V_{-1.414}$$

$$V_{0.707} = (0.5-0)(0.707+1.414)/1.414 + 0 = 0.75$$

% NaCOOH = 0.75 %

According to the equation of the fitted model to describe the relationship between pH and independent variable of % NaCOOH through a multiple linear regression model as defined in 10.2.1, the optimal conditioning pH of pelts previous to the pre-tanning process with tara tannins is:

$$\mathbf{pH =} 3.15 + 2.78*\text{NaCOOH} \mathbf{= 5.23}$$

According to the formulas for Codification Table, Design III, Table 40, for sodium formate:

$$V_x = (V_0-V_{-1.414})(x+1.414)/1.414+V_{-1.414}$$

$$V_{0.707}= (0.6-0.2)(0.707+1.414)/1.414 + 0.2 = \mathbf{0{,}80\%}$$

According to the regression equation of the fitted model to describe the relationship between pH and independent variable of % NaCOOH and % HCOOH as defined in 10.2.2, the optimal conditioning pH of pelts previous to the pre-tanning process with tara tannins is:

$$\mathbf{pH\ final =} 3.65 + 0.31*\%\ \text{NaCOOH} - 0.16*\%\ \text{HCOOH} - 0.19 * (\%\text{NaCOOH})^2 =$$
$$\text{pH final} = 3.65 + 0.23 - 0.13 - 0.11 = \mathbf{3.64}$$

These results applied to the recipe for wet-white with tara tannins are shown in table 46.

Operation	**%**	**Product**	**T °C**	**Running time**	**Control**
Conditioning	50	Water	20		
	4	Sodium chloride			
				10 min.	°Bè=6
Add hides to drum				10 min.	pH= 3.3
Depickling	**0.75**	**Sodium formate**			
	0.38	Sodium bicarbonate		120 min.	**pH= 5.23**
Drain					
Pretanning	50	Water	20		
	12	**Tara powder**			
	7	**Naphthalene sulphonic syntan liquid**		Overnight	
	0.8	**Formic acid 85%**		120 min.	**pH=3.64**
Drain					
Washing	300	Water	20	20 min.	
Drain					
Horse up. Samming. Shaving.					

Table 46: Final recipe for wet-white with tara tannins

11. Thesis practical validation: Manufacturing a sustainable automobile-interior leather article.

Beyond the mathematic models used to validate this thesis, the latest section of the research intends to present the manufacture an automobile-interior leather article base on the results from previous sections. Therefore, a full bovine hide was processed with a wet-white formulation based on tara tannins at pilot scale. The hide was split in two sides for better handling. After pretanning according to the findings developed during the experimental designs, sides were shaved to the thickness for the required car upholstery, retanned, fatliquored and dyed following a standard formulation. One of the sides was finished to manufacture a headrest of a car seat, while samples were prepare according to International Standard EN ISO 2419 / IUP 1 and IUP 3, "Leather – Physical and mechanical tests – Sample preparation and conditioning"[51, 52].

Material: Pickled pelt from Russia bovine hide. pH = 3.5. Total weight 11.580 kg. Side 1: 5.260 kg. ; side 2: 6.320 kg.)

Equipment: Simplex DF drum.

Procedure: Drums are empty. Pelts horsed up.

Operation	**ºC**	**%**	**Product**	**Time**	**Remarks**
Conditioning	20	200 12	Water Common salt Add pelts to the drum	 10 min Over night	 ºBè = 5.5.
Drain					
Depickling	20	50 4 0.75 0.38 1.2 0.6	Water Common salt Sodium formate Sodium bicarbonate Sodium formate Sodium bicarbonate	 10 min 2 h. Over night	 ºBè = 7 pH = 3 pH = 3.78 *Note 1* pH = 5.20
Drain					
Pretanning	20	50 12 7 0.5 0.6	Water Tara powder Naphthalene sulphonic syntan (1:10) Formic acid 85% (1:10) Formic acid 85% (1:10)	 6 h 30 min. 2 h	*Note 2* *Note 3* pH = 3.82. *Note 4* pH = 3.6
Drain					
Washing	20	200	Water	15 min.	
Drain					

51 Normas IUP. Ensayos físicos de curtidos. Asociación Química Española de la Industria del Cuero. Octubre 2001. Pag, 3 and 12.

52 Journal of the Society of Leather Technologists and Chemists (JSLTC). Volume 82. September-October 1998. Number 5. ISSN 0144-0322. Pages 190. 192 and 199.

Washing	20	200	Water	15 min	
Drain.					
Horse up (*Note 5*). Samming. Shaving to 1.2 mm thickness (*Note 6*)					

Note 1: Due to the high acidity from preserving pickle, % of sodium formate and % of sodium bicarbonate have to be increased to achieve the desired pH of 5.23. To ensure pH is completely through the pelt section, drum is running over night.

Note 2: At the pH of 5.2, collagen does not swell thus addition of common salt is not necessary[53,54]. Volume of bath has to be minimized to increase mechanical action and aid the penetration of the chemicals in the inner layer of the collagen structure.

Note 3: Tara powder is added in solid form to avoid a quick reaction on the pelt surface, thus blocking tannins to be diffused inside the structure.

Note 4: The tanning completion was visually checked. A thin layer remained white but, checking with ferric sulphate (dark blue indicator), it showed a complete vegetable tanning through the cross section of the leather. % of formic acid needed to be adjusted to achieve the pH of 3.64.

Note 5: Leather was very clean with uniform light brown color. Shrinking temperature achieved 70º C considering that the tanning was completed. Bath contained a high amount of insoluble matter. Superficial astringency on leather surface was characteristic of leather tanned with vegetable tannins.

Note 6: After shaving leather was completely stained with dark blue spots. After cleaning with a chelating agent, e.g. ethylenediaminetetraacetic acid (EDTA), stains were removed and the even light brown color was fully recovered. Leather resisted and damage of shrinking was not observed. The behavior for shaving operation was optimal due to the superficial astringency.

The two shaved sides were weighted. Total shaved weight 5.650 kg (50% of pelt weight). Sides were loaded to the Simplex DF drum.

Operation	**ºC**	**%**	**Product**	**Time**	**Remarks**
Washing	35	300 0.5 0.5 0.3	Water Oxalic acid EDTA Non-ionic degreasing agent (45%)	30 min.	
Drain					
Washing	35	300	Water	15 min	
Drain					
Retanning	30	150	Water		

53 E. Gratacos, J. Boleda, M. Portavella, J.M. Adzet, G. Lluch. Tecnología química del cuero. Barcelona 1962. Pag. 47

54 Antoni Ylla-Catala. La Ribera. Grup Colomer. Vic. 2008. Pag. 34.

		3	Neutral salt of dicarboxilic acid with buffering effect. Powder		
		1	Sodium formate		
		0.3	Sodium bicarbonate	30 min	pH = 4.7
Fatliquoring I		1	Anionic phosphoric ester 55%		
		3	Animal sulphitated oil 80%		
		3	Mixture of synthetic oils	40 min	
		1.5	Neutral salt naphtha. sulphonic acid		
		6	Synthetic substitution syntan 96%		
		0.5	EDTA		
		10	Tara powder	60 min	
Dyeing		0.5	Neutral salt naphtha. sulphonic acid		
		3	Metal-complex grey dye	60 min	
				Overnight	15 min/hour
	50	80	Water		
		1.5	Formic acid 85% (2x15 min)	60 min	
Drain					
Washing	50	300	Water	15 min	
Drain					
Fatliquoring II	50	200	Water		
		7	Animal sulphitated oil 80%		
		4	Anionic phosphoric ester 55%	60 min	
		4	Protein based syntan	15 min	
		2	Tara powder	20 min	
		1	Formic acid 85% (2x10 min)	30 min	pH = 3.4
Drain					
Washing	20	300	Water	20 min	
Drain					
Horse up 24 hours. Samming. Vacuum dry. Hang for drying. Toggling. Staking. Conditioning. Thickness: 1.5 mm					

Samples were prepared and conditioned from one of the sides according to “EN ISO 2419 IUP 1 & IUP3, Leather – Physical and mechanical tests methods – Sample preparation and conditioning” for quality testing. The rest of the side was finished by coating polyurethane resins, cross-linkers and auxiliaries to obtain the final feel and esthetics required for a commercial article. The side was milled, shaved to 1.2 mm of thickness and printed. See photo 15.

The European standard “prEN 14906 – Leather – Leather for automotive – Tests methods and testing parameters” gives guidelines to select the test methods to assess the performance of leather for automotive. The parameters for testing are divided in fundamental and complementary properties. Fundamental properties consider basic parameters (apparent density mass per unit area and thickness), tensile properties, stiffness in blending, durability/wear, ageing, lightfastness, fastness, emission behavior and others. Most of these parameters refer to the finishing properties or substances beyond the scope of this thesis. For this reason, quality tests focus on tensile and ageing properties that can be influenced by the pretanning operations. Furthermore, lightfastness is also assessed as an added value of tara tannins to the final article despite the latest rating is obtained when coating with pigments. In any case, it is well known that higher lightfastness in crust can avoid excessive use of pigments, thus, natural aspect of the final article can be preserved if the quality of the grain is acceptable.

Photo 15: Car-interior leather from pretanning with tara tannins.

Top: crust after wet-end. Down: finished article

Test methods and results, according to prEN 14906 guidelines are indicated in table

Test method	Concept	Expression of results	Result
EN ISO 3376 / IUP 6	Tensile strength	NPa	10.2±0.1
EN ISO 3376 / IUP 6	Percentage elongation at break	%	41.1±1
EN ISO 3377 / IUP 8	Tear load at single edge	N	54.6±0.1
ISO 105-B02/IUF 402	Lightfastness (photo 16)	Blue scale	3
EN ISO 17227/IUP 35	Dimensional stability	% 150ºC/15 min % 150ºC/30 min % 150ºC/60 min % 200ºC/15 min	2.8±0.2 2.8±0.2 3.4±2 burning

Table 47: Quality test results. Car-interior leather from pretanning with tara tannins.

Photo 16: Blue scale for lightfastness

Those quality results can be compared with the technical specifications that car manufactures request to their suppliers to be completely fulfilled according design car models. For this reason three European Original Equipment Manufacturers (OEM) of automobile groups were approached to obtain information on engineering material data that have to be conformed to the Companies in leather deliveries to the vehicle manufacturing chain. Those groups were Volkswagen, Ford and PSA Peugeot – Citroën.

Due to industrial confidentially, the whole documents cannot be reproduced in this research report.

Despite each OEM have its own standards for testing, Volkswagen and Ford follow the ISO standards or values that can be compared, while PSA cannot be considered in this assessment.

<u>Tensile strength:</u>

Volkswagen: ≥ 130 N

Ford: ≥ 125 N

Manufactured leather article pre-tanned with tara = 10.2 Npa

The tensile strength, T_n, in NPa is calculated using the equation:

$$T_n = F / w * t \rightarrow F = T_n * w * t$$

F = highest force recorded in N

w = is the mean width of the test piece, in mm. 10 mm has been applied

t = is the mean thickness of the test piece, in mm. 1.5 mm as indicated

T_n = 10.2 NPa * 10 mm * 1.5 mm = 153 → **Pass**

Tensile elongation at break:

Volkswagen: 35 – 60 %

Ford: 30 – 70 %

Manufactured leather article pre-tanned with tara = 41.1 % → **Pass**

Tear load:

Volkswagen: ≥ 25 N

Ford: 70 N (ASTM D 5733 not comparable with ISO 3377)

Manufactured leather article pre-tanned with tara = 54.6 N → **Pass** (for VW)

Lightfastness:

Volkswagen: ≥ 3 rating

Ford: 225.6 kJ/m^2, rating 3; 488.8 kJ/m^2, rating 4

Manufactured leather article pre-tanned with tara = 3 → **Pass**

Considering that manufactured leather article pre-tanned with tara is not finished and selected pigments of normal application in tanneries increase this property.

Dimensional stability:

Volkswagen: ≤ 5 % (120ºC/168 h)

Ford: ≤ 5 % (100ºC/3 cycles)

Manufactured leather article pre-tanned with tara = 3.4 (150ºC/60 min).

Test methods differ, but shrinking, in any case, is lower that requirement → **Pass**

These results confirms that pre-tanning (wet-white) with tara tannins and according the proposed technology described in this thesis, the quality requirements for leather articles for vehicle interiors can be achieved. It is important, however, to point out that the final properties will also depend on other substances and operations during the whole processing, e.g. fatliquors, retanning agents and finishing.

12. Final conclusions

This thesis has validated the compliance of the two major hypotheses of sustainability and innovation implicit in the title of the work. It proves the fact that tannins from the pods of tara fruits are able to respond as newest technologies of tanning leather complying article quality standards and meeting the highest exigencies of sustainability required by consumers and general community.

The tara sourcing of tannins has been assessed by approaching the values to the “Triple Boton Line” objectives of environment (planet), social (people) and economic (profit) while experiments have been designed in order to optimize a wet-white recipe to be submitted to the chemical and mechanical treatments in order to manufacture all kind of articles and able to meet the physical requirements for consumer leather goods.

- Environment: The agro forestry of the tara tree benefits to the environment with important contributions to the fixation of carbon and nitrogen to the soil, as alternative to reforestation and protection to soil erosion. It enables ecosystems to survive and minimize consumption of materials which exploitation requires energy and water among other resources or, contrary to other vegetable tannins, production does not depend from other industries or implies deforestation. Tara tannins are renewable as they are available in a continually renewing matter. Regulations of chemicals, mainly in Europe, recognize the use of non-hazard substances from natural origin if not chemically treated.
- Social: The tara tree is suitable for agro forestry and represents a source of economical activities for Andean Regions by exporting products to the leather markets. Also, other products from the fruit of tara are very valuable in other industries as gum for food and industrial applications and polyphenols with properties in medicine. Its application in tanneries and leather articles is safe for workers and consumers.
- Economic: The fruits of the tara tree contain valuable substances. Among them, the pods are high concentrated in tannins. Agro forestry is the solution to ensure quality and consistency on production volume and prices to supply the high potential demand of tannins for the world wide leather production. Leather treated with tara tannins are white and had excellent light fastness and, therefore, are specially suitable for pastel shades in articles submitted to extreme atmospheric conditions. The automobile industry is concerned on green issues and strictly claims to suppliers recyclable materials or, if disposal, the lowest environmental impact. The wet-white leather solves these requirements. Tanners manufacturing this kind of leather articles use tara as a retanning agent while glutaraldehide is the main tanning agent.

The hypothesis of tara pre-tanning process as innovative technology in the leather making is proven with the analysis of the performance of the pelts submitted to the treatment of tara, blended with general synthetic tannin groups, at different ratios and application conditions.

Tara commercial samples from various suppliers were analytically characterized by means of pH, and content of water, total solids, soluble solids, non-tannins, tannins and insoluble matter, and compared to determine significant differences among them. All these variable results from the chemical tests did not showed significant statistic differences and deviations among them did not exceed the limits of a normal distribution.

Commercial tara powders currently available in the market are reach in tannins (ca. 50%) and content a high amount of insoluble matter (>20%).

The normal distribution was used for comparing further characterizations of tara powder processed in the laboratory from fruits obtained in different regions of Bolivia. Despite their natural origin of tara powder, composition of ingredients maintained consistent ratios. Therefore, agro-forestry of tara is suitable in a wide range of climate conditions without significant deviation in their composition.

A correlation of non-tannins content and the Gallic acid hydrolyzed from tannin molecule was tested but not proven as the null hypothesis could not be statistically rejected. However, the hydrolysis of Gallic acid can be explained after the treatment of tara powder exposed to time and temperature according to the lineal function:

$$\text{Content of free Gallic Acid (mg/kg)} = 1{,}224.1 + 15.9\ T$$

The hypothesis of tara pre-tanning process as innovative technology in the leather making has been proven with the analysis of the performance of the pelts submitted to the treatment of tara, blended with general synthetic tannin groups, at different ratios and application conditions.

The tara tannins are suitable to transform collagen protein into leather by stabilizing its structure from hydrolysis, mainly bonding the CO-NH linkage of the protein through the phenolic hydroxyl group, among other side reactions.

Experimental Design I, blend of tara powder with syntans, naphthalene sulphonic or auxiliary type and phenol condensation or substitution type have shown that the tara powder has good properties because its tanning effect, but it has certain limits to react in the interior of the deeper layers of the collagen structure. Results have demonstrated that the blend with naphthalene sulphonic syntan is the most suitable for tanning with tara tannins acting as a dispersant auxiliary.

Design II has optimized the ratio of components of the blend of tara tannins with a naphthalene sulphonic syntan.

- Synergy is obtained by increasing the values of naphthalene sulphonic when tara has limits: shrinking temperature due the improvement of the tara tannin penetration, tensile elongation an tear load.
- Considering the optimal combinations for each variable, the mean of the variables and the concentration of tannins, the calculated ration among them is:

67 parts of tara tannin

33 parts of naphthalene sulphonic syntan

Design III has optimized the conditions for best application of the bend obtained in the Design II, by means of measure of pH at the beginning and at the end of the process using a blend of sodium formate and sodium bicarbonate (2/1) and formic acid, as pH regulator agents. The calculated optimal pH has been:

$pH_{initial} = 5,23$

$pH_{final} = 3,64$

The results of the experimental research have been validated with the complete manufacture of a leather article for automotive interior and physical tests reject the null hypothesis (tara tannins are not suitable for wet-white).

13. Recommendations for new researches.

The conclusions of this thesis can support further experiments to develop technologies for a new range of leather articles. Their objectives need to focus on satisfying increasing demands of sustainable and safe material used for manufacturing goods like shoe, apparel or upholstery.

Design of new formulations using sustainable vegetable tannins to manufacture eco-friendly leather articles by improving the competitiveness of SMEs in the International leather market have to be evaluated as a substitution of the chrome tanning for high quality leather. Limits of the cross-linking between the tara tannins and the collagen structure have been solved in this research by blending them with synthetic tanning agents, naphthalene sulphonic syntan, mainly. This was due to the current situation of the supply chain of the tara fruit by-products and the simplicity of the process also constrained by costing factors. However, new researches are necessary to obtain and concentrate the tannins with better properties according the final leather articles quality requirements. Therefore, new works can focus on:

- Removal or reduction of insoluble matter from tara powder, either by sieving or filtering a solution. In any case, the filling effect of insoluble matter during the tanning operation has to be considered for certain articles. Solubilization technologies of this matter with certain chemical, e.g. sulphitation commonly used for other vegetable extracts as sweet quebracho, has to be observed if further commercialization is possible or registrations are required due to the subsequent chemical molecule modification.
- Extraction of tannins to increase the active matter for commercial products. As tara tannins are hydrolysable, water solution at certain temperature and concentration by evaporation or atomization can be processed without the need of registration in REACH. Hydrolysis conditions need to be considered to avoid an excess of non-tanning matter (e.g. Gallic acid and polymers of low molecular size).
- Research of properties of tannins according to their molecular size. Fractions of tannins can be separated by, e.g., reverse osmosis, and tanning properties can be assessed from light to heavy portions to be applied according the needs of specific articles.
- Other blends, besides the syntans analyzed in this thesis, can be assessed considering other environmental needs. E.g., mixtures with other vegetable tannins either hydrolysable like chestnut or polyflavonoids tannins like quebracho or mimosa.

The first part of this thesis focuses on the concept of sustainability in general terms with the aim to validate the hypothesis within the scope of this research. However, new researches are necessary to assess all the aspects of the concept according to the sections 1 and 2.

- Life cycle assessment to the three bottom lines: social, environmental and economic. The holistic approach have to include not only the raw material production that has also other considerations mentioned underneath, but manufacture, logistics, uses and disposal of the consumer articles.

- A very special emphasis requires the strategies to mitigate the climate change and the reduction of greenhouse gases. Forestry plays a critical role in the carbon cycle by absorbing carbonic dioxide from the atmosphere through the photosynthesis mechanism and accumulating carbon as biomass. Currently, carbon market regulations are under big discussion in international forums or become voluntary as a sustainable responsibility of corporations and societies. The contribution of the tara agro-forestry could be assessed under the United Nations Framework Convention on Climate Change (UNFCCC) and/or the Kyoto Protocol (PK) to fight global warming. Therefore, despite the incipient and complexity of forestry projects, it is necessary to include tara agro-forestry to pull towards international investments and support the use of natural substances for traditional and well established industries like tanning, as alternatives to expensive synthetic materials.
- Assessment of leather article consumer good disposal after their use-life. Differently from other tanning substances, mainly chromium, tanning with tara leather maintains as organic material. Disposal of leather and by-products like shavings and trimmings can find further uses like fertilizers or, at least, high disposal costs.

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Photos: Joan C. Castell, Dr. Fimo Aleman, AIICA, David Solano, CTFC

Tara (Caesalpinia spinosa):

The sustainable source of tannins for

innovative tanning processes

ANNEXES

Annex 1: Botanic characteristics of Caesalpinia spinosa

Etymology:

- Caesalpinia in honor to Andrea Caesalpini (1524 – 1603), Italian botanic and philosopher.
- Spinosa: from Latin *spinosus – a – um*, spiny
- Origin: Unknown (Cardenas, 1989).

The tree:

Photo 17: Caesalpinia spinosa (tara): the tree.

The tara tree is small, only 2 – 3 meters high, but oldest species can achieved up to 12 meters; short, cylindrical and sometimes twisted trunk with a dark grey bark with scattered prickles, with dense and rising branches and twigs, sometimes from the lowest part, and leafy and umbrella-shaped top. Pivot roots and abundant secondary roots. It is a leguminous plant and fixes the nitrogen. BASFOR[55] reports selected trees to supply germoplasma of 3 – 11 m. high, trunk diameter average 22 cm, and top diameter of average 5 m.

55 BASFOR: Semillas Forestales – Plantas y Asesoramiento técnico. Centro de Semillas Forestales. ESFOR (School of forest science. Universidad San Simón. IC / Cosude. Avda. Atahualopa, final norte s/n. Cochabamba. Bolivia. (Date of consultancy June, 12, 2009) http://www.umss.edu.bo/Academia/Centros/Basfor/

Leaves:

Photo 18: Caesalpinia spininosa (tara): leaves.

Alternate composed, like feathers, slightly prickly, ovoid and brilliant leaflets of dark green color measuring 15 cm of length.

Flowers:

Photo 19: Caesalpinia spinona (tara): flowers

Hermaphrodites, yellow to red color, grouped in grapes at the extreme of the terminal branches. Flowers are 15 to 20 cm long, irregular and tubular calyx, short twice bigger than stamens, long sepals, corolla with free petals, grapes 8 – 15 cm. long.

Fruits and pods:

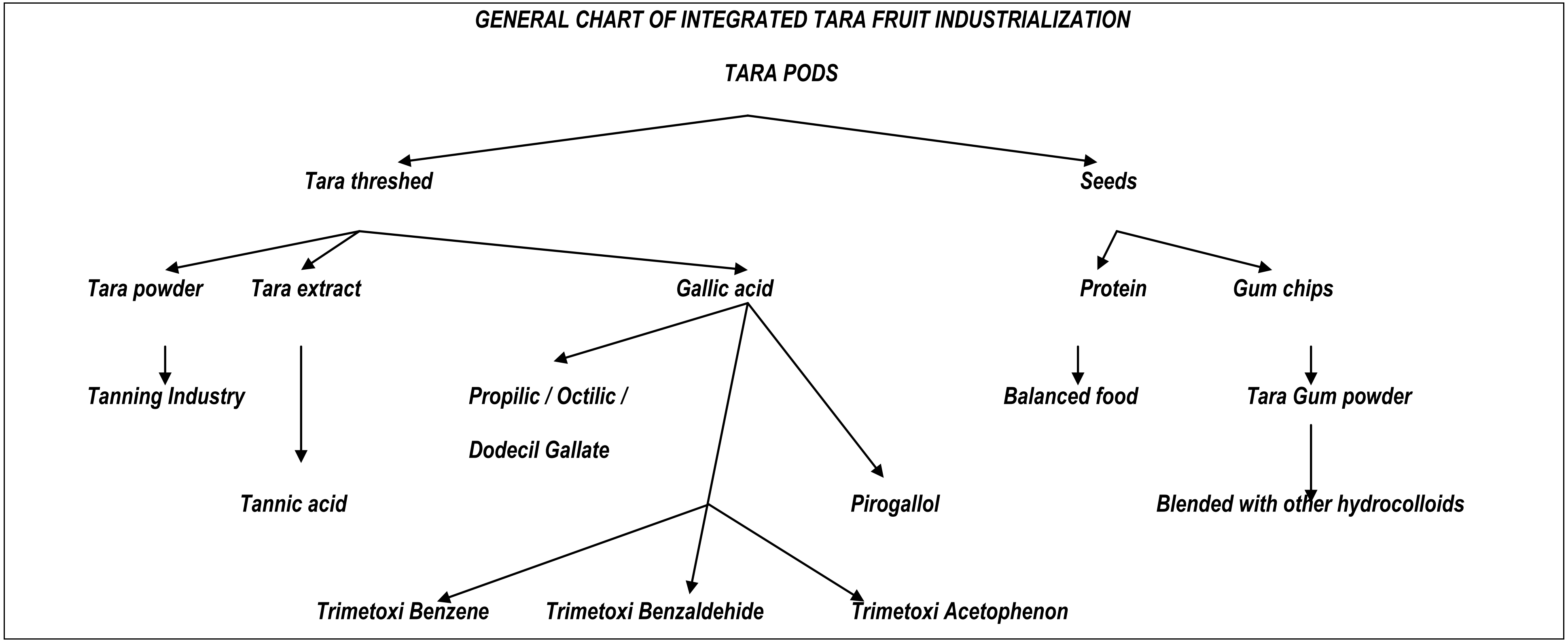
Photo 20: Caesalpinia spinosa (tara): the fruit

The fruit of Caesalpinia spinosa is a flat yellow to orange pod up to 10 cm long and 2 cm wide. They are fragile when are dry. Every pod contains up to 7 round seeds with a diameter of 5 to 7 mm. The color of the seeds is dark red when mature.

They weight 3,3 g average, what means one kg of seed needs 305 fruits.

Photo 21: Tara agro forestry exploitation in Peru

Annex 2: General chart of integrated tara fruit industrialization



TARA Y SU INDUSTRIALIZACIÓN INTEGRAL. Luís Germán Zúñiga Sánchez. Sociedad Mercantil Exportación (SOMEREX). October 2009

Annex 3: Pretanning-retanning recipe for leather car upholstery

Article: Soft nappa, chrome-free for car interior.

% calculate on pelt weight

Hides are soaked, limed, unhaired, delimed, bated and pickeld as usual process in factory.

pH before pre-tanning = 3 – 3,1

Operation	%	Product	Time	Control
Pre-tanning	2,5 2 3	Glutaraldehyde 30% Basifying Sulphonic syntan	2 hours 3-4 hours 3-4 hours	pH = 3 pH=3,9
Run 10 1t 10 rpm minutes every hour overnight. Next morning: adjust pH=4–4,1 Wash and drain. Shaving to 1,2 mm. thickness to obtain WET-WHITE				
Washing	200	Water 30ºC	10 min.	
Drain				
Retanning	200	Water 30ºC		
	0,3	Sodium formate		
	0,3	Sodium Bicarbonate	20 min	pH 4,9
	6	Liquid sulphonic syntan	20 min	pH 4,5
	2	Synthetic oil	20 min	
	8	Liquid sulphonic syntan		
	5	Granulated sulphonic syntan	20 min	
	5	Tara powder		
	8	Liquid sulphonic syntan		
	5	Granulated sulphonic syntan		
	5	Tara powder	60 min	
Dyeing	1	Amphoteric dyeing auxiliary		
	1	Dyes	360 min	
		Overnight. Run every 10 min		
	1	Formic acid 85%	60 min	pH 3,8
Drain				
Washing	200	Water 50ºC	10 min	
Drain				
Fatliquoring	200	Water 50ºC		
	8	Synthetic oil		
	2	Lecithin oil	60 min	
	1,5	Formic Acid 85%	30 min	
Drain				
Washing	200 0,2	Water 40% Anionic tensoactive	10 min	
Drain Unload Horse up and mechanical operations				

Photo 22: Automobile car interior. Auto leather upholstery

Annex 4: Tara fruit supply chain.

Forestry farmers:

Photo 23: Young tara forestry. Cochabamba. Bolivia

The forestry farmers own or rent areas where tara trees grow, either in plantations or wildly. When pods are ripe, they fall down and farmers harvest them to be traded in local markets or to be sold to the collectors.

Most of these farmers have 4 or 5 trees in their properties but also big farms growing up large forests can be found.

During the execution of this thesis, it was possible to visit a farm 100 kg south Lima. The farm includes a huge production of sugar-cane with mechanized harvest. The areas where machines are not able to work properly, it is used for growing tara forests but profiting, also, manpower and other equipment like watering facilities.

Production is responsibility of the farmers. The farmers prepare the soil, weed, sow, fertilize, irrigate, trim and harvest. The farmers also sort the production.

Collectors / wholesalers

Photo 24: Collectors and wholesales dealing with tara pods

Collectors, known in the Andean regions as a “acopiadores”, buy and gather the pods from different farmers. They organize bulk, unload, sort, store, load and transport the products. Collectors / wholesalers may be:

- *Local collectors*: they buy from small farmers and sell to intermediates. Most of them deal with more than one single intermediate of directly to the exporters. Generally, they are financed by intermediates that advance capital to deal with farmers.
- *Intermediary collectors*: They obtain the pods directly from farmers or local collectors and they are the linkage with the transforming industries or the exporters.

The farmers and collectors that harvest the tara fruits sell them to the open market to the highest bidder. Supplies of tara from these producers do not meet demand and large buyers that purchase large amounts of tara.

Transforming industries:

Photo 25: Tara powder mill. El Callao. Peru

Transforming industries process the pods of the harvested tara trees to obtain the products ready to supply the different industrial sectors.

They receive the raw material from their own collectors, from intermediaries or directly from the farmers. They control the quality and the weight of the batches of pods, before processing and packaging. At the end, they deal with exporters.

Processing adds value to the physical product. Processing mainly takes place in Lima, where the companies are located with the equipment which is required for processing tara. The activities undertaken by processors are unloading, storage, processing, selection, packaging and transport.

Exporters

They are dealers. They buy tara tannin powder from manufacturers and sell to customers, mainly in foreign countries were product is distributed.

Export is the last step in the supply chain before the product enters in the targeted market. Exporters arrange international transport and deal with customs. They also coordinate the wholesale and processing of the product to be able to supply their customers on time.

Other actors:

- *Transport and logistics*: Either some private and other public companies transport the products from the farms to the local markets in provinces or from them to the manufacturers or to the exporters..
- *Technical services*
- *Forest* Caesalpina spinosa plants
- *Cattle farms:* manure
- *Nurseries:* seeds
- *Equipment suppliers*: manure, equipment

Other activities to be considered during the value chain include alternatives like organic production, grading tara seeds according to origin, resistance to illnesses, and ration of target products to be obtained, minimizing contamination by improving hygienic production conditions (HACCP), grinding of the endosperm to produced a powder, further grinding with finer mesh sizes, blending tara with auxiliaries to produce formulations which tailor to specific needs of end-users, packaging in paper bags with polyethylene lining (plastic inner bag), information provision (improving documentation), improving test method for analysis and quality control, etc.

Annex 5: Tara production in Peru, Bolivia and Equador

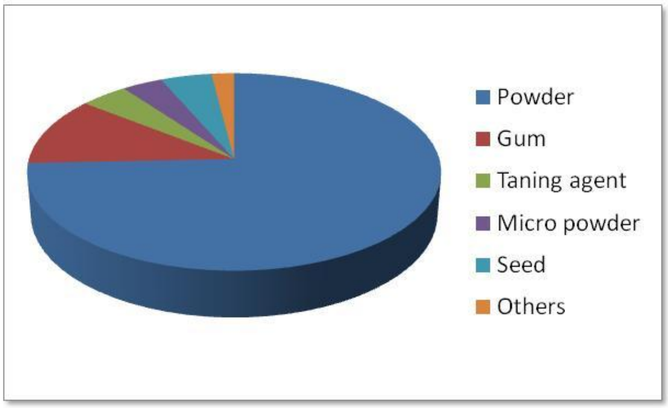
Production in Perú

According to Prompex[56] Perú produced in 2005, 13.264 tons of tara pods. The primary production regions were Cajamarca (36%), La Libertad (22%), Lambayeque (21%), Ayacucho (7%) and Huánuco (5%).

ECOBONA[57] estimated a production of 24.038 tons of tara fruits in 2007, 100% processed in the country.

Region	Ha	Production	%
Cajamarca	1328	10624	48%
La Libertad	427	3418	15%
Huánuco	311	2489	11%
Ayacucho	542	4338	20%
Other	159	1270	6%
	2767	**22139**	**100%**

The transformation of tara fruit resulted in 17.033 tones of tara products, distributed as 75% in tara powder, 11% in tara gum, 4% as a tanning agent, e.g. tara extract, 4% as a micro powder, 5% seeds and 2% others.



56 Comisión de Promoción del Perú para la Exportación y el Turismo. Ministerio de Comercio Exterior y Turismo. 2005

57 Almeida e. Taller Regional de la Tara. ECOBONA. Cajamarca 24-27 october 2007.

In 2005, Italy was the major destination of Peruvian tara products, 17%, followed by Argentina 16% and Brazil 15%. China imported that year 6% of the total production of tara products. However, during the last 3 years, exports to China increased from 1.000 tons in 2005 to 6.000 in 2009, half of the total exports. Argentina reduced drastically imports in the period 2008 – 2009 near 40% due to the strong reduction of leather for automobile. Argentina was the main supplier for automotive leather since the decade of the nineteen's but due to the international crises that affected automotive industry, especially in the USA, production went back to classical articles as shoe, clothing and leather goods. This situation affected the demand of tara either because formulations of these articles do not consider wet-white as intermediate commodity, nor tara is used for vegetable tanning but, mainly, quebracho.

Since 2003, the Consejo Nacional de la Cadena Productiva de la Tara (CONATARA) is the platform for the cooperation and dialog between the economic agents in the tara commercial chain and includes, also, institutions from administration and academy. The goal of CONATARA is to generate specific competitive commitments to add value to the tara products in its promotion in the international markets.

Production in Bolivia

Bolivia produces 200 tons of tara fruit per year. Exports go to Argentina, Uruguay and Chile, and to Peru in informal commerce practices. Bolivian tara seeds are exported to Switzerland as tara gum. There is a tendency to cultivate tara trees and to increase from the current 180 Ha to 2000 Ha in the coming years.

The two main regions of tara productions are Cochabamba and Potosi.

According to the ECOBONA-INTERCOOPERATON Regional program (2007) volume of tara products, after transformation of tara pods, is 115 Tm, 100 tones of tara powder, 30 tons of seeds and 21 tons of tara pods.

The Asociación Boliviana de Tara (ABT) was founded in 2007. Its members are ECOBONA, BASFOR, the Agronomy Faculty of the University of San Simon in Cochabamba, ESFOR (Forestry School), the University City of Sucre among other public and private institutions.

Production in Ecuador

Only two provinces in Ecuador, Imbabura and Chimborazo, produce tara fruit to the volume of 84 tons per year. A Spanish company, Cobad Export[58], purchases 75% of this production to be

58 Programa Nacional ECOBONA. Portal de Bosques Andinos (Date of consultancy December, 1, 2009) http://www.bosquesandinos.info/ECOBONA/TARA/TARABAJAIIIop.pdf

transformed in 68 tons of tara products. Tara powder is exported to Spain (17 tons) and commercialized to the tanneries in Ambato and Salcedo clusters. This company also produces 30 tons of seeds that are sold to Peru. The rest of 21 tons of tara pods are for local consumption, mainly in artisanal leather.

The CONAPROG (Consorcio Nacional de Productores de Guarango) is an organization to facilitate and promote the commerce of tara products.

Annex 6. International leather production. Figures and statistics

The best comprehensive source of information on production and trade in the leather sector is the "World statistical compendium for hides, skins and leather footwear", produced every two years by the Food and Agriculture Organization of the United Nations (FAO)[59].

The value of international trade of hides, skins achieves near 22,5 billion USD (average 2003-2005).

Commodity	Value	Volume
Raw hides & skins	5.008,5 Million USD	2675 Kt
Wet blue, crust and finished leather	17.477,7 Million USD	15.218 Million sq ft

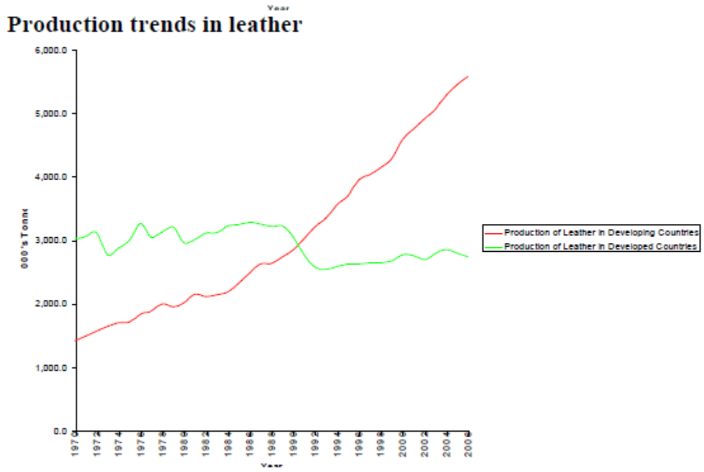
There are no statistics to comprise the internal trading and information on production and trade on a country basis will not be in the scope of this work. However, estimations from FAO account for a world production of 6.319,6 thousand tones of bovine hides corresponding to 344 million pieces.

Bovine hides and skins account for 65% of the worldwide leather production, while sheep skins 15 %, Goat skins 9 % and pig skins and other 11%

According to FAO statistics, the worldwide leather production in 2006 was 22.700.5 million of square feet (2.109 million of square meters). The main producer was China with a share of 29%. Italy was the second producer with 9,5 %, India (7,6%) and Brazil (7,2%). Thirty countries produced 91,7% of the global leather production.

Trends of production leather is quite stable in developed countries while increases in developing countries as a result of the FAO statistics analysis:

59 Chief, Raw Materials. Tropical and Horticultural Products Service. Commodities and Trade Division (ESC). FAO. Viale delle Terme di Caracalla. 0100 Rome. Italy. ESC-Registry@fao.org.



The tanning industry in Europe (E27) reports revenues for 10.365 million euro with a value added at factor costs of 1.975 million euro. There exist more than 3.000 tanneries, mostly in Italy and employees 50.800 persons, according to Eurostat 2007 statistics..

Europe is the largest market for leather goods production with 13.924 enterprises, employing 108.500 persons and invoicing 12.097 million euro.

According to COTANCE[60] President Johansson, "*about 1 million jobs depend in Europe on the sector and the EU market for leather and leather products is worth some 60 billion Euro. European Tanners are at the root of this wealth and industry leaders at global level with some 15-17% of leather sales world-wide"*.[61]

The chemical supply chain for the leather industry

The leather industry is a global industry which is affected by events occurring around the world such as BSE and Foot & Mouth Disease crisis.

Leather chemical consumption is directly linked to the availability of hides (skins of animals slaughtered for meat, primarily of bovine and ovine origin). The world trend is towards lower red meat consumption per capita which is just about compensated by growth in the population (1,7 to 1,9 per cent).

According to the "Frost&Sullivan "SWOT"analysis carried out in year 2000, the main aspects are:

60 COTANCE: Confederation of National Associations of Tanners and Dressers of the European Community. The European Leather Association: 3 reu Belliard, B-1040 Brussels, Belgium. Tel: 32 2 512 7703 – Fax: 32 2 512 9157. cotance@euroleather.com

61 COTANCE meets European Commission Vice-President Günter Verheugen. http://www.euroleather.com/index.php?option=com_content&view=article&id=103:high-level-meeting-at-the-commission&catid=29:trade&Itemid=53.

Strengths:

Production of bovine and ovine hides as a result of meat consumption

Continuing demand for leather goods, from shoes, over upholstery through garment to bags, belts, etc.

Weakness:

Strong dependence on raw hide availability and prices

Leather production causes environmental and safety issues and is restrained legislation.

Opportunities:

New technology and product development can resolve some environmental issues.

Threats:

The strong purchasing power of large end-users causes lower average prices for leather chemicals.

Increased of usage of synthetic leathers or alternative materials.

However, due to this unique character, there are very few real drivers and restrains to the global market.

Market trends and impact

Frost & Sullivan[62] analyzes the European markets for four groups of specialty leather treatment chemicals, including beamhouse chemicals, tanning chemicals, fatliquors and dyestuffs. The report discusses market drivers and restraints, charts trends, and examines challenges that market participants will face. It identifies areas for growth, provides expert forecasts, examines end-user issues, monitors customer demands, and presents strategic recommendations. Profiles of key industry participants are included. Comments have been modified by the author after more than 30 years of experience in the leather chemical industry and focusing to the most relevant and useful issues for the marketing of tara tannins.

Raw hide availability and prices affect leather production:

Most important restrains.

Outbreaks of BSE in EU countries other than the UK and FMD throughout the EU, as well as Asia, South America and South Africa, have exacerbated the already deteriorated raw material situation for tanner worldwide.

62 Frost & Sullivan is a global services enterprise with 1800 analysts, consultants, and visionaries that cover more than 300 markets and 250,000 companies from our 40+ global offices. www.frost.com.

Facing a building demand for leather for the garment and upholstery segments, coupled with a perceived diminishing of raw material drives up raw hide prices, which ultimately limits the demand for leather as tanneries cannot pass the higher cost to their customers, e.g. fashion designers, who will instead look for alternative materials.

Environmental and safety issues and legislation affect global competitiveness:

Important restrains, especially at regional level.

European Union and USA have strict environmental rules and regulations concerning waste streams from tanneries, the necessity of waste management and ecological audits of the full processing protocols.

The costs of effluent treatment, dust extraction, settling tanks for organics, chrome extraction and personal safety equipment all add the cost of the production of leather treatment chemicals, thus negatively affecting prices and competitiveness,

In developing countries, legislative safety issues associated with leather treatment chemicals are generally no so extensive, giving the manufacturers in those countries a competitive advantage with regards to pricing. However, safety and environmental conditions in these countries are expected to improve in the coming years.

Relocation of leather producers to developing countries drives exports of leather chemicals and increases competition in Europe and North America

Important restrains, especially at regional level

There is a general trend for end-users (primarily garment, shoes and furniture manufacturers) to relocate to low labor cost countries. Leather production in these low cost countries is therefore growing at a faster rate than elsewhere.

The access to the development resources is critical to most customers –they have primarily “skilled labor” with too few technically qualified professional staff. Therefore, the ability to offer the know-how of a full product range with service is becoming increasingly important in securing loyalty.

Technology trends and product development trends emerging markets.

Continuing driver at global level..

In general, there is only a limited scope for technological break-thoughts (either product or process); the base technologies are well established.

The major technology trends can be summarized as follows:

Product substitution, such as the trend towards more environmentally friendly products, which favors non-chrome and solvent-free products

Products that allow the use of less water.

On the customer side, process changes in tanneries (particularly automation) require suppliers to be able to offer reliable and constant quality chemicals.

<u>Raw material cost and source availability drives relocation of industry.</u>

Driver or restrain at regional level.

To improve the overall economy of production of leather treatment chemicals a number of producers have moved their production facilities closer to the raw material sources and the end-user markets.

<u>One stop shopping requirements of buyers.</u>

Important competitive factor.

Similar to other industries leather treatment chemicals customers are seeking buyer friendly solutions which require a full range of wet-end leather treatment chemicals and appropriate technical service to solve specific customer queries.

<u>Technical and customer service are key of success factors.</u>

Important competitive factor

Customer service and high quality are pre-requisites for success in both mature and developing regions.

<u>Stabilizing prices.</u>

Low impact driver

After continued decreases in prices for leather chemicals in the past this trend is expected to be slightly in the near future duo to prices increases in raw material prices from the petrochemical industry.

<u>Trend to natural look limits usage of sinishes</u>

Low impact restrain to the finishing sector.

The trend of the past to keep and emphasize the natural leather character is still going on.

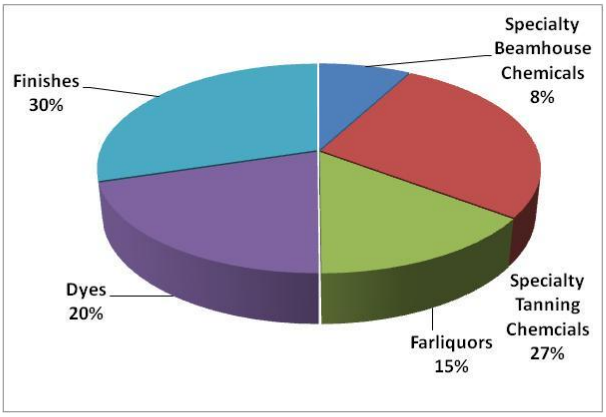
Customer structure:

The overall customer structure of the leather chemical industry is very fragmented with very few large tanneries and small family owned enterprises. The consolidation process among the customers has been very limited.

Leather chemicals. Total market size:

Frost & Sullivan estimated the total market size of leather treatment chemicals of 3.500 million USD and more than 2 million tones, with annual grow rates of 1,4 to 2,3 %. These growing rates not only depend on the total leather production. Approximately, upholstery, furniture and auto, consumes around 30 % more chemicals that shoe leather production. Therefore, the mix of leather articles has an impact on the consumption of chemicals.

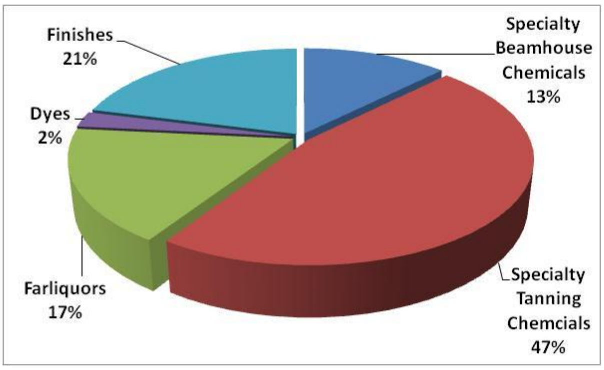
Leather treatment chemicals can be segmented in specialty chemicals for beamhouse and wet-end operations, excluding chromium salts and other basic auxiliaries, wet-end dyes and finishing:



Leather treatment chemicals by value (Source Frost&Sullivant)

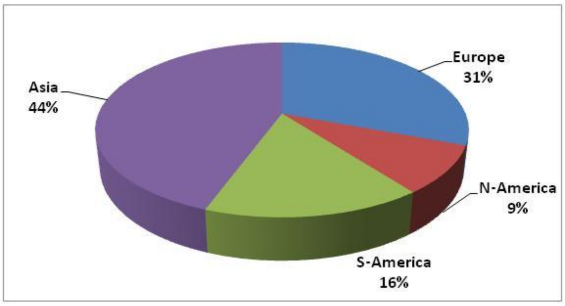
The figure is expressed in values and chemicals include specialty beamhouse chemicals, specialty tannage chemicals and fatliquors. Approximately, half of the value of chemicals corresponds to the value of tannins, either vegetable extracts or synthetic that in value can be calculated 945 million USD.

In volume, the product type distribution defers considerably due to price differences between them:



Leather treatment chemicals by volume (Source Frots&Sullivant)

Trends by geographic region:



Leather treatment chemicals. Market by Regions (Source: Frost&Sullivant)

Europe (31%):

A slightly decreasing (-1% to 0%) is forecasted for the European leather market. This reflects the decrease in raw leather treatment in Europe which involves specialty beamhouse, tanning liquors and fatliquors products.

The most important markets in Europe are Italy, Spain and Germany.

Italy: is the only market that has survived the decline of western European leather industry. It now accounts for around 10% of world leather production, and 50% of European leather production. Italy produces shoes upper and upholstery leather and is famous for its highly fashionable luxury garment and bag leathers which are susceptible to the unpredictable changes seen in leather fashions.

Spain: is the second market in Europe. Due to the high quality of the skins (entrefino and merino) garment leather was very much appreciated. But during the last years this production has been relocated in Asian countries and clothing leather companies has become distributors and designers of finished articles. Also, shoe leather has decreased considerable as shoe manufactures have relocated the production plants to third countries. However, high quality leather for leather goods has found its market niches with global luxury enterprises and production has grown during the last years and it is maintained in a high level.

Germany: has the larges production of automotive and airplane upholstery leather in Europe which, along with shoes upper and garment leather, makes up the majority of its production. Auto sales affecting the demand of automotive upholstery in Germany have been suffering from the financial crisis and consumers have been postponing the purchase of new cars. Therefore, is a noticeable fall in leather production.

North America (9%):

The North America market comprises USA, Canada and Mexico. The decline in the USA market is partly compensated by shift to Mexico. This has contributed to move production from low-medium quality leather for shoe to high standards leather for auto upholstery.

South America (16%)

The market also shows growing rates attributable to the increasing focus on automotive upholstery.

Brazil: Stable after some years of uncertainness.

Argentina: Has suffered several internal crises due to the devaluation of the local currency but has been stabilized. Argentinean tanneries focused on automotive leather but, during the last two years have moved back partially to shoe and leather goods.

Asia market (44%)

China: is by far the largest leather producer of all kind of leather and continues growing due to the low labor costs, government policies such as tariff reductions and investment incentives, resource advantages in pig and sheep skins and that most of the global leather good manufactures have been relocated in China.

India: is also a growing leather producer because of low labor costs, largest market for vegetable tanning agents due to the availability of raw materials for vegetable tanning extracts and growing domestic market for leather products.

Competition:

Traditionally, the leather treatment chemical suppliers have been multinational chemical companies, based in developed countries and, most of them, in Germany. During the twentieth century, these companies have supported all the knowledge and R&D activities related with the leather process technology, among production and distribution. The advances of the modern leather technology were linked to the research of new chemicals and the application of the increasing knowledge of synthesis based on phenol, naftalen and polymer science. Also, synthesis of dyes and fatliquors were fully applied during more the hundred years by the chemical industry.

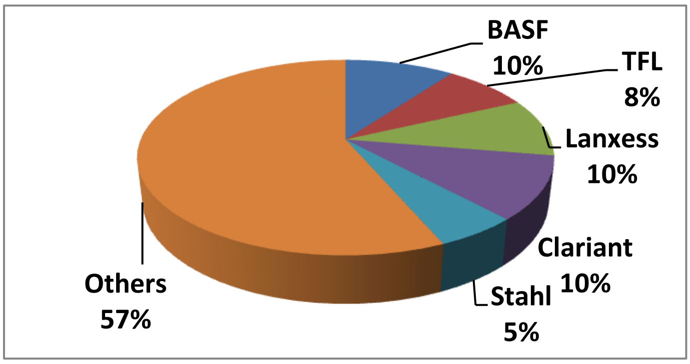
These companies actively were supporting the market offering a broad product range for the complete process of leather making and technical services.

Since chemical specialties have become commodity products and leather industry has been constrained by costs, the supply chemical chain has been spread with new competitor either product-focused (e.g. dyes manufacturers) or regionally focused (typically around tanneries in Asia, Latin America and Italy).

Currently, the chemical suppliers can be considered as:

Global broad product range companies: Most of them with headquarters in Europe and production sites distributed worldwide, mainly in developing countries, according their own production strategies that do not consider the leather sector as priority. They use to have daughter companies for marketing and distribution, sometimes, not located in leather production clusters and, therefore, the use to have distributors for warehousing and often, invoicing and servicing tanneries.

This figure shows the market share of BASF, Lanxess, Clariant, TFL and Stahl in the global market and in the Specialty chemicals for beamhouse and wet-end operations where tara tannins can be included:



The three market leaders, with revenues between 300 to 340 million euro do not exceed a market share more that 10% and this shows that there is a very spread market with no a strong leader position.

Global broad product range companies (TFL, BASF, Lanxess, Stahl, Clariant) account for approximately 50 per cent of the total market.

Smaller competitors tend to be either product-focused (e.g. dyes manufacturers) of regionally focused (typically around tanneries in Asia, Latin America and Italy).

Relevant trade related issues[63]

Registered Trade Marks in connection with Tara

The World Intellectual Property Organization (WIPO) is an agency of the United Nations, established to develop and international intellectual property (IP) system. A trade mark is a

63 Tara Casealpina spinosa. Market Survey. Compiled by Swiss Import Promotion Programme (SIPPO) by ProFound – Advisers In Development 2008/2009.

distinctive sign which identifies certain goods and those produced by specific person or enterprise. Through a trademark, the owner is protected by having the exclusive right to use the mark to identify goods.

In the databeses of OHIM and WIPO, no trade names were found for tannins from tara. Howver, internet searches gave the following results: Ormotan™ from Silvatem, Tanosin from Sochive, Lecosin from FGL, Fortan from A-Forte, Chimitan from Stefani Chimis, Floretan from Codyeco and Chemitan from Chemipol.

Registered patents in connection with Tara

A patent search was done at ESP@CENET[64]. Searching for the term tara in the titles and abstracts of patents results in 222 patents in total.

Specifically, for the term "tara tannin" in the titles and abstracts of patents results in 9 patents.

Two results come from the searh of tara, selecting the European Classification conde C14C, which is defined as "Chemical treatment of hides, skins or leather, e.g. tanning… compositions for tanning".

Tariffs, quotas and taxes

Tariffs on raw materials are generally low, in particular for ingredients originating in developing countries. In order to support supplies from developing countries, the EU operates the Generalized System of Preferences (GSP). Under the GSP scheme of the EU, imports from a number of developing countries are admitted at the reduced tariff or at a zero tariff. Andean countries belong to the GSPE group of counties.

A "EUR-1" form hat to be provided by the exporter to take advantage of the GSP tariff. The EUR-1 form is a certificate of origin that is issued in preferential trading between the EU and associate countries.

Packaging

Tara powder for the leather industry is packaged in polypropylene (PP) of polyethylene (PE) bags (plastic) of 25 or 50 Kg.

Documents

Tara powder importers can demand a certificate of analysis (stating tannin content, solubility, pH value in a certain solution). A packing list and a bill of lading are also required for the transport of tara products.

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64 http://ep.espacenet.com

Cash-Against-Documents (CAD) and letters of credit are both used for payment of the goods. Some importers prefer CAD, as it is a faster payment method for them.

Marking

The required marking mostly depends of the specific requirements of the importer. Information that is often required includes date, supplier name, address, product name, net weight, if the product is intended for food use, grade, recommended storage conditions. The information should be in English and using EU measures (e.g. grams).

Labeling

Quality labels, such as a label for organic products could also be put on the packaging. Sometimes, the attachment of certain documents can also be required. These may include a certificate of analysis of a certificate of origin. Depending on the sourcing methods of the importer, documentation might be important and elaborate of obsolete. Some importers prefer to visit companies from which they have received interesting offers, while others prefer to gather documentation which proves that the company can meet their requirements.

Prices

According to industry sources, the price for tara powder fluctuates approximately from € 0,70 / kg FOB Callao, early in the 2007 and roses in 2008 to € 1,70 FOB / kg FOB Callao. During 2009, due to the lower production of leather articles, price went down again to € 0,76 / kg FOB Callao.

The variation in price quotations has a large impact on the trade in tara powder. Industry sources have become frustrated from the price fluctuations. Purchasing tara for a good price became more difficult and long deliver times (4-5 months) combined with price fluctuations made tara procurement a speculative business. Importers place very irregular orders, to profit most from low prices.

The unreliable prices have resulted in the abandonment of the market by various traders. Consequently, end-users have more difficult in sourcing tara powder and tend to switch to alternative products. Industry sources have indicated that € 1,40 is the absolute price maximum for importers. Tanneries will switch to other tannins when prices exceed the € 1,40 price level. The substitution of tara, coupled with decreased demand, due to the financial crisis, has led to sharp price decreases in the past year.

Tara products have to compete in established markets where margins are generally low. Prices are based on actual costs of business operators (e.g. producers of processors). This kind of price-setting is called cost-based or cost-plus pricing. Many suppliers compare their prices with the prices of competitors and adjust their prices to improve their price performance ratio.

However, one should bear in mind that competitive pricing requires extensive knowledge of the products and services of competitors, as there are many value addiction activities which influence prices.

For price information, it is possible to be obtained from reliable sources like Promperú, IMR Internation, Online market places.

Quality requirements

In the leather manufacturing, variance of quality of the powder must be minimized as it can affect the quality of final articles. Tanneries cannot adopt their formulations accordingly to the lack of consistency of the suppliers and, therefore, the reliability of supplies is indispensable.

The main industrial requirements for tara are:

Tannin content: must be at least 50%.

Iron content: must not exceed 200 mg/Kg. Iron is a contamination from mills and shall be minimized using stainless steel grinding machinery.

Color: must be as light as possible.

Mesh size: <200

Some traders in Europe supply tara tannin liquid form. The tannin of tara is extracted and diluted with water and, in some cases, blended with other tannins or auxiliaries, formulated ready to be used.

Marketing requirements, strategies and sales promotion

Critical requirement to supply EU markets is the ISO certification of the provider and manufacturer.

Also, technical data sheet is required, containing product specification, product features such as description of production process and applications fields and recommendations.

Marketing efforts need to focus on restoring confidence to importers. Prices must become more stable and delivery times have to become shorter. For a sustainable trade in tara, profit-making has to be based on long-term business relationships instead of short-term selling to the highest bidder. Contract-farming offers a safe solution for both suppliers and buyers. Note, however, that not all buyers are willing to make long-term commitments.

The price fluctuation of the past years is strongly related to the availability of tara on the global market. Stocking tara can be an effective tool to stabilize prices. Stocking has to start a minimum price levels while stocks must be sold at maximum price levels.

The value of international trade in hides, skins and leather footwear average 2003-2005 (Million US Dollars)			
	Developing countries	Developed countries	**World**
Raw hides and skins	598.4	4,410.1	5,008.5
Wet blue, crust and Finished leather	9340.0	8137.7	17,477.7
Leather footwear	13,990.9	17,347.7	31,338.6
Total	**23,929.3**	**29,989.5**	**53,824.8**
Meat from Cattle, Sheep and Goats	5,264	18,841	24,105
Rubber	6,859	162	7,022
Cotton	3,086	6,122	9,208
Coffee	6,738	2,869	9,607
Tea	2,567	691	3,258
Rice	5,779	1,231	7,01
Sugar	6,93	4,222	12,281

Source FAO

Production of bovine hides (million pieces)										
	1998	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
WORLD	**314.8**	**316.8**	**319.2**	**315.6**	**321.3**	**330.0**	**329.8**	**333.0**	**335.2**	**344.0**
Developing countries	**190.5**	**195.5**	**200.2**	**201.2**	**205.7**	**213.0**	**214.5**	**224.9**	**226.1**	**232.8**
Developed Countries	**124.3**	**121.2**	**118.9**	**114.4**	**115.6**	**117.0**	**112.3**	**108.1**	**109.0**	**111.2**
Latin America	62.7	64.8	66.1	66.1	67.4	69.4	71.7	74.3	75.2	77.1
Africa	19.4	20.0	19.6	20.1	21.2	21.4	21.5	21.9	21.9	21.9
Near East	13.1	12.5	12.8	12.6	12.7	12.8	13.0	12.8	13.0	13.1
Far East	95.6	98.4	101.2	102.4	105.6	107.4	111.8	115.8	115.9	120.6
Other Developing	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
North America	40.9	41.6	41.4	40.3	40.7	40.1	38.7	36.6	38.1	38.4
Europe	37.0	36.4	35.0	33.9	34.3	33.5	32.8	32.0	31.1	32.0
Former USSR	29.7	27.0	26.4	24.3	24.6	26.0	24.7	22.6	23.2	23.2
Oceania	13.1	12.6	12.0	12.4	12.1	13.3	12.9	12.7	12.2	13.0
Other Developed	4.2	4.2	4.2	3.5	4.0	4.0	4.2	4.3	4.5	4.6

Source: FAO

Production of bovine hides (000's Tonnes)											
	1997	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
WORLD	**5722.9**	**5774.5**	**5814.4**	**5863.2**	**5783.9**	**5870.3**	**6103.5**	**6059.4**	**6098.8**	**6159.3**	**6319.6**
Developing countries	**2885.5**	**3019.0**	**3112.9**	**3209.7**	**3230.7**	**3284.2**	**3499.4**	**3551.1**	**3681.4**	**3709.7**	**3821.9**
Developed Countries	**2837.4**	**2755.6**	**2712.1**	**2662.7**	**2562.5**	**2591.1**	**2610.0**	**2508.2**	**2417.4**	**2449.6**	**2497.7**
Latin America	1238.0	1303.8	1380.5	1443.4	1454.6	1432.9	1585.2	1566.6	1632.3	1653.7	1696.3
Africa	244.0	260.2	269.5	262.4	268.3	281.3	284.5	285.6	291.7	291.1	292.7
Near East	201.6	205.2	198.8	203.9	201.6	193.1	201.7	207.3	205.4	208.8	211.2
Far East	1171.7	1220.1	1260.5	1296.9	1320.4	1369.7	1419.6	1488.4	1549.0	1553.1	1618.5
Other Developing	3.0	3.0	2.9	3.0	3.0	2.9	3.0	3.0	3.0	3.0	3.2
North America	1032.7	1011.1	1027.6	1024.1	995.9	1007.1	993.2	930.9	902.5	939.1	948.6
Europe	879.9	858.5	840.2	810.3	789.8	799.9	789.5	781.5	761.7	742.8	764.2
Former USSR	618.8	563.7	516.7	505.3	460.4	467.9	494.6	469.4	428.3	438.8	439.1
Oceania	221.8	239.2	231.1	219.2	227.4	221.2	241.9	233.0	230.3	229.6	244.3
Other Developed	84.2	83.1	85.9	93.7	81.3	89.9	89.5	93.1	94.5	99.2	101.6

Source: FAO

Leather production -Top 30 countries - million square feet

Country	1998	1999	2000	2001	2002	2003	2004	2005	2006
China	3285.9	3892.8	4138.5	4487.1	4525.3	4893.5	6124.1	6382.5	6599.3
Italy	1981.6	1918.7	2055.3	2060.6	2013.2	1934.8	2218.3	2219.1	2146.9
India	1377.7	1403.5	1448.3	1460.7	1460.1	1458.5	1233.8	1248.2	1738.6
Brazil	690.8	760	829.1	814.2	863	883.1	1326.8	1433.4	1647.3
Korea	1369.2	1336.4	1286.4	1373	1394	1367.9	1659.5	1641.9	1446.4
Former USSR	917.9	998.5	1061.3	1216.4	1361.2	1612.9	1640.1	1651.7	1224.5
Argentina	423.7	460.1	509.4	516.5	468.3	508.3	653.2	690.5	712.7
Mexico	683	680.5	719.8	759.8	756.9	780.9	535.1	555.9	591.8
Turkey	448.9	343.2	420.1	436.4	502.4	616.8	557.3	584.6	547.7
USA	845.7	933.1	862.6	819.9	786.2	813.6	563.2	475.0	477.0
Spain	534.8	489.3	542.2	551.2	528.5	521.9	484.4	464.0	442.0
Pakistan	288.8	297.8	327.3	339.7	357.1	358.2	336.0	357.2	363.0
Japan	282.5	268.7	280.9	284.9	262.6	270.7	398.8	318.3	315.1
Germany	266.3	297.8	316.8	322	287	280.4	288.0	253.0	280.9
Iran	128.3	133.2	133.6	133.1	146.3	158.2	323.5	265.0	250.2
Thailand	292.5	293.3	314.4	329.5	324.2	298.4	243.3	236.9	220.8
Uruguay	140	136.7	138	136.2	136	142.5	163.4	169.3	172.0
New Zealand	99.1	134	167.4	158	149.6	137.7	167.2	161.7	164.2
Egypt	117.3	124.8	147	157.7	163.4	167.8	155.3	156.1	155.5
Bangladesh	148.1	148.9	150.1	150.9	157	157.6	148.1	148.1	148.0
France	185.8	175.3	160	140.5	133.5	131.5	149.5	169.2	143.7
Sudan	82.4	84.9	91.1	90	90.9	89.2	130.4	136.2	139.2
Indonesia	121.2	131.9	132.7	132.1	135.5	140.6	139.0	135.0	138.5
United Kingdom	150	170	156.2	165.2	163.0	152.0	137.0	133.0	137.8
Australia	167.4	196.6	189.9	191.6	156.9	159.8	173.8	160.2	134.4
Colombia	96	90	99.54	92.84	93.68	95.12	101.2	102.1	115.5
Nigeria	112.1	114.3	118.5	102.2	103.8	108.4	99.7	99.8	102.7
Algeria	69.3	79.7	82.9	81.8	84.8	83.5	87.1	89.5	92.5
Morocco	88.9	90.6	89.04	89.94	86.58	84.08	79.9	83.1	80.7
Poland	89.5	87.7	92.7	91.7	88.9	90.6	83.9	79.6	79.6
Top 30 Countries	**15484.8**	**16272.2**	**17061.3**	**17685.7**	**17707.3**	**18435.6**	**20355.7**	**20545.0**	**20808.5**
Others	**3084.2**	**2760.8**	**3254.7**	**3346.5**	**3370.2**	**3487.0**	**1681.2**	**1761.6**	**1892.0**
World Total	**18569.0**	**19033.0**	**20316.0**	**21032.2**	**21078**	**21922.6**	**22036.8**	**22306.6**	**22700.5**

Source FAO 2008

Annex 7. General overview of making leather from raw hides

<u>*Beamhouse:*</u>

Sorting: On receipt, hides and skins may be sorted into several grades by size, weight, or quality. Hides are also sorted by sex.

Trimming: Some o the edges (legs, tails, face, udders, etc.) of the raw hides and skins can be cut off.

Curing & storing: Curing is a process that prevents de degradation of hides and skins from the time they are flayed in the abattoir until the process is the beamhouse are started. When the raw material cannot be processed immediately ("green") it must be cured. The methods for curing for long-term preservation are: salting, brining, drying and salt drying. Methods for short-term preservation are cooling, using crushed ice or refrigerated storage and biocides. Hides and skins are generally stored as they are received by the tannery on pallets in ventilated or air conditioned and/or cooled areas, depending on the method of curing chosen. From storage the hides and skins are taken to the beamhouse.

Soaking: Soaking is carried out to allow hides and skins to re-absorb water, to clean and to remove interfibrillary material from them. The soaking methods depend on the state of the hides. The process is mostly carried out in two steps: a dirt soak to remove the salt and dirt and a main soak. The process is carried out in processing vessels, such as mixers, drums, paddles or pits. The duration of soaking may range from several hours to a few days. Depending on the type of raw materials, soaking additives can be used such a surfactants, enzyme preparations and bactericides.

Unhairing & liming of bovine hides: The function of liming and unhearing is to remove hair, interfibrillary components and epidermis and to open up the fiber structure. Hair removal is performed by chemical and mechanical means. The keratinous materials (hair, hair roots, epidermis) and fat are eliminated from the pelts mainly with sulphides (NaHS or Na_2S) and lime. Enzymatic preparations are sometimes added to improve the performance of the process. The process of liming and unhearing can be carried out in process vessels such as drums, paddles, mixers or pits.

Pinting & liming of sheepskins: The aim of painting is to bring about the breakdown of the wool root within the skin so that as much undamaged wool fiber as possible can be pulled easily from the pelt. Paint, generally, consisting of a mixture of sodium sulphide and lime, is applied to the flesh side of the skin and left for several hours. Application of the paint can be through a spraying machine or manually. After several hours the wool can be "pulled" from the skin, either manually or mechanically. After pulling, the skins are limed in process vessels, with the same purpose as the liming of bovine hides. Wool-on skins are not painted, unhaired or limed.

Fleshing: Is a mechanical scraping off of the excessive organic material from the hide (connective tissue, fat, etc). The pelts are carried through rollers and across rotating spiral blades by the fleshing machine. Flashing can be carried out prior to soaking, after soaking or after pickling.

Splitting: By mechanical splitting the thickness of hides and skins is regulated and they are split horizontally into a grain layer and, if the hide is thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in limed condition or in the tanned condition.

Tanning operations:

Deliming: To remove residual lime from the pelts and to take them to the optimum condition for bating. This involve a gradual lowering of the pH (by means of washing and addition of deliming chemicals), an increase in temperature and the removal of residual chemicals and degraded skin components. Generally, deliming is performed in a processing vessel such as a drum, mixer or paddle.

Bating: Is a partial degradation of non- collagenic protein achieved by enzymes to improve grain of hide and the subsequent run and stretch of leather. In this process the rest of the unwanted hair roots and scud can be removed.

Degreasing: Excess grease must be eliminated from fatty skins (sheep, pig) to prevent the formation of insoluble chrome-soaps or prevent the formation of fat spots at later stage. Degreasing is most relevant in processing sheep skins, where the natural fat content is about 10-20% on dry weight. The nature of this fat makes it difficult to remove because of the presence of cerides and a high melting temperature. The three methods commonly used for degreasing are: with organic solvent and non-ionic surfactant, in aqueous medium with non-ionic surfactant and in solvent medium.

Pickling: Is carried out to reduce pH of the pelt prior to mineral tanning and some organic tannages. The choice of the exact pickling parameters depends on the subsequent tanning step. Very often is carried out in the tanning liquor; however, pickled pelts can be traded, especially sheepskins, using fungicides to protect them from mould growth during storage.

Tanning: In the tanning process the collagen fiber is stabilized by the tanning agents such that the hide is no longer susceptible to putrefaction or rotting. In this process the collagen fibers are stabilized by the cross-linking action of the tanning agents. Furthermore their dimension stability, resistance to mechanical action and heat increase. Various agent can be categorized in three main groups: mineral tannins, vegetable tannins, alternative such as syntans, aldehydes, oil… Chromium and vegetable tanning agents are the most commonly used tanning agents.

Draining, samming and setting: After tanning, the leathers are drained, rinsed and either horsed up to age, or unloaded in boxes and subsequently sammed to reduce the moisture content prior to further mechanical action, such as splitting and shaving. The setting our operation can be carried out to stretch out the leather. There exist machines which combine the samming and setting action. After samming and setting, hides and skins can be sorted into different grades after which they are processed further or sold on the market.

Shaving: The shaving process is carried out to achieve an even thickness throughout the skin/hide, and it can be carried out on tanned or crusted leather. Shaving is carried out where splitting is not possible or where minor adjustments to the thickness are required.

Post-tanning operations:

Post-tanning involves neutralization and washing, followed by retanning, dyeing and Fatliquoring, mostly done in a single processing vessel. At this stage of the process, specialist operations may also be carried out to add certain properties to the leather such as water repellence or resistance, oleophobing, gas permeability, flame retarding, abrasion, anti-electrostatics, etc.

Neutralization: Is the process by which the tanned hides are brought to a pH suitable for the process of retanning, dyeing and Fatliquoring.

Bleaching: Vegetable tanned skins and leathers with wool or hair may need to be bleached in order to remove stains, or to reduce the coloring in the hair, wool or leather prior to retanning and dyeing.

Retanning: The retanning process can be carried out with the following objectives:

To improve the feel and handle of the leathers

To fill the looser and softer parts of the leather in order to produce leathers or more uniform physical properties and with more economical cutting value to the customer

To assist in the production of corrected grain leathers

To improve the resistance to alkali and perspiration

To improve wetting back property of the hides which will help the dyeing process.

A wide variety of chemicals can be used for the retannage of leather. They can generally be divided into the following categories: vegetable extracts, syntans, aldehydes, mineral tanning agents and resins.

Dyeing: The dyeing process is carried out to produce level colors over the whole surface of each hide and skin and exact matching between hides in a commercial pack. Typical dyestuffs are water-based acid dyes.

Fatliquoring: Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils.

The retanned, dyed and fatliquored leather is usually washed before being horsed up (piled on "horses") to rest.

Drying: The objective is to dry the leather whilst optimizing the quality and area yield. There is a wide range of drying techniques and some may be used in combination. Each technique has a specific influence on the characteristics of the leather. The most used drying techniques include samming, setting out, hang drying, vacuum drying, and toggle drying. Generally samming and setting out are used to reduce the moisture content mechanically before another drying technique is used dry the leather further. After drying, the leather may be referred as curst. Crust is a tradable intermediate product.

Finishing:

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished with respect to: color, gloss, handle, flex, adhesion, rub fastness, as well as other properties including extensibility, break, light and perspiration fastness, water vapor permeability and water resistance as required for the end use. Generally, finishing operations can be divided into mechanical finishing processes and applying a surface coat.

Mechanical finished processes: a wide range of mechanical finishing operations may be carried out to improve the appearance and the feel of the leather. The following list includes, among others, commonly used mechanical finishing operations:

Conditioning: optimizing the moisture content in leather for subsequent operations

Staking: softening and stretching of leather

Buffing/de-dusting: abrading of the leather surface and removing the resulting dust from the leather surface.

Dry milling: mechanical softening

Polishing

Plating / embossing: flattering or printing a pattern into the leather.

These operations may be carried out before or after applying a coat, or between the applications of coatings.

Applying a surface coat: The purpose of applying a surface coat is:

To provide protection from contaminants (water, oils, soil…)

To provide color either to modify dyed color or reinforce that provided by the dyes, to even the color or to disguise defects.

To provide modifications to handle and gloss performance

To provide attractive fashion or fancy effects

To meet other customer requirements

There is a wide range of application methods each of which has its advantages and disadvantages. A combination of methods can be used to achieve the desired effect on the finished product. In principle, the following types of application methods can be distinguished:

Padding or brushing the finishing mix onto the leather surface

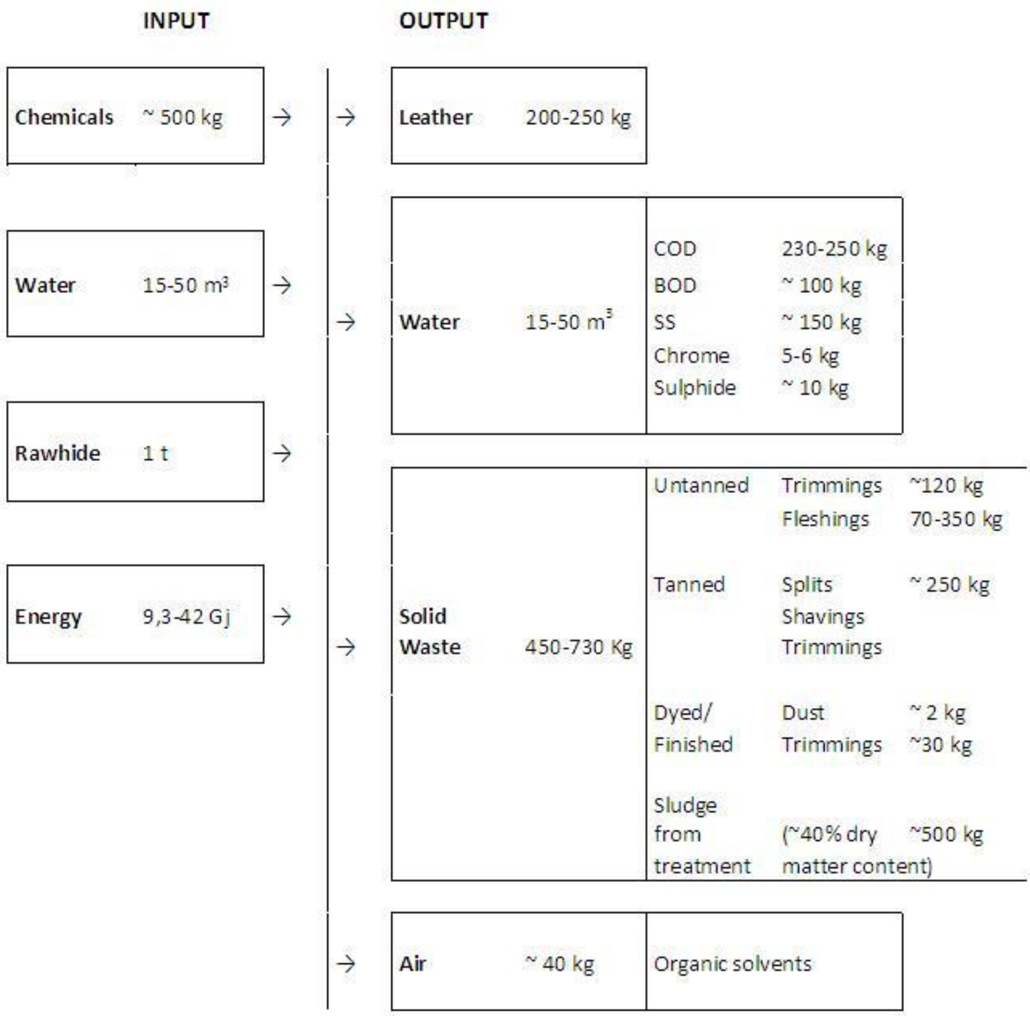
Spray coating which involve spraying the finishing material with pressurized air in spry cabinets.

Curtain coating, which is passing the leather through a curtain of finishing material

Roller coating, which is an application of finishing mix through a roller

Transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive.

Annex 8: Environmental considerations for the leather industry



This table expresses the input and output overview for a conventional (chrome tanning) process for bovine salted hides per ton of raw hide treated. The quantities and qualities of emissions and waste produced by tanneries strongly depend on the type of leather processed, the source of hides and skins and the techniques applied.

Environmental concerns in a tannery include waste water, solid waste, air pollution, soil protection and safety aspects. The releases potentially contain toxic, persistent or otherwise harmful substances.

Most of the steps of the tannery's operation are performed in water. Consequently waste water effluent is one of the major concerns in tanneries. The characteristics of waste water are a high chemical and biological oxygen demand, high salt content and toxic releases. The table bellow shows the consumption level of the main process chemicals, tanning agents and auxiliary chemicals for a conventional tanning process for salted bovine hides.

A further aspect to be aware of in the tanneries is the potential hazard to human health and the environment for handling, storing, transporting and packaging of chemicals.

When effluents discharge to water treatment plants, either municipal or plants operated for large tanning complexes, it is produced a high amount of sludge, about 5 to 10% of the total volume of effluent being discharged. The settle sludge resulting is normally in the form of a liquid with a solids content of 3-5% dry solids. Typically, sludge are dewater to have a dry matter content if 25-40%.

For sludge and other residues further re-use and recycling options exists. The viability of these options is strongly dependent on the composition of the residues. Landfilling of wastes with high organic content and toxic substances is increasingly coming under pressure in many countries. Other strategies include reduction measures by means of recycling, composting, biogas production or materials/energy recovery. However, an average of more than 80% of these solid residues and sludge contain chromium.

Probably, the most debated issue with regards to the leather industry impact in the environment is the chrome tanning, thus the utilization of chromium (III) salts. They are used in the tanning industry and its toxicity shall not be confused with chromium (VI). Hexavalent chromium is known to be a skin irritant and thought to be carcinogen.

Despite toxicity of chromium (III) salts is similar to the table salt, there are concerns because potential oxidation, either in leather articles, effluents after chrome tanning or solid wastes. It is know the effect of certain fatliquors and other chemicals to oxidize tanned leather, but also, some other that prevent such formation. Polyphenols, contained in vegetable tannins have shown anti-oxidation properties.

Due to the fact that chromium has been under pressure from regulatory authorities, and other collectives, some leather users are beginning to demand the use of alternative tanning agents, such as glutaraldehyde, aluminum and vegetable tannins. In any case, nowadays, chrome tanning is the most efficient and versatile tanning agent available and it is relatively cheap.

The amount of chemicals used varies significantly with the specification of the final product, the pelts treated and the process chosen. Figures for consumption of chemicals can therefore only be given within a broad range. Besides the main process chemicals, a great variety of substances is used for auxiliary process purposes. For reasons of workplace health and safety, some barely soluble agents are applied as aqueous suspensions or dispersion, which may have to be stabilized with auxiliaries, thus adding even further to the number of chemicals used.

It is common for tanneries to use more than 300 different chemicals in the lather making process. The potential impact of chemicals will depend of many factors:

- The selected chemicals
- The medium in which it is released (solid waste, atmosphere, effluent, soil…)
- The actual concentration received by the environment. It should be noted that the quantities in the waste water are not strictly a function on the input quantities. Some agents are almost totally absorbed, react in the process or are precipitated in the waste water treatment.
- Transformation of the chemicals due to chemical and biological process before and after discharge o the environment. The substances might react during the process or with other constituents; or they are degraded in the waste water treatment plant; they can also be distributed to different outlets of a factory.
- Continuous or batch discharge.
- Characteristics of the receiving environment. For example in a water course, essential factors are: the stress of organisms due to other constituents; inhibitory or synergetic effects due to other chemicals; flow characteristics; light and temperature.

Chemical consumption	**%**
Standard inorganic (without salt from curing, acids, bases, sulphides, ammonium-containing chemicals)	40
Standard organic, not mentioned bellow (acids, bases, salts)	7
Tanning chemicals (chrome, vegetable and alternative tanning agents)	23
Dyeing agents and auxiliaries	4
Fatliquoring agents	8
Finish chemicals (pigments, special effect chemicals, binders and crosslinking agent)	10
Organic solvents	5
Surfactants	1
Biocides	0,2
Enzymes	1
Others (sequestering agents, wetting agents, complexing atents…)	
Total	100

Consumption of chemicals in leather processes (Source Bref)

Annex 9: The application of the vegetable tannins in the leather industry

Vegetable tannins are niche products, compared to chrome salts. The main advantage of vegetable tannins is that they are supposed more environmental friendly. With increasing strict EU legislation regarding waste and waste water treatment, vegetable tannins offer specifically interesting solutions for tanneries aiming to reduce their pollution.

Tannins displace water from the interstices between the protein fibers in the skin and cements the fibers together, preserving its flexibility and making it resistant to rot. Vegetable tannins get deeply and uniformly dispersed in the hide, resulting in roundness and feel properties.

Most of the plants contain tannins. However, only a small number of them have shown true value as commercial products in the vegetable tanning. Currently, most of the commercial tannins are offered as extracts from different parts of the plants:

- Bark: pine and mimosa
- Wood: Chestnut, quebracho
- Leaves: Sumac
- Fruits: Valonia, tara

Quebracho:

Quebracho is the most important and most widely used extract in the tanning industry.

The tannin is extracted from the wood of the Qhebrachia lorentzii, a tree that grows in South America, predominantly in Argentina. It is a very slow-growing tree, taking approximately one hundred years to reach maturity.[65] The extract contains about 63-70% good quality tannins, condensed or catechol type.

The natural tannin of quebracho is soluble in hot water but condensates when it is cooled. In this stage, having a very low content of non-tannins, is used to obtain heavy leather articles, such sole leather. Its pH is higher than 6 and has an average molecular weight of 2400. The leathers tanned with quebracho trend to have a red color.

In order to increase its solubility, the extract needs to be clarified by treatment with bisulfite. This reduces its astringency and decreases the insoluble matter but increases the non-tannin content. Sulfited quebracho has a pH higher that 6 and average molecular weight between 700 and 800. The strong tendency to fix with the hide is reduced and, therefore, the tannin penetrates easily and a softer leather, but emptier, is obtain. The color of the tanned leather is quite light.

65 Thomas C. Thortensen. Practical leather technology. Robert E. Krieger Publishing company, Malabar. Florida. USA. Third Edition. 1985. Page 149.

Mimosa:

Mimosa, wattle extract, is the second most important extract, coming from the bark of the trees of the various acacia species, but principally from Acacia mollissima. The extracted tannin is catechol type. The plant is originally from Australia, but is grown commercially in South Africa, an in a small quantity in Brazil.

It contains about 60 % of tannins and 18-20% of non-tannins. The extract contains some sugars and has a very small amount of insolubles. Its average molecular weight is between 1600 and 1700.

For leather articles manufacturing, mimosa extract has low astringency, thus good penetration and is often used in the re-tannage of upper leathers.

Leathers tanned with mimosa extract have a beige-yellow color, lighter than the treated with quebracho. However, oxidizes easily when articles are exposed to the light and color turns to violete.

Chestnut

The chestnut wood extract is obtained from the chestnut tree Castanea dentate, the grows in the United States, France and Italy, among other countries in the Mediterranean bank. It was the most important source of vegetable tannins until sources of chestnut wood became too expensive due to the blight and the cost to obtain the wood.

The tannin is hydrolysable and has a natural pH value of about 3 in solution and a molecular weight of 1500. Due to its astringency, chestnut extract is sweeten with reductive and alkaline matters, until pH reaches 4,5 value.

Leathers treated with chestnut have a better light fastness that mimosa and quebracho and have a certain waterproof behavior. Color trends to be between light red brown and green.

Annex 10: Equipment for experimental tests

Photo 26: Fave drums, stainless steel, 500x2mm (DxL).

Photo 27: Simplex drums, stainless steel, 4 T.D.F.

Annex 11: I am a tree and you too

YO SOY UN ARBOL, Y TU TAMBIÉN

AMARU CHOLANGO. QUITO. 1996.

Ahí yace muerto	There lies dead
Sus manos no alcanzan el cielo y	His hands do no reach the heaven
Sus raíces no alcanzan	His roots do not reach
El fuego de la tierra.	the fire of the earth.
Lo tomo con mis manos	I take him in my hands
para quemarlo	to burn him
Lo alzo	I leave him.
Lo tomo de nuevo y muchas veces más.	I take him and many times.
Con mis manos	With my hands
lo lleno de ternura	I give him tenderness
al fin	at the end
Lo bautizo con fuego.	I baptize him with fire.
¡Ahora vive él!	Now he lives!
¡Ahora él es!	How he is!
Ahora es arte.	Now he is art.
Ahora es más que un árbol.	Now he is more than a tree.
¡Ahora él es todos los árboles!	Now he is all the trees!
A través de sus venas no corre savia	Through his veins runs no sap
corre leche	runs milk
del tiempo. El silencio	of time. The silence.