PROCESSSING AND APPLICATION OF *ZOGALE* (*Moringa oleifera*) SEED OIL IN TANNING PROCESS

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A THESIS PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF MASTER OF TECHNOLOGY (M.TECH.) IN INDUSTRIAL CHEMISTRY.

MARCH, 2011

CERTIFICATION

This is to certify that the research work **'' Processing and Application of *Zogale (Moringa oleifera)* Seed Oil in Tanning Process ''** has been presented by Suleiman Salihu (M.TECH/CH/07/0163) of the Department of Chemistry, Federal University of Technology, Yola and has been read and approved as meeting the requirement for the award of Masters of Technology (M.TECH) degree in Industrial Chemistry.

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DEDICATION

This research work is dedicated to Almighty Allah, the provider and the protector.

ACKNOLEDGEMENTS

I would like to express my profound gratitude to Almighty Allah who make it possible to accomplish this work. I most specially express my sincere gratitude and appreciation to Dr. J.T. Barminas who through the period of carrying out this research work was extremely patient, tirelessly and consistently held himself to suggest, contribute a lot to my work. I also extend my gratitude to the entire lecturers who have enriched us with knowledge and made us what we are today. These include Dr. H M. Maina, Dr. S. A. Osemeahon, Dr. Buba Aliyu, Dr. Dimas Kubmarawa, Mr. Iliya K. to mention but few. I extend my appreciation to the Director General/ Provost, Dr. Isuwa I. and Mr. Cornelius Chris Maju both of Federal College of Chemical and Leather Technology (CHELTECH) Zaria.

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However, I wish to thank the management of my institution, The Federal Polytechnic, Mubi for allowing me obtain this higher qualification.

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ABSTRACT

The *Moringa oleifera* seed oil was extracted and analyzed to establish its physico-chemical properties in order to investigate the possibility of its fatliquoring characteristics on leather. The seed has 38 % oil content reasonably high to be used on commercial basis. The saponification value(183.4 mg KOH/g) suggest the use of this oil also in liquid soap, shampoo and oil based ice cream production. Six different proportions of the sulphating agents were added to sets of six batches of oil . The reaction times were 60 and 120 minutes for the sets of first and second batches respectively while in each set the proportions used were 10, 15, 20, 25, 30 and 35 %. The products obtained for 20-30 % sulphating agent were found to have adequate oil-in-water emulsion stability. The 25 % product obtained was adequate as a fatliquoring agent in leather manufacture and its fatliquoring characteristics compared favourably with groundnut fatliquor commonly used in Nigeria tanneries.

CHAPTER ONE

INTRODUCTION

2.0 BACKGROUND OF THE STUDY

Leather is a material created through the tanning of hides and skins of animals, primarily cattle hide. The tanning process converts the putrescible skin into a durable, long- lasting and versatile natural material for various uses. Together with wood, leather formed the basis of much ancient technology, the leather industry and the fur industry are distinct industries that are differentiated by the importance of their raw materials. In the leather industry the raw materials are by-products of the meat industry, with the meat having higher value than the skin. The fur industry uses raw materials that are higher in value than the meat and hence the meat is classified as a by-product. Taxidermy also makes use of the skin of animals, but generally the head and part of the back are used. Hides and skins are also used in the manufacture of gud and gelatin. (Tuck, 1981).

Nigeria is blessed with many oil bearing seeds from which variety of vegetable oils and fats can be sourced for lubrication of leather during tanning process. Groundnut is one of the most abundant of these seeds, other notable seeds in this category include cotton seed, soybeans, palm fruit, kernel, castor oil, etc. (Tuck, 1981).Groundnut oil, cotton seed oil and palm oil are some of the oils that have been used in their natural forms for lubricating purposes in our traditional tanning industry. The mechanized

tanneries also incorporate the neutral groundnut in fatliquoring formulations. This might be due to the fact that the oil imparts fullness on leather when used as a lubricant and it is readily available in the country. Dilution of lubricant makes it possible for the oil molecules to penetrate the leather layers more easily and spread more uniformly among the fibres of the leather to ensure good lubrication (Drake, 1981). Oils are rendered self emulsified in water either by chemically incorporating a surface active group (e.g. OSO_3^{2-} , SO_3^{2-}) in the moiety of the oil or by mixing emulsifiers with the neutral oil.

Emulsification of oil in water makes it possible to use water-based fatliquoring process in leather manufacture. This fatliquoring process is cheaper, safer and more convenient than that using organic solvent as the oil/fat diluents because water is the diluents of the lubricating base. Sulphation process is one self emulsifying in water. The resulting product is called sulphated fatliquor (Drake, 1981).

The importance of lubrication or fatting process in leather manufacture is derived from the physical properties of the leather. While the lubrication characteristics of a sulphated fatliquor, like other fatliquor types is dictated by the nature of the base lubricant (i.e. neutral oil), the emulsifiability of the oil which dictates and imparts the penetration of the lubricant into leather, is influenced by the extent to which the neutral oil can be sulphated. Factors such as the proportion of the sulphating agent added, the

temperature and time of reaction are known to influence the quality of the fatliquor produced (Drake, 1981).

Many industries rely on crude oil which could be converted easily into fuels, chemicals, fibres, fertilizers, pesticides, etc. However, this conversion processes depend on non-sustainable resource whose reserves are being depleted at high rates. The major oils fields are on the declining production levels, locally and internationally. It is then imperative to develop alternatives, which are cheap and renewable and have minimal impact on the environment.

Tanning process consists of inspection of the hides for defects as they come into the tannery and the cutting off the ears and ends. Next, the hides are cleaned to remove dirt, manure and salt, in order to get the hide in the form of natural soft hydrated state. Cleaning of hides is carried out by paddle washing or soaking in vats.

Soaking as well as washing of the hides is very important, because if moisture is not restored, the hide will not respond properly to different tanning operations. Soaking can be increased by adding small amounts of sodium poly sulphide and surfactants as accelerators.(Keller, 1973). Disinfectants have also been used in soaking so as to check bacteria present from delayed or inadequate curing. Properly soaked hide contains about 65% water while over soaked hides are generally soft.

Liming is done for loosening and removing the epidermis and hair from the hide and usually carried out in paddles, drums and pits. The hides are tied or hooked together and kept in the vats containing water with 10% of the weight of hides in lime and 2% of the hide weight in sodium sulphide (accelerator). Other accelerating or sharpening agents used are dimethylamine cyanide salt and sulp-hydrate etc. The hides are moved ahead daily in a series consisting of 3-7 vats, remain in each for one day and the then enter a fresh lime vat.

The epidermis and hair are mainly composed of a protein known as keratin. The latter is readily attacked by alkali lime thus attacks the disulphide linkage of the keratin of the epidermis and the cortical layer and the hair. As a result hairs are softened and epidermis is removed.

$$R - S - S\,CH_2R + H_2O \longrightarrow RSH + RCH_2SOH$$

$$RCH_2SOH \longrightarrow RCHO + H_2S$$

After the above process, hides are usually placed in a vat of warm water, which permits an easier removal of the hair in a dehairing machine. The skins are brought into contact with a roller set with dull knife blades, which run off the loose hair and epidermis.

Tannins are complex mixtures of glucosides of various polyphenols and combine with collagen fibres of the skins. During tanning these tannins liberate sugars. The pH of the tanning process is controlled by adding sulphuric acid.

Skin + Tannin ⟶ Leather + Sugar

In short, liming operation in leather is a drum/paddle or pit based operation where four main objectives are met. The objectives are (Sharphouse, 2008)

i Removal of interfibrillary proteins.

ii Removal of Keratin proteins.

iii Collagen swelling due to the alkaline pH.

iv Collagen fibre bundle splitting. Liming operations of cattle hides usually last 18 hours and are generally associated with the alkaline phase of beamhouse operations. Historically, the liming pits were used and were one the longest operations.

Important operations include:

1 Preliminary preparations such as washing and cutting of unwanted parts.
2 Soaking and cleaning of skin so that it is free of flesh and grease
3 Hair removal of skin (optional) or liming
4 Tanning
5 Oiling and finishing.

1.4 DESCRIPTION OF *Moringa oleifera* PLANT

The plant occurs in practically most tropical and sub-tropical areas, either wild or cultivated. It is also found widely as both an ornamental and cultivated plant in temperature zones where because it is frost sensitive, it is grown commonly from seed. The seeds are capsulated and bitter to taste. The leaves are highly nutritional and the parts of the plant are medicinal.

1.5 STATEMENT OF THE PROBLEM

Cost and availability of raw materials are important factors in the production of fatliquors. On the other hand, hides and skins are found in most parts of Northern Nigeria in abundance. The *Moringa oleifera* plants are grown or cultivated in most parts of Adamawa State, and some seeds are large and abundant in nature, hence the need to extract and determine the properties of the seed oil for its possible usage in leather tanning process as an alternative source.

1.6 AIM AND OBJECTIVES OF THE STUDY

This work is concerned with the:

1) Extraction and characterization of the oil from Zogale (*Moringa oleifera).*
2) Development and evaluation of fatliquor from the oil.
3) Application of the fatliquor in leather tanning process.
4) Analysis of the treated leather.

CHAPTER TWO

LITERATURE REVIEW

3.0 VEGETABLE OILS

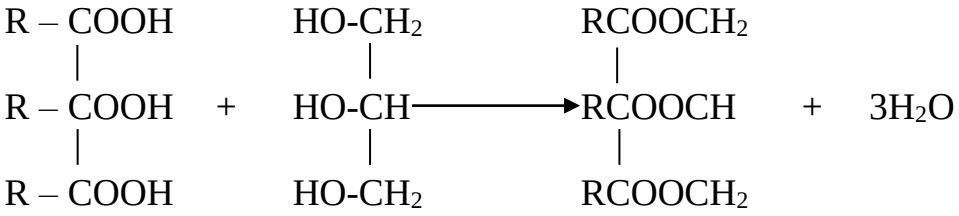
Vegetable oils are complex mixture of esters (triglycerides) which are formed from high molecular weight carboxylic acids called fatty acids e.g. palmitic acid, $C_{15}H_{31}COOH$, stearic acid, $C_{17}H_{35}COOH$ with glycerol. Plants constitute the most important source of edible oils and fats. Most vegetable oils are extracted from seeds, nuts and kernel (Cameron, 1966). They are usually liquid at room temperature with the exception of palm oil. In Nigeria common sources include groundnut (Arachis hypogea), ogbono (Irvingia gabonensis), melon seed (Cucumeros edulis), water melon (Citrullus lanatus) and guineacorn (Sorghum durra).

Vegetable oils have in the past been converted to biofuels (Drake, 1981). The growing interest in the production of alternative renewable and environmentally friendly lubricants serves as the basis for this research work. Fats and oils have found numerous applications in addition to their role as food for man. These include their application in medicine, chemical industry, etc. Studies on the chemical composition and physico-chemical characteristics of the fruits and seeds of some wild plants have proved the presence of high level of ascorbic acid in edible oils.

Vegetable oils from fast growing plants are considered promising biomass materials that could find use as renewable energy resource (Barminas et al., 2001).

2.1.1 CLASSIFICATION OF VEGETABLE OILS

Oil is simply an ester of alkanoic acid. This is normally produced through the reaction with glycerol. The esters are known as triglycerides from high molecular weight alkanoic acid (fatty acids) e.g. palmitic acid, $C_{15}H_{31}COOH$.



Below are the main classifications of oils:

2.1.1.1 Essential oils

These are highly volatile on exposure to air and have pleasant taste with strong aromatic odour. They possess antiseptic qualities and are stored in any part of the plant.

2.1.1.2 Fatty oils

They are non-volatile with no taste or odour. They do not possess antiseptic qualities and are stored in seeds (with a few exceptions).

2.1.1.3 Drying oils

They readily absorb oxygen on exposure to air, form tough elastic resistant films and are used as solvents for pigments in paints and varnish manufacture e.g. soybean.

2.1.1.4 Non-drying oils

They are liquids at room temperature and do not form elastic film on exposure to air. These include groundnut oil, olive oil, palm oil, cotton seed oil, etc.

2.1.1.5 Semi-drying oils

They absorb oxygen slowly after a long time when exposed to the atmosphere, form soft films and are used as polymers. This class of oils includes sunflower, cotton seed oil, etc.

The vegetable oil and animal fats having either drying or semi-drying properties are suitable for use as base of paints and other coatings. However, this property restricts their use as fuel. (Knothe, 1997).

2.1.2 LUBRICANTS FROM VEGETABLE OILS

Lubricant is primarily aimed at separating two surfaces sliding past each other with a film of some materials that can be sheaved without causing damage to the surfaces (Cameron, 1966). As secondary functions, lubricating oils have to cool, clean and seal engine components (Drake,

1981). Not much has so far been published about using animal fats and vegetable oils in the lubricant industry.

Lubricity measures the lubricating property or local carrying ability of a fluid. A low lubricity may cause high wear and sealing of the engine while a high lubricity may result in reduced engine wear and longer component life.

For over a century, lubricants derived primarily from mineral oils or petroleum distillates have been used to lubricate internal combustion engines. Mineral oil reserves are non-renewable and in an effort to address the problem of environmental pollution caused by the use of these petroleum derivatives, attempts have been made to find renewable alternatives, like vegetable oils, to replace mineral oil as fuels and lubricants. Soybean oil is currently been used successfully as a lubricant in various components of irrigation systems and it has good potentials to be used as a lubricant in internal combustion engines (Green, 1967).

The effectiveness of lubricating oils from vegetable oils was studied by Green (1967). He pointed out that the actual performance can only be discovered after the oils have been studied in machines under operating conditions over a period of time and in addition should possess the following:

i) The oil must be capable of maintaining an efficient lubricating film between all pairs of working surfaces in the engine under operating conditions.

ii) It must be chemically stable, anti-corrosive and show good chemical resistance to oxidation in the working environment and through the temperature range over which the engine will operate.

iii) It should have a high viscosity index, combining easy cold starts and low oil shearing losses with adequate viscosity at maximum running temperature.

iv) It should preferably have detergent properties capable of inhibiting deposit formation in the engine over range of operating conditions.

v) It must have film strength adequate for bearing surfaces that have very high loadings.

vi) It must be miscible with gasoline.

vii) The lubricity (i.e. film strength) values of soybean have been formed to be as that of mineral oil. During preliminary studies, the miscibility with gasoline, lubricity values, and viscosity values of different soybean oil forms were investigated. The results of these paved the way to using soybean oil in the two-stroke gasoline engines (Sims, 1985). Considering the growing concern regarding climate change, utilization of renewable energy in general and biomass in particular is expected to grow further in the future for industrial application.

2.2.0 FATLIQUORS

The fibre elements dehydrated by tanning are coated with a fat layer to give leather the desirable softness and handle by a sort of lubrication. Surface-active or other agents that are added to an emulsion to increase its stability by interfacial action is known as emulsifiers or emulsifying agents. In the fatliquoring process, oils/fats are employed as oil in water emulsion known as fatliquor. Fatliquor may be anionic, cationic or non-ionic. Anionic fatliquors are commonly employed for fat binding with chrome-tanned leather, which is cationically charged. Anionic fatliquors are commonly prepared by sulphation, sulphonation, or bisulphitation of oils/fats. Depending upon the source of oils/fats used, the fatliquor can be classified as vegetable, synthetic and semi-synthetic. Generally, castor oil is used as a source for vegetable based fatliquors. The synthetic fatliquors are usually obtained by sulphochlorination of C_{lO}-C_{20} fractions obtained through the FischerTropsch method of paraffin synthesis or from the petroleum industry (Dutta, 1985). Semi-synthetic fatliquors are prepared from both the vegetable and synthetic sources. Characterization and possible use of oil extracted from seal hides as leather fatliquor has also been studied (Cuq et.al., 1998). At the same time, fatliquoring influences the physical properties of the leather, such as extensibility, tensile strength, wetting properties, waterproofness and permeability to air and water vapour.

2.2.1 FATLIQUORING PROCESS

The process of fatliquoring entails the treatment of leather with a warm dilute emulsion of oil in water. The process is usually the last one prior to drying and finishing. As the range of emulsifying agents is constantly increasing, the treatment of leather with emulsions can now be done from the bating stage onwards. The functions of fatliquoring according to Hollstein (1972) are as follows:

a. **Lubrication.**

The fibres are coated with a film of oil which acts as a lubricant while the leather is in use. It reduces internal friction and increases the durability of the leather.

b. Adjustment of physical properties

The coating of the leather fibres with oil prevents them from sticking together and forming chemical or physical cross-links when the leather is dried. Thus increasing oil content induces increasing softness, stretch, pliability, compressibility, and increased tensile strength.

c. Regularization of physical properties

By increasing the oil content of the leather in winter and reducing it in summer, the effects of seasonal temperature changes in the liming and tanning processes can be nullified. In the ideal air-conditioned factory such changes would not occur, but in the average factory, where seasonal

temperature fluctuations occur, fatliquoring plays an important part in keeping the production at a uniform condition throughout the year.

d. **Waterproofing**

According to Keller (1973) the water repellency and waterproofness of leather can be influenced by fatliquoring. When leather is treated with molten and liquid fats in drum stuffing, a high degree of water repellency can be induced due to the hydrophobic nature of the hydrocarbon chains in the fat. The presence of either increasing numbers of hydrophilic groups in the oil molecule, for example, the sulphonic acid and sulphate groups in chemically treated oils, or the presence of stable emulsifying agents, can reverse this effect. Thus a highly sulphated oil can increase the wettability of chrome leather and make it unsatisfactory to wear, while the presence of a large proportion of raw oil makes it more waterproof.

e. Filling effects

The use of solid and semi solid fats, e.g. tallow, in fatliquoring will cause filling of the air spaces in the looser parts of the leather and improve the cutting value of the stock. This effect can be increased by adding small quantities of colloids to the emulsion, such as china clay, soya bean flour, or flour.

f. **Protection**

The presence of a film of fat in the leather structure gives protection to the

leather against all harmful chemicals. It will protect the fibres against acids, alkalis, water, and many other chemicals to which the leather may be exposed.

2.2.2 Principles of Fatlquoring

The principle of fatliquoring is the application to the goods of an oil-in-water emulsion, which is subsequently induced to break, thus depositing a film of fatty matter over the fibre structure. In the initial stages of the process, the fatliquor emulsion must be compatible with any other chemicals in the same bath so that it remains stable. It must have controllable affinity for the leather so that controlled layer wise deposition of the fat can be obtained. The leather can be considered to be either negatively, positively, or in a balanced charged state, depending on the type of tannage and the pH of the leather. Consequently, by formulating emulsions of an ionic, cationic, non-ionic, and multi-charged charges, varying degrees of affinity between the leather and the oil emulsion can be produced. When the leather and the emulsion have the same charge, good penetration and slow exhaustion of the liquor occurs. Conversely when a leather, or any layer of the leather, has an opposite charge to that of the emulsion, then rapid fixation and deposition of fat occurs. Examples of this effect in work practice are the rapid penetration of sulphated (anionic) oil emulsions into vegetable and semi-chrome leathers and the necessity for neutralising full chrome leather to prevent surface deposition of fat from

anionic emulsions. Likewise, cationic emulsions applied during cationic chrome tannage will penetrate well and give very soft leathers. A high ratio of emulsifying agent to raw oil tends to give emulsions of small particle size and vice versa. Such fine emulsions are very stable and tend to penetrate deeply into the leather to produce soft and loose results. Coarser and less stable emulsions are apt to break more easily, producing firm light leathers tending to be greasy on the surface. For leathers to be paste dried, a very common practice is to fatliquor the leather first with an anionic emulsion, and then to treat the leather subsequently with a small amount of cationic emulsion. This then precipitates on the surface of the leather and act as a barrier to excessive penetration of the paste, thus facilitating removal of the dry leather from the drying plates.

2.2.3 Selection of Fatliquoring Material

The choice of agents for fatliquoring depends on cost and availability, interfacial tension, viscosity, acid value, iodine value, colour imparted to leather, volatility, and method of emulsification and application.

2.2.3.1 Cost and Availability

Economic factors are important and must always be borne in mind. The ever rising demand for edible fats has increased the price of many fats and the leather trade is using increasing amounts of the cheaper oils and fats. In general, hydrocarbon and marine oils are the cheapest materials, vegetable

fats are in the middle price range, with animal and synthetic fats in the most expensive ranges.

2.2.3.2 Interfacial tension

Fats and oils with low surface tension are able to spread easily over the fibre structure and give excellent stretch and softness. Conversely, materials with high interfacial tension give a lower degree of lubrication, firmer leather, and a dry handle. Fish oils are examples of the former group of oils and the vegetable oils are typical of the latter.

2.2.3.3 Viscosity

The viscosity of an oil or fat is one of the factors governing its ability to penetrate into the fibre structure. A high viscosity material tends to have poor penetrating power and remains in the outer surfaces of the leather. It may make the leather feel greasy on the surface, but will have good filling properties. The viscosity of fatliquoring materials is influenced by the temperature of the process and decreases as the temperature rises. Greasy effects can be caused by the use of too low temperatures in the fatliquor float.

2.2.3.4 Acid Value

The presence of free fatty acids in a material for fatliquoring can lead to fatty acid spue formation and lack of adhesion in cemented and vulcanised shoe construction methods. When required for the latter purposes the

leather should not contain more than 3% free fatty acids, but for other purposes high fatty acid values can be tolerated. The fatty acid spue formation causes most trouble to upper and soft leather tanners and can be traced to the use of high quantities of unsuitable fats or incorrect pH gradients inside the leather. The fish oils, with the exception of sperm whale oil, and neatsfoot oils are the most likely oils to have high fatty acid values. The use of vegetable, synthetic, and mineral oils will generally reduce the danger of fatty acid. spue formation.

2.2.3.5 Iodine Value

The iodine value indicates the degree of unsaturation of the hydrocarbon chains in the fat. It is these unsaturated groups which oxidise and cause yellowing of the leather on ageing. When selecting oils for use on leathers to have aniline finishes or for white leathers, the iodine value should be as low as possible.

2.2.3.6 Colour imparted to Leather

This factor is important in all white and pale coloured leathers. The danger of initial yellowing or dulling of the colour must be considered, as well as the subsequent yellowing from oxidation referred to in Iodine value (above).

2.2.3.7 Volatility

The possibility of loss of the 'more volatile oil fractions must be borne in mind when fatliquoring leather for vacuum drying, as it may cause hardening of the leather during drying. It can also cause hardening on ageing and is most likely to occur with fine mineral oils containing short carbon chain oils.

2.2.3.8 Method of emulsification and application

The suitability of the material in actual use is important. It may control the method of emulsification, e.g. the use of chemically treated oils, the use of external emulsifiers, and the conditions of application, with special reference to pH and temperature conditions and compatibility with previous or subsequent treatments.

2.2.4 Fatliquoring Materials

a. Mineral oils:

These oils are widely employed on many types of upper leather. They are cheap, good lubricants, and reduce the danger of fatty acid spue formation. They are useful for leathers which are to be friction glazed as they tend to remain in the outer layers. For the same reason they can be used to control adhesion in paste drying and to lubricate the grain during grain correction processes.

b. Synthetic oils.

These oils are expensive but very useful in producing high quality leathers. They are constant in composition, colourless, chemically stable, and adjusted for specific uses on different types of leathers.

Hydrocarbon oils are not recommended for leathers to be solvent lacquer finished, as they cause poor adhesion of solvent based films

c. Marine oils

These oils are widely used for soft and waterproof leathers. They are powerful lubricants and so can cause looseness of the fibre structure and undesirable stretch in the leather. The common oils met with are cod and other fish oils. Marine oils tend to be low in price and are widely available; however, their colour, smell and high acid value call for special care in their use.

Traditionally sperm whale oil has been used widely in the leather industry. However, there is international concern over sperm whale stocks and many countries have banned its use. It is therefore no longer recommended for use in the leather manufacturing industry. Substitutes for sperm whale oil are now available which are claimed to have the same characteristics of producing a full round leather with good upper leather characteristics. These substitutes should be used instead of sperm whale oil.

d. Vegetable oils

The non-hardening vegetable oils are widely used for producing firm dry leathers with a non-greasy handle. They are particularly useful for fatliquoring all types of suede leathers, white, and pale coloured aniline finished leathers. The most commonly used oils in this class are castor, coconut, olive, and rice bran. They tend to be expensive in industrialized countries but are often locally available at reasonable cost in developing countries (tuck, 1981).

e. Animal oils

The most common oil in this class is neatsfoot oil obtained by boiling the hooves and horns of cattle. It contains large quantities of stearin and is usually filtered at low temperatures (cold tested) before use. It is expensive but has good filling and good lubrication powers. It is the ideal fatliquor for high quality upper leathers. The other material in this group of commercial interest is egg yolk. This contains lecithin and when incorporated into fatliquor emulsions, greatly increases their stability. It can be used alone for fatliquoring white leathers. It is claimed that when used on box calf, a tighter grain break is obtained. Egg yolk preserved only with boric acid should be used for leather. In order to avoid coagulation of protein the egg yolk should never be heated above 60° C. Many egg yolk substitutes based on lecithin are more stable and do not coagulate (Tuck, 1981).

f. Proprietary Products

A large number of proprietary materials is offered to the leather industry for fatliquoring purposes. These consist of straight oils, blended oils, emulsifiable oils, emulsified oils and fats, and auxiliary agents. Some approximate indication of their composition and recommended methods of application is available from the manufacturers.

2.2.5 Fatliquor Formulation

A fatliquor mixture can consist of chemically treated oils, raw oils, emulsifying agents, and auxiliary materials.

2.2.5.1 Chemically Treated oils

Sulphated oils: These are oils treated with sulphuric acid and neutralised in order to produce self emulsifiable products. The degree of sulphation is expressed by the combined sulphate (SO_4^{2-}) factor, for example:

Lightly sulphated oils contain 1—2 % combined sulphate

Medium sulphated oils contain 2—4 % combined sulphate

Highly sulphated oils contain more than 4 % combined sulphate

The effect of increasing the combined sulphate is to reduce the filling properties and increase the fineness of emulsion giving better penetration. These oils give negatively charged emulsions, and are therefore called anionic oils.

2.2.5.2 Sulphited oils:

These oils give anionic emulsions of low polarity and are therefore more stable to oppositely charged materials. They can be applied over a wide range of processes to give softer more mellow leathers than can be obtained by conventional means.

2.2.5.3 Raw oils

These ingredients give the main filling and lubrication effects and have to be carried into the leather as an emulsion, or they can be introduced into the leather by the aid of suitable solvents.

2.2.5.4 Emulsifying agents

Soaps. A number of soaps are used in fatliquoring upper leathers. The most popular are soft and medium soaps, e.g. Marseilles soap — a green olive oil soap and triethanolamine oleate. They are sensitive to acid and hard water and are precipitated by chromium and aluminium ions, Thy give some filling effect and a less greasy surface. Some of the emulsifying agents in tanning processes are synthetic in nature. A very wide range exists and for general purposes is divided into three main groups:

a. Anionic

This is the most important group of emulsifying agents. The earliest members were the sulphonated primary fatty alcohols, and the range now includes secondary alkyl sulphonates, aryl sulphonates, and petroleum

sulphonates. They are extremely useful as emulsifying agents and can be used either to emulsify oils or they can be added in small amounts to increase the stability of emulsion produced by other means, e.g. sulphated oils. If used in excessive amounts they may make the leather soft and loose grains, as well as making it permanently very hydrophilic. This latter effect increases the suitability of the leather for paste drying and aqueous finishing, but may cause trouble to the wearer.

b. Cationic

The most common group of materials in this class are the quaternary ammonium compounds. They are expensive and their use is restricted to special effects, such as emulsifying oils used in mineral tanning, as secondary fatliquors for leathers pasted to dry, and as mordant for leathers subsequently dyed with anionic dyestuffs (Tuck, 1981).

c. Non-ionic

The most common group of materials in this class are the polyethylene oxide-based materials. They produce very stable emulsions for general use over a wide range of leather making processes.

2.2.6 Solvent fatliquors

The fact that leather fibres do not stick together when dried out from a non-polar hydrocarbon solvent has prompted investigation of this phenomenon and efforts have been made to produce commercial product and processes

on this basis. There are processes, in which a solvent of the white spirit type is included in a conventional type of fatliquor, or efforts have been made to use short float solvent based processes; according to Norton (1966).

2.2.7 Emulsion Preparation and Application

The best method of preparing an emulsion for use in fatliquoring is first to boil together untreated oils, synthetic emulsifiers, alkalis, and soaps for 15 minutes. Then chemically treated oils are added and boiled for a further 5-10 minutes. Finally the mixture is cooled to 60°C and any egg yolk or similar material added. The use of high speed homogenizers is recommended to give finer and more stable emulsions, as well as to allow the use of a greater quantity of untreated and cheap oils and fats.

When incorporated into general processing for economic reasons, the diluted product is added to the normal bath. When fatliquoring is a separate process the following factors must be controlled for proper application.

i. Float

A fresh float free from electrolytes is best. The minimum quantity of float gives the best result.

ii. Temperature

Modern fatliquors are not very heat sensitive but for general use on upper leathers the temperature range of 40-65° C is used.

iii. pH

With the general run of anionic fatliquors, the pH of the leather lies in the range 5.0-6.5. For special uses, sulphited and cationic oils can be applied at pH values as low as 3.0-3.5.

iv. Time

If the process is carried out under optimum conditions, a time of 45 minutes in a drum running at 15-20 rpm should be satisfactory.

2.2.8 Fatliquoring Recipes

During pickling and pretannage to produce increased softness, 0.5-1.0 % sulphited, cationic, or non-ionic oil can be added (Hollstein, 1972).

During tannage, to reduce astringency, reduce friction and give softer leather, 0.5-1.0% cationic, non-ionic, or sulphited oil can be added during cationic tannage.

During tannage to reduce astringency, 0.5-1.0 % sulphited oil can be added to the retanning liquor and then a normal fatliquor can be given after retannage is complete.

To control physical properties there are various basic formulae that can be used.

2.3 STUFFING OF LEATHER

In the manufacture of heavy side leather for boots for the armed forces, for agriculture, and for winter sports, it is common practice to make this leather waterproof by treating with molten fats in a hot air stuffing drum. Usually between 15 % and 25 % of stuffing mixture on the shaved weight of leather is employed. The difficulties encountered are to ensure good penetration of stuffing mixtures and to avoid the formation of fatty acid spues on the finished leather. For good results the leather must be well buffered to pH 5.0-6.0 and the stuffing mixture should contain mineral oils and hydrocarbon waxes, which act as solvents for free fatty acids in the oils. In addition, 0.2 % para-nitrophenol dissolved in alcohol (percentage on leather weight) must be added to the stuffing mixture in order to prevent mould formation, which will also cause the formation of fatty acid spue on the leathers (Tuck, 1981).

2.4 SHOWERPROOFING

Upper leathers can be made water repellent before drying and finishing. The best results are obtained with straight chrome tanned leathers, completely free from vegetable tannins, synthetic tannins, dyestuffs and oils, all of which contain strong hydrophilic groups. It is particularly important that the leather does not contain wetting agents. The shower proofing treatments can be done either by drumming the agent into the

leather or by treating the dry leather by pad or spray with a solution of the agent in a suitable solvent mixture.

2.5 PREPARATION OF LEATHER FOR DRYING

After the completion of the drumming processes, the goods are horsed up overnight or for a longer standardized period. This will allow the leather to drain free of excess water and allow time for fixation of process chemicals.

2.5.1 Samming

This process removes surplus water to about 55 % and can be achieved by a number of machines, the commonest being the loose felt sleeved machine. The preliminary removal of water will allow more efficient and more permanent setting out to take place.

2.5.2 Setting out

This process removes further quantities of water to a level of about 40 %, stretches the leather to maximum area and mechanically smoothes the grain side. It must be carefully done for leathers which will be hung or toggled to dry; during vacuum paste drying further smoothening and removal of grain creases and folds will take place so making the setting out less critical. The most efficient machines have heated top rollers and sometimes a

combination of wide and narrow width machines are used in order to get maximum setting out over the whole leather area.

2.5.3 Drying

The factors that have to be considered in drying leather according to Aritz (1969) are:

i. Quantity of water to be removed.

ii. Air temperatures.

iii. Relative humidity of air.

iv. Air speed over leather surfaces.

v. Speed of drying.

vi. Type of installation to be employed.

The quantity of water to be removed from leather is considerable, the leather after setting out containing about 60-65 % water; leather is normally dried down to between 10 % and 20 % water. It is obvious that as much water as possible should be removed from the leather before it enters the drying plant.

Most drying plants use warm air as the means of drying. The temperatures that can be used are governed by the type of goods and the type of tannage. With full chrome leathers, high temperatures can be employed and air temperatures of 70-85° C dry bulb are common; for combination tanned leathers lower temperatures are safer, due to the possibility of migration of

water soluble to the leather surface and edges during drying. In this case, temperatures of 50-70° C dry bulbs are more usual.

The relative humidity of the air and its actual temperature control the amount of water it can hold before becoming saturated. The easiest way of decreasing the relative humidity is to heat the air and this also increases its capacity to carry water vapour at saturation. The air used in drying cabinets will have relative humidity values of 20 % to 50 % and this can be monitored using a wet and dry bulb thermometer and suitable hygrometric tables.

The speed of air flow over the leather surfaces plays an important part in controlling drying. The general trend is to use high speeds, e.g. 90 m/min (300 ft/min) and to blow the air downwards. This takes advantage of the fact that damp air is heavier than dry air. By removing the air quickly from the leather surfaces, it is never allowed to approach saturation and one can, in fact, obtain very good drying results by using large quantities of quite cool natural air, as in the old ‘weather drying’ method.

The speed of drying has important effects on the physical properties of the resultant leather. A slow gentle drying gives soft supple stretchy leather with a poor grain break. Conversely, rapid drying gives a tighter firmer leather with the fibres having a higher angle of weave. Most modern

cabinet and tunnel dryers work on a 3-4 hour drying period and must be used continuously for the most economic results.

The type of installation used for drying varies a good deal; although paste drying is tending to become the most common method.

2.5.3.1 Hanging in cabinets and tunnels

This is the classical method for chrome calf and goatskins. It allows contraction of the leather during drying, giving a plump leather with a tight grain break and classical springy ‘handle’.

2.5.3.2 Toggling in cabinets and tunnels

This method is used by some side leather tanners. It gives a flat firm lather and a higher area yield than hanging. It may lead to distortion of the soft flank areas. It can be used for full grain aniline finished leathers.

2.5.3.3 Paste drying

This method gives the smoothest surface and maximum area yield of all known drying methods. It is recommended for all corrected grain leather but paste residues can interfere with full grain leather finishing. Leathers to be pasted must be plump, well tanned, and contain 30% more fat than leathers dried by other means.

2.5.3.4 Vacuum drying

This is the latest method of drying upper leathers. The leather is set out grain down on a heated plate (70-90° C) and a vacuum is created from the

flesh side. It gives smooth grained leathers, softer than the equivalent pasted leather and the loss of area over a pasted leather is only 3-5 %. It is particularly suitable for all full grain aniline and semi-aniline finished leathers, as there are no paste residues to cause difficulties.

2.5.3.5 Hot water tank drying

The use of hot water tanks as pasting surfaces has been patented and gives very good results (Tuck, 1981). It is very rapid and saves a heavy capital cost. It is widely used both for drying grain and flesh split leathers. Full chrome leather with highly substantive fatliquors are the easiest to process. The presence of synthetic and vegetable tannins in the leather surface can cause it to become hard and brittle when dried in this way; this remark also applies to vacuum dried leathers.

After drying it is general practice to pile the leather in a cool place for as long as possible. This allows the tannage to stabilise and the leather to reach equilibrium moisture content with the surrounding atmosphere. This storing is most essential for full chrome leathers, but as the degree of retannage increases, the advantages to be gained by storing gradually disappear.

2.6 BASIC FATLIQUORING AGENTS

The basic Fatliquoring Agents are summarized below according to Sevim and Liu (2007)

A. Biological fatty substances

1. Vegetable oils

a. Drying oils: linseed oil, hemp oil, poppy oil, nut oil, wood or tung oil. (Limited use)

b. Semi-drying oils: colza or rape oil, maize oil, sunflower oil, soya bean oil, cotton seed oil, rice oil.

c. Non-drying oils: olive oil, castor oil, ground nut oil (arachis oil), fruit kernel oils.

2. Vegetable fats Coconut fat, palm kernel fat, palm oil fat, Japan tallow.

3. Animal oils

a. Marine animal oils: seal oil, whale oil, dolphin oil (no technical use) Fish oils: herring oil, sardine oil, menhaden oil. Liver oils: cod liver oil, shark liver oil

b. Land animal oils: neatsfoot oil, lard oil

4. Animal fats Beef and mutton tallow, lard, butter fat, bone fat, horse grease.

5. Waxes

a. Vegetable: carnauba wax, candelilla wax, montan wax.

b. Animal: beeswax, wool grease.

c. Non-biological fatty substances, paraffin waxes, mineral oils, olefins, processed hydrocarbons, synthetic fatty acid esters and waxes, fatty alcohols, alkyl benzenes.

2.6.1 Chemical characteristics of some fatliquoring agents are provided in Table 1 and 2 (Sevim and Liu, 2007)

Table 2.1. Properties of some fatty acid substances used as fatliquors.

Product	Density	SV	UM (%)	IV	AV	SR (^{0}C)
Cod liver oil	0.921 – 0.928	179 – 193	0.7 – 3.0	140–181	0.5 –1.7	–10 to 0
Shark oil	0.865 – 0.929	85 – 188	2.0 – 56.0	100–200	0.1 –3.0	–20 to +10
Herring oil	0.917 – 0.931	179 – 194	0.7 – 2.4	108–155	1 – 19	-
Menhaden oil	0.925 – 0.935	189 – 198	0.6 – 1.6	139–193		ca. +17
Sardine oil	0.928 – 0.935	186 – 193	0.5 – 1.8	154–196		1 – 19
Ground nut oil	0.916 – 0.921	188 – 197	0.3 – 1.0	83–103 ca.		1 – 3 to 0
Olive oil	0.914 – 0.929	191 – 195	0.5 – 1.4	80– 185		–16 to 0
Castor oil	0.950 – 0.974	176 – 191	0.3 – 0.4	81– 186		–18 to –10
Cotton seed oil	0.913 – 0.927	191 – 199	1.0 – 2.0	101–121		– 16 to – 1
Maize oil	0.920 – 0.928	188 – 198	1.3 – 1.6	117–123		–15 to –10
Rape oil	0.911 – 0.918	172 – 176	0.5 – 1.6	94–105	0.5 –6.0	–10 to 0
Sesame oil	0.921 – 0.925	187 – 195	0.5 – 1.0	103–112		– 16 to – 3
Soybean oil	0.922 – 0.934	188 – 195	0.5 – 1.5	124–133		–18 to – 8
Wood oil (Chinese)	0.936 – 0.945	188 – 197	0.4 – 1.0	150 – 160		– 18 to + 2
Linseed oil	0.930 – 0.936	187 – 195	0.5 – 2.0	172–196		–27 to –16

Table 2.2 Other fatty acid substances used as fatliquors.

Product	Density	S V	U M (%)	IV	AV	S R (^{0}C)
Coconut oil	0.920 – 0.938	246 – 268	0.2 – 0.3	8 – 10	–	+14 to +25
Palm oil	0.921 – 0.948	196 – 210	0.2 – 0.3	51 – 57	–	+31 to +41
Neatsfoot oil	0.913 – 0.919	192 – 196	0.1 – 0.6	68 – 81	1.0 – 6.0	– 12 to – 6
Sperm oil	0.875 – 0.890	125 – 149	35 – 44	71 – 93	0.1 – 0.4	+ 7 to +10
Beef tallow	0.936 – 0.953	190 – 200	0.1 – 0.3	32 – 47	0.5 – 5.0	+30 to +38
Horse grease	0.915 – 0.933	195 – 200	0.4 – 0.7	74 – 94	–	+22 to +37
Egg yolk (egg oil)	0.914 – 0.917	184 – 198	0.2 – 4.2	64 – 82	–	+ 8 to +10
Wool grease (wax)	0.940 – 0.970	77 – 130	39 – 50	15 – 29	1.0 – 3.0	+30 to +40
Beeswax	0.950 –0.966	99– 100	52 – 55	6 – 15	17– 24	+60 to +63
Carnauba wax	0.990 – 0.999	78 – 93	52 – 56	8 – 14	4 – 8	+83 to +86
Japan wax	0.963 – 1.006	207 – 238	0.4 – 1.6	4 – 15	–	+50 to +54
Montan wax	1.000 – 1.030	60 – 90	25 – 60	8 – 15	28 – 32	+78 to +90

SV = Saponification value, UM = Unsaponifiable Matter in %, IV = Iodine Value, AV = Acid Value , SR = Solidification Range in ^{o}C.

2.7.2 Classification of Leather Fatliquoring agents.

These are outlined below

1. Untreated oils, fats and waxes: These are all round fatliquor based on oil, fat and waxes. They have very low odour, resistant to yellowing by light and at high temperatures, very low fogging. It is used to fatliquor all types soft leather like automotive, upholstery and garment leather.

2. Emulsified oils and fats: This type makes it possible to use water based fatliquor in leather production. This process is cheaper, safer and more convenient than that using organic solvent as the fat/oil diluents.

3. Sulfonated oils, fats and fatty alcohols: This is one self emulsifying in water and the resulting product is known as sulfated products involving - C-O-S bond, ester-like, splittable and sulfonated products which involves - C-S bond, true sulfo acid, unsplittable.

4. Chlorinated oils and fats: This involves the production of chlorinated products and sulfochlorinated products by treating fatty substance with sulphur oxides and chlorine.

2.8 Fatliquoring Methods

Some of the most common methods are summarized

1. Oiling-off : This is mainly for oiling of vegetable tanned leathers. It has excellent grain lubrication without imparting the adhesion of finishing coat and is mainly for sole leather (Tuck, 1981).

2. Cold stuffing on the table: This involves impregnating the leather with lubricant on the smooth surface.

3. Hot stuffing by the dipping process: This is a process by which leather is impregnated with fatliquor, generally in a stuffing drum at fairly high temperature.

4. Fatliquoring (principal method): The most common method is fatliquoring in float. It is a treatment with fatty substances emulsifiable in water which are introduced into the inter-fibrillary spaces in an aqueous float. It can be done in warm or cold float. It can also be carried out by dry fatliquoring (without float) oiling by brush.

2.9 Some Commercial Formulations used as fatliquor agents Baden Aniline and Soda Factory (BASF) are the sole producers of the following fatliquor agents.

2.9.1 Fatliquors based on natural oils

These include:

i. **Lipoderm Liquor 1C** All-round fatliquor based on fish oil. Fat content approx. 90 %.

ii. **Lipoderm Liquor A1** Chrome-resistant fatliquor with very low odour. Resistant to yellowing by light and at high temperatures, very low fogging. Lipoderm Liquor A1 can be used to fatliquor all types of soft leather such as automotive, upholstery and garment leather, nappa shoe uppers and soft, milled leathers. Fat content approx. 70 % (Erhan 2004).

iii. **Lipoderm Liquor LA** Leather treated with Lipoderm Liquor LA has a silky surface texture and a handle which is pleasantly soft, full and supple. It can be used to fatliquor all types of soft leather, especially upholstery leather and garment leather. Lipoderm Liquor LA's excellent fastness and very low fogging make it an ideal choice for fatliquoring automotive leather. Lipoderm Liquor LA can also be used to improve the handle of nubuck.

iv. **Lipoderm Liquor PN** Fatliquor for soft, stretchy leathers with a tight grain, a slightly greasy handle and high fastness. Fat content approx. 60%.

v. **Lipoderm Liquor WF** Reduces the water absorption and wettability of the leather, enhances the fatliquoring effect, and gives a tight grain and a greasy handle. Recommendable for use with the Densodrin system for water-resistant leathers. Fat content approx. 50 %.

2.9.2 Fatliquors based on synthetic oils

The common types available include:

i. **Lipoderm Liquor FP** Polymeric fatliquor mainly used in combination with other fatliquors. High fullness, high exhaustion, odourless, low fogging, high yellowing resistance. For automotive leathers, shoe uppers and leathers that are washable and resistant to dry cleaning. Recommendable for use with the Densodrin system for water resistant leathers.

ii. **Lipoderm Liquor PSE** Lightfast, synthetic fatliquor for soft leathers. High penetration, high emulsifying power for synthetic oils, resistant to chrome. Fat content approx. 60 %.

iii. **Lipoderm Liquor SAF** Recommended for fatliquoring high-quality leathers such as aniline, softy, nappa and suede. Penetrates well and gives the leather a greasy handle and an elastic grain. Fat content approx. 80%.

iv. **Lipoderm Liquor SLW** Lightfast, synthetic fatliquor with very high penetration for soft, washable leathers. Can be used in combination with

Densodrin types to enhance the softness of water-repellent leathers. Fat content approx. 60 %.

v. **Lipoderm Liquor SOL** Leather treated with **Lipoderm Liquor SOL** has a tight grain, a full handle and high fastness. It responds very well to dyeing. Lipoderm Liquor SOL can be employed as the main component of mixtures of fatliquors which can be applied to all types of leather, especially shoe upper leather. We would recommend combining Lipoderm Liquor SOL with selected fatliquors from our range in order to control the handle and specific properties of the leather.

2.9.3 Fatliquors based on natural and synthetic oils

The two most versatile agents used are:

i. **Lipoderm Liquor CMG** Gives very soft leather. Odourless, low-fogging and high fastness. Especially recommended for automotive leather, upholstery leather, garment leather and nappa shoe uppers. Fat content approx. 60 %.

ii. **Lipoderm Liquor SC** Mixture of natural and synthetic oils. Can be used as the sole fatliquor applied to shoe uppers. Fat content approx. 70 %.

2.9.4 Cationic Fatliquors

i. **Lipamin Liquor NO** Lightfast, natural fatliquor, suitable for use in multicharge liquors, especially on leathers that are vacuum dried. Fat content approx. 60 %.

ii. **Lipamin Liquor SO** Lightfast, synthetic fatliquor. Resistant to yellowing at high temperatures, suitable for use in multicharge liquors. Fat content approx. 60 %.

2.9.5 Water-insoluble fatliquors

This product is lightfast. It inhibits exudation and increases the tensile strength of the leather. Examples of these products are:

i. **Lipoderm Oil N1** is natural raw oil with characteristics similar to those of neatsfoot oil. The leather gets a full, supple handle and a particular smooth, fine grain. Lipoderm Oil N1 can be recommended as a fatliquoring additive for all types of chrome leather, but especially for shoe uppers. If it is used as a "grain oil" on vegetable tanned leather, such as sole leather and case leather, higher elasticity and gloss are achieved.

2.9.6 Fatliquoring Auxiliaries

i. **Lipoderm N** Anionic emulsifier and stabilizer for anionic fatliquors, with an additional fatliquoring action can be applied to washable leathers.

ii. **Lipamin OK** Cationic stabilizer for cationic fatliquors, with an additional fatliquoring action.

iii. **Siligen HS** Cationic emulsifier for fats and oils.

2.10. QUALITY OF LEATHER FATLIQUOR

To assess the qualities of leather fatliquors, the under listed tests are normally required according to Leticia and Matrix (2007).

1. Water-insoluble fatliquoring agents

a. Determination of water content

b. Determination of non-volatile, non-fatty organic substances (The insolubles in ether minus ash give the non-volatile, non-fatty substances)

c. Determination of total volatile substances (Water and organic solvents)

d. Determination of content of mineral matter

e. Fatliquoring substances (Product weighed out minus water, volatile and non-volatile organic substances and mineral matter)

f. Determination of fatty acids

g. Determination of unsaponifiable matter

2. Water-soluble Fatliquoring agents

a. Determination of fatliquoring substances (100 minus water, mineral matter and volatile organic substances = % fatliquoring substances)

b. Separation into emulsifying and emulsified components (according to Panzer-Niebuer) Emulsified proportion = neutral fat, unsaponifiable matter, free fatty acids (in petroleum ether solution) Emulsifying proportion = emulsifiers (in aqueous/alcoholic solution)

c. Testing for sulfonation

d. Determination of degree of sulfonation (total SO_3^{2-}, inorganically and organically bound SO_3^{2-})

e. Determination of degree of neutralization

f. Determination of neutral salts in sulfonated oils

3. Characteristics of Fats and Oils required are:

a. The iodine value (IV) specifies the amount of unsaturated compounds.

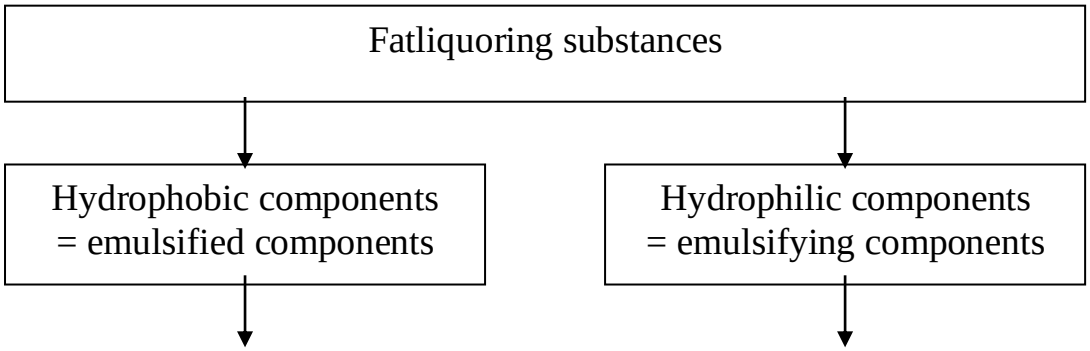
b. The acid value (AV) specifies the amount of free fatty acids contained in the fat.

c. The saponification specifies the amount of potassium hydroxide in value (SV) mg necessary for neutralizing 1 g fatty acid.

d. The ester value (EV) is a measure of the ester content of fats or waxes. It is identical to the saponification value of acid-free fats.

e. The peroxide value (PV) is a measure of the peroxide-bound oxygen contained in fats or oils. It is used to assess the degree of oxidation.

2.11 GENERAL STRUCTURE OF FATLIQUORS



consisting of:
unsaponifiable and
saponifiable substances
=

a. Biological fatty substances
(animal and vegetable oils/fats)

b. Non-biological fatty
substances (paraffins,
processed
hydrocarbons, synthetic
fatty acid esters, fatty
alcohols, alkyl benzenes,
polyethers)

consisting of:
emulsifiers and
fatliquoring auxiliaries
=

a. Anionic substances
(sulfates, sulfonates,
carboxylic acids)

b. Cationic substances
(amine salts, suphonium and olefins,
phosphonium compounds,
polyamines, fatty amines)

c. Nonionic substances
(substituted polyalcohols,
polyglycol ethers)

+

Mineral matter

= inorganic salts

+

Volatile matter

= water, solvents

2.12 REACTIONS IN THE PRODUCTION OF FATLIQUORS

Sulphation process

The reaction of oils with sulphuric acid is an addition reaction. Normally the oil is an unsaturated oil as saturated oils are less chemically active and therefore difficult to sulphate .

- $R - CH = CH - R + H_2SO_4 \longrightarrow R - CH_2 - \underset{\displaystyle OSO_3H}{\underset{|}{CH}} - R + NaOH$

  $\longrightarrow R - CH_2 - \underset{\displaystyle OSO_3Na}{\underset{|}{CH}} - R + H_2O$

  Sulphated oil

- Side reaction

  $R - CH = CH - R + H_2SO_4 \longrightarrow R - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle SO_2OH}{\underset{|}{CH}} - R$

  Sulphonated oil

- With some oils such as castor oil , the main reaction is esterification of the hydroxyl group.

- $CH_3(CH_2)_5 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH = CH\,(CH_2)_7 - COOH + H_2SO_4$

  $\longrightarrow CH_3\,(CH_2)_5 - \underset{\displaystyle OSO_2OH}{\underset{|}{CH}} - CH_2 - CH = CH\,(CH_2)_7 - COOH + H_2O$

Sulphated castor oil (Turkey red oil)

Turkey red oils can form alkali metal salts (saponification) which are known as Turkey red oil soaps, widely used as surface active reagents in the fatliquoring of chrome tanned leathers.

2.13 OIL LUBRICANTS

Oil lubricants are classified into mineral oils, natural oils, synthetic oils and emulsions natural oils are regenerative and renewable through improved agricultural techniques. Mineral base oil lubricants for engineering mechanisms formulated from hydrocarbon mineral oils are expensive to process and use. Whole or partial substitution with natural oil by blending will not only reduce processing and use cost but also enhance downstream relevance of the botanical plants and encourage the upstream primary producers to expand their agricultural activities.

Erhan *et al* (2004) suggested that the polar functionality of natural oil structure provides a surface protection film with strong adsorption energy arising from greater lateral interaction between the polar heads and long hydrocarbon chains of the ester group. The coefficient of friction and wear rate are dependent on the strength of the fluid film and extent of adsorption on the metal surface. However, the cold flow behaviour of natural oil derivatives poses a rheologic and challenge. Sharma *et al* (2004) suggested improvement in flow behaviour by structure modification using anhydrides.

The rheology of oil lubricants indicates the flow and deformation characteristics of the lubricant during processing, transport and use. The rheology of the oil lubricant showed maintain the integrity surfaces under operating conditions of sliding speed, contact pressure, temperature and humidity, and atmospheric cleanliness Sivakumar (2004).

Rheological behaviour of oil lubricants is most relevant in the hydrodynamic and elas to hydrodynamic lubrication regimes. Harris and Busby (1973), Spikes (1994), Taylor (2002) and Bames *et al* (2001) among others, have studied various aspects of mineral oil lubricants rheology and have concluded that mineral oil have good wear and friction properties because of their inherent lubricity, adequate low temperature flow behaviour and good oxidation property; but are not environmentally friendly. Alakali *et al* (2003) and Satimeluis *et al* (2003) worked on the rheology of palm oil and canarium oil respectively with relevance to processing and transport and found their low temperature instability a major hindrance to processing. Similar conclusions were drawn by Adhavarya *et al* (2004), Sharma *et al* (2004) and Castro *et al* (2006) in their work on the oxidation and wear properties of soybean oil. They suggested the modification of the chemical or generic composition of the oil to improve its oxidation and wear properties. The rheology of a great variety of natural oils from tropical plants amenable to short rotation

plantation deserve more research in order to reduce lubrication costs and down times of production equipment.

Indiscriminate disposal of spent lubricating oil into the surrounding ecosystems has contributed immensely to the level of environmental pollution in the society (Akpan and Frank, 2003; Okelana *et al* 2003). Certain analytical studies had shown that spent lubricating oils contain certain chemical constituents with biocidal properties.

2.16 OIL EMULSION

An emulsion is a fine dispersion of one liquid in another liquid with which it is immiscible. Surface active or other agents that are added to an emulsion to increase its stability by interfacial action is known as emulsifiers or emulsifying agents. In the fatliquoring process, oils/fats are employed as oil in water emulsion known as fatliquor. Fatliquor may be anionic, cationic or non-ionic. Anionic fatliquors are commonly employed for fat binding with chrome tanned leather, which is cationically charged. An ionic fatliquors are commonly prepared by sulphation, sulphonation or bi-sulphifation of oils/fats. Depending upon the source of the oils/fats used, the fatliquor can be classified as vegetable, synthetic or semi synthetic.

Generally, castor oil is used as a source for vegetable based fatliquors. The synthetic fatliquors are usually obtained by sulphochlorination of $C_{10} – C_{20}$ fractions obtained through the Fischer – Tropsch method of paraffin

synthesis or from the petroleum industry (Dutta 1985). Semi-synthetic fatliquors are prepared from both the vegetable and synthetic sources. Characterization and possible use of oil extraction from seal hides as leather fatliquor has also been studied (Cuq *et al*, 1998).

2.17 ULTRASOUND – APPLICATION IN FATLIQUORING EMULSION PREPARATION

The application of power ultrasound in process industries has a significant role in the concept of 'Clean technology' ultrasound is a sound wave with a frequency above the human audible range (16 HZ to 16 KHZ). Ultrasound having frequency range of 20 KHZ to 100 KHZ is termed as power ultrasound (Mason, 1990) and commonly employed for improving the efficiency of physical processes such as cleaning, emulsification, degassing, crystallization, extraction, etc (Contamine *et al*, 1994) and for accelerating/performing chemical reactions (Ando and Kimura, 1990). Ultrasound having frequency range of 1 – 10 MHZ is termed as diagnostic ultrasound and used in medical field and non-destructive testing (Xie *et al*, 2000). The main advantage of physical methods such as use of power ultrasound over chemical means of activation of reactions is that they do not contribute to pollution load in the form of chemical entities (Sivakumar and Rao, 2001). The potential use of ultrasound in process industries such as leather with the aim to improve the quality, improve diffusion rate,

reduce process time and pollution load have been investigated extensively (Sivakumar and Rao, 2004).

Fatliquoring emulsion was earlier prepared using natural and sulphated fats and by exposing the mixture to ultrasonic waves for 10 – 15 min. (Senilov and Obukhov, 1990). Fat emulsion of alkyl phenol ethylene oxide condensates and surface – active agents was prepared using ultrasound (Timochin *et al* 1961), which lowers the sulphated oil requirement for fat liquoring by 25 – 30 %. Fatliquor emulsion was also successfully prepared quickly and economically using ultrasound (Gourlay, 1959). Fat liquor emulsion preparation based on castor oil using ultrasound has been discussed (Sivakumar *et al*, 2007). The use of ultrasound for enhancing the fatliquoring process has also been studied (Sivakumar *et al*, 2005). Due to the growing demand for the good quality leather auxiliary chemicals, newer processing techniques are gaining importance. Although earlier work has been carried out, some of the important aspects have not been addressed so far. The aspects in the present study include, influence of process parameters such as ultrasonic output power, time of emulsion formation, emulsion particle size, stability of the emulsion and suitability of the emulsion for application to leather. Vegetable oil – water emulsion based on castor oil has been studied (Sivakumar *et al*, 2007). The ultrasonically prepared fatliquor has been employed to leather and their

applicability has been studied through the strength properties of fatliquor leather.

2.17.1 Need for power ultrasound in emulsification process

1 Sulphation is the general method followed to prepare fatliquor emulsion based on castor oil where sulphuric acid is used. The use of sulphuric acid in fatliquor preparation reduces the neutral oil component in fatliquor, which is very essential for importing good feel and better properties to leather.

2 Therefore, alternative method, which uses sulphation free process for preparation of fatliquor, would be beneficial.

3 An emulsifying agent is required to increase the stability of oil in water emulsions. The emulsifying agents generally used are chemicals or metal soaps which result in increased pollution.

4 The potential use of ultrasound in the preparation of table oil in water emulsion (as non-ionic vegetable fatliquor) without sulphation process and with minimum use of additional emulsifying agents has been studied (Sivakumar *et at*, 2007).

5 The possible benefits in leather due to the use of the fatliquor so prepared using ultrasound have also been investigated.

2.15.2 Relevant sonochemistry

The sonochemical activity arises mainly from acoustic cavitation in liquid media, which are nucleation, growth and explosive collapse of microbubbles on a microsecond time-scale. The cavitational collapses occurring near a solid surface will generate microjets and shock waves (Suslick and Casadonte, 1987). Moreover, in the liquid phase surrounding the particles, high micro mixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid. The intense agitation and dispersion effect which is brought on by the effects of cavitation, results in an increase in the number of collisions between the oil droplet and water and hence better emulsification of oil in water.

Generally, the sonochemical activity arises mainly from acoustic cavitation in liquid media explained as nucleation, creation, growth and collapse if micro second time scale (Mason 1999), (Suslick *et al* 1986) and (Diderko *et al* 1999). Then further pore diffusion is dependent mainly on the concentration gradient across the layers and degree of binding on the fibre surface (Sivakumar *et al* 2000). Modeling of batch sonochemical reactor considering the acoustic cavitation parameters for a liquid phase reaction was made earlier (Rajan *et al* 1998). In the leather state, localize temperature raise and swelling effects due to ultrasound may improve the diffusion (Sivakimar and Rao, 2003).

Summary of benefits obtained due to the use of ultrasound in various unit operation related to leather processing. Venkatasubramanian and Paruchuri (2009)

S/No.	Unit Operation	Mechanism
1.	Soaking	Cleaning action
2.	Liming	Hair dressing
3.	Degreasing	Fat removal after emulsification
4.	Tanning: vegetable tanning	Penetration of tanning (polyphenolics) and binding with collagen
5.	Dyeing	Diffusion electrostatic binding
6.	Fatliquoring	Diffusion and lubrication of Leather fibre
7.	Tanning extraction: solid-liquid leaching	Leaching of tanning agents from plant material
8.	Natural dye extraction from plant materials	Leaching of colorants from plant materials
9.	Emulsification: fatliquoring emulsion preparation	Oil water emulsification process
10.	Precipitation: chrome recovery	Better setting rate of $Cr(OH)_3$ precipitate due to better dispersion of alkali MgO

Ultrasonic pulse mode operation is found to be useful for reducing the electrical energy consumption in ultrasound aided leather dyeing (Sivakumar and Rao, 2003). Use of external aids such as air-bubbles or surfactant in the dye bath give significant improvements in ultrasound aided leather dyeing process due to the formation of more number of soft cavitation bubbles, which have been found useful in the process (Sivakumar and Rao, 2003). Photomicrography analysis of cross-section of

dyed leather show better penetration and distribution of dye for the ultrasound aided process (Sivakumar *at al* 2005). Scanning electron microscopy (SEM) analysis indicates leather fibre structure is not affected due to ultrasound (Sivakumar and Rao, 2004). The effect of dual as well as higher frequency system Vil. 58KHZ, 1132 KHZ, 192 KHZ and 58 + 198 KHZ has also been studied in leather dyeing process and found to be beneficial (Nagarajan *et al.,* 2006).

The influence of ultrasound on leather fatliquoring process has been studied with different types of 'fat liquor' such as vegetable, synthetic semi-synthetic having varying degree of penetration ability (Sivakumar *et al.* 2005). Significant improvements have been observed in leather fatliquoring process as well as for pre-sonication of substances such as vegetable 'fatliquor' due to considerable reduction in emulsion particle size aiding penetration through the matrix.

Physical effects of ultrasound such as cleaning, micro-stirring, emulsification have been gainfully employed in pre-tanning operations such as soaking (Sivakumar *et al.* 2004) for removal of non-collagenous materials, liming for hair loosening and fibre opening, degreasing (Sivakumar *et al. 2004*) for removing natural fat respectively to improve the efficiency of these processes. There is also found to be enhanced rate of rehydration of air dried skin in the soaking process due to the use of ultrasound.

2.15.7 Vegetable Tanning Process

Vegetable tanning is one of the versatile tanning methodologies involving natural materials. The problem associated with this tanning method is that it takes longer time for diffusion of vegetable tanning agents (VTA) through the part matrix. Diffusion rate enhancement with ultrasound has also been observed in vegetable tanning (Sivakumar and Rao, 1999) and (Sivakumar *et al.2008*). There is about 30 – 40 % increase in % uptake of VTA due to the use of ultrasound for 120 – 210 w under the given process conditions. There is an appreciable reduction in the particle-size of VTA due to sonication prior to tanning process aiding penetration.

2.15.8 Oil-Water Emulsification Process

Oil-water emulsion known as 'fatliquors' are employed in leather making for softening the leather. The application of ultrasound in oil-water emulsification process has been found to give suitable emulsion with minimal use of surfactant and without using conventional sulfation process (Sivakumar *et al.* 2008). The emulsion so obtained by the ultrasonication method is found to be suitable for leather application. The intense agitation and dispersion effect, which is brought on by the effects of cavitations, results in an increase in the number of collisions between the oil droplet and water and hence better emulsification of oil in water (Sivakumar *et al.* 2008). Ultrasonic cavitation at castor oil-water interface is found to

significantly enhance the emulsification rate, useful for scaling up of the process.

2.15.9 **Preparation of Fatliquor Emulsion**

Experiment has been carried out for the preparation of fatliquor emulsion with 80% castor oil for application to leather fatliquoring process. The details of the experiment are as follows:

i) Total amount of vegetable oil and water = 80 g;

ii) Composition of vegetable oil = 80 % (64g);

iii) Composition of water = 20 % (16 g); and

iv) Ultrasound output power = 100 W

Time taken for complete emulsification was recorded.

2.15.10 **Stability of the Fatliquor**

The stability of the prepared fatliquor emulsion has been studied by observing phase separation (as oil and water if any takes place with respect to time.

CHAPTER THREE

MATERIALS AND METHODS

3.1 PREPARATION OF SEED SAMPLES

The Zogalle (*Moringa oleifera*) seeds were identified and collected at Modire in Girei Local Government and Dirma in Song Local Government Areas of Adamawa State in Nigeria because of their size and relative abundance. They were dried, the outer cover removed, then pre-heated and pulverized into paste form.

3.2 EXTRACTION OF OIL

The solvent extraction (soxhlet method) was used. In this method, 40 g of the ground seed sample was wrapped in the cellulose paper, then placed in the thimble, and extracted using lighter petroleum ether (40-60^{o} C) in a 5L soxhlet extractor for 8 h according to Pena *et el.,* (1992).The oil was then recovered by evaporating the solvent using vacuum evaporator and the residual solvent was removed by drying in an oven at 60^{o} C for 1 h.

3.3 DETERMINATION OF OIL CONTENT.

Harold *et al*., (1990) method was used. A clean dry 200 ml conical flask was used to weigh the extracted oil. The calculation below was used to obtain the percent oil content.

$$\% \text{ oil content} = \frac{\text{Weight of oil obtained}}{\text{Weight of sample used}} \times 100$$

3.7.0 DETERMINATION OF THE PROPERTIES OF THE OIL

3.4.1 Determination of Density of Oil

The procedure by Gunstone (2004) was adopted. In this method a clean measuring cylinder was dried in an oven at 105 – 110^{o} C and weighed. A volume of 5 cm^{3} of oil was measured into the cylinder using pipette and weighed again, then the density of the oil calculated using the relation:

Weight of cylinder = w_2

Weight of cylinder + oil = w_1

Weight of oil = $w_1 - w_2$

Initial volume of oil = v_1

Density of oil = $\frac{w_1 - w_2}{V_1}$

using the relation,

Density = Mass/Volume at 30^{o} C.

3.4.2 Determination of Moisture Content

The procedure used was in accordance with SLTC UK (1996). Here, 1 g of oil sample was weighed onto a dry evaporating dish. The oil was dried in an oven at 105^{o} C for 3 hours. The dish was removed and cooled in a desiccator, weighed, taken back to the oven and heated for another one

hour. This was done to achieve a constant weight and the following calculations performed:

Weight of dish = a

Weight of sample = 1 g

Weight of dish + sample before drying = b

Weight of dish + sample after drying = c

Weight of moisture = (b – c) – a

$$\% \text{ moisture} = \frac{(b-c) - a \times 100}{\text{Weight of sample}}$$

3.4.3 Acid Value

The method already outlined by Harold *et al.*, (1990) was adopted: 1g of the oil was weighed into a conical flask and 50 ml of petroleum ether was then added and then mixed gently. This was followed by the addition of 50 ml of ethanol and titrated against 0.1 M NaOH to obtain a pink colour.

$$\text{Acid value} = \frac{V \times \text{Normality of NaOH} \times 5.61}{\text{Weight of sample used}}$$

where V = Volume of NaOH used

3.4.4 Free Fatty Acid

The data obtained for the determination of the acid value was used as suggested by Baker (1964).

Free fatty acid = $\frac{\text{V x Normality of NaOH x 28.2}}{\text{Weight of sample}}$

3.4.5 Determination of Saponification Value

This was carried out according to the method described by Harold *et al.*, (1990). A portion of 2.0 ml of oil was measured into 25 ml of 0.5 M ethanolic potassium hydroxide in a 250 ml conical flask and refluxed on a heating mantle for one hour after which the content of the flask was titrated against 0.5 M HCl using phenolphthalein as indicator. The difference between the titre values of oil sample and the blank was recorded.

Weight of sample = w (g)

Volume of HCl used in the test = V_1 ml

Volume of HCl used in the blank = V_2 ml

Molar concentration of HCl = M (mol/dm^3)

Saponification Value (SV) = 28.05 ($V_2 - V_1$)/w

3.4.6 Determination of Iodine Value

Harold *et al.* (1990) method of analysis was used. 1ml of oil was measured into an empty conical flask and 15ml of Wij's solution was then added. The flask was Stoppered and then shaken gently. It was allowed to stand in the dark at room temperature for one hour. 20 ml of 10 % potassium iodide solution was added followed by 150 ml of distilled water. The mixture was titrated against 0.05 M thiosulphate solution using starch as indicator.

Weight of oil (1.0 cm^3) = W

Volume of sodium thiosulphate used in the test = V_1

Volume of sodium thiosulphate used in the blank = V_2

Concentration of sodium thiosulphate = M

$$\text{Iodine value (IV)} = \frac{2[1.269(V_2 - V_1)\,M]}{W}$$

3.4.7 Determination of Unsaponifiable Matter

The Harold *et al.* (1990) method was used. A portion of 2 g of oil was weighed into 250 ml flask. 25 ml alcoholic potassium hydroxide solution (0.5 M in 95 percent ethanol) was then added and boiled gently under reflux for 1 hour and transferred into a separating funnel, using 50 ml water to wash the flask The solution extracted was warmed 3 times with 50 ml diethyl ether. The third extract was added, then shaken the combined ether extract with the first 20 ml of wash water and then vigorously with two further 20 ml quantities. Ether extract was washed twice with 20 ml of aqueous 0.5 M potassium hydroxide solution and at least 20 ml of water until the wash water was no longer alkaline to phenolphthalein. Ether extract was poured into a weighed flask and the solvent evaporated off. The residue was then dried at 80^o C in the oven to constant weight. Unsaponifiable matter was dissolved in neutral alcohol and titrated with 0.5 M NaOH.

3.4.8 Measurement of Peroxide Value

The Harold *et al.* (1990) method was adopted. About 2 g oil sample was weighed into a dry 250 ml stoppered conical flask. 10 ml Chloroform was added to dissolve the fat by swirling and 15 ml glacial acetic acid, 1ml of fresh saturated aqueous potassium iodide solution were added. The content was shaken for 1min and placed in the dark for 5min. About 75 ml of water was added, mixed and the freed iodine was titrated with 0.01M sodium thiosulphate solution using soluble starch solution (1 %) as an indicator. A reagent blank determination (V_0) was done with 0.5ml of 0.01M thiosulphate solution and used in the calculation of peroxide value.

$$\text{Peroxide Value} = \frac{(V - V_0)\, T \quad X\, 10^3\, \text{mEq/kg}}{M}$$

T is the molarity of the thiosulphate solution.

3.4.9 Determination of Kinematic Viscosity

This was carried out in accordance with Nouredini *et al.*, (1992) method. A Canon – Fenske routine viscometer was used for these measurements, where suction was applied to cause the sample to rise above the first marking line. The sample was then allowed to flow down past the second marking line. The efflux time were calculated as the time required for the oil to pass between the two marking lines and the kinematic viscosity calculated as the product of the efflux time and the viscometer constant.

$V = K(t - q)$

where: V = Kinematic Viscosity

K = Constant printed on the viscometer

t = Average flow time

q = Correction factor (Hagen –bath correction)

3.4.10 Determination of the Ash Content

The method used by Maduako *et al.,* (2000) was adopted. In line with their method, the specimen was put in an oven crucible, weighed and heated in a furnace at 1000^{o}C for 24 h to drive off all volatile matter in the sample. The specimen was removed with the crucible every 6 h, cooled in a desiccators and reweighed, until a constant weight was recorded three times, which was the weight of the remaining ash crucible. The ash content was determined by subtracting the initial and final weight of oven crucible. The weight of the oil ash was then expressed as percentage of the initial weight of the specimen.

3.5 DEVELOPMENT OF FATLIQUORING AGENT

About 50 g of oil was added into a clean beaker and 10 % H_2SO_4 V/V (sulphating agent) was added and allowed to react for one hour. One piece of dried sheep skin was treated with 5% V/V of the product. The experiment was repeated with 15 %, 20 % 25 % and 30 % V/V H_2SO_4.

3.5.2 Leather Fatliquoring Procedure

In order to find out the applicability of prepared oil-water emulsion on leather, fatliquoring process was carried out. Sheep skins treated, tanned using basic chromium (iii) sulphate retanned with syntan (synthetic agent) and then taken for the fatliquoring experiment. The skins were cut into two halves through backbone as left and right hand sides for the comparison of the process with and without chromium. The leathers were then cut into 6 x 6 cm size samples and then neutralized to the pH of 6.0 – 6.5 using sodium formate and sodium bicarbonate. The shaved weight of the leathers were recorded. The effect of amount of fatliquor 2 – 10 % (% based on shaved weight) on fat uptake in leather were studied according to Sivakumar *et al.* 2008. Fatliquoring experiments were carried out with 500 % water as float for 2 h in a sample drum with 45 rpm having 22 cm diameter x 8.5 cm width.

3.6 ANALYSIS OF TREATED LEATHER

3.6.1 Strength Properties of the Leather

Strength characteristics of the fatliquored leathers such as tensile strength and torgue tear strength (SATRA, 1992) were tested using an instron tensile tester and grain crack and grain burst were also tested using castor meter. Leather samples for the physical testing were taken parallel to

backbone from the leather samples following the IUP/1 procedure for sampling and testing as published (IUP, 1958).

3.6.2 Stability of the Fatliquor

The stability of the prepared fatliquor emulsion was studied by observing phase separation (as oil and water) if any takes place with respect to time.

3.6.3 Fat Content Determination

The fat content in the leather (dried leather weight basis) was determined by following the soxhlet extraction method (SLTC, 1996). The fat content in the leather was determined by soxhlet extraction method using dichloromethane as a solvent (SLTC, UK, 1996). The wet leather sample was cut into small pieces and taken in an evaporating basin and dried at 30-35^{o} C for 16-18 h. The actual weight of the leather was recorded (W_1). Then the dried leather was transferred to the extraction thimble made out of Whatman No.1 filter paper. The extraction flask was cleaned and dried in the oven at 105^{o} C, cooled in a desiccator and its weight along with porcelain was noted (W_2).

$$\% \text{ fat content} = W_2\text{-}W_1 \times 100/W.$$

3.6.5 Measurement of Tensile Strength, Percent Elongation and Tear strength

The above parameters were determined using the procedure according to Mahdi *et al.*, (2009), IUP (1958) as detailed in the following.

$$\text{Tensile strength in N/mm}^2 = \frac{\text{Breaking load N}}{\text{thickness in mm x width in mm}}$$

Breaking load N = highest load reached at break.

$$\text{Elongation at break in \%} = \frac{\text{mm length at break} - \text{mm initial length}}{\text{mm initial length}} \times 100$$

3.6.5.1 Tensile Strength

The samples were cut parallel and perpendicular to the backbone using a dumbbell shape. The thickness and width of the specimen was measured in the same position using standard thickness gauge and Vernier calipers respectively i.e. measured one at the mid−point and the other two midway. The width was measured on the flesh and grain side, and then the mean thickness (mm) and width (cm) was calculated. The area of cross section of each specimen was also calculated by multiplying its width by its thickness. The jaw of the tensile machine (Instron l026) was set 50 mm apart, and then the sample clamped in the jaws, so that the edges of the jaws lie along the mid line. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load.

Tensile strength load is in Newton's or kilograms according to Official Method (SLTC, 1996).

3.6.5.2 Percent Elongation at Break and Grain Crack Load Testing.

The initial free length between the clamps before and after final free length at the instant of break was measured. The initial free length was set at 5 cm and the elongation calculated from graphical read out according to the Official Method (SLTC, 1996).

3.6.5.3 Measurement of Tear Strength

This method is intended for use with any types of leather. The specimens were cut as a rectangle 50 mm long and 25 mm wide by use of a press knife which cuts out the specimen and slot in one operation parallel and perpendicular at each position. Instron l026 having a uniform speed of separation of the jaws of 100±20 mm per minute was used, and the readings of load till in that part of the scale which has been shown by calibration to be correct within 1%. The machine was run until the specimen was torn apart and the highest load reached during tearing was recorded as the tearing load. Tearing load is in Newton's or kilograms

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF Zogale (*Moringa oleifera)* SEED OIL

From the study of the physical and chemical properties of the seed oil shown in Table 4.1, the oil content of *Moringa oleifera* was determined to be 38.0 %. This reasonably high oil content of *Moringa oleifera* indicated that the oil could be used on commercial basis. Generally, the oil content and properties of seed oils showed a wide variation depending on the species and environmental conditions (Ibrahim *et al.*, 1974). The sample used was said to have greater yield of the seeds, big in size and very abundant.

The iodine value is a measure of the unsaturation of fats and oils. Low iodine value indicated that lower unsaturation (Knothe 2002; Kyriakidis, 2000). The iodine value of *Moringa oleifera* seed oil was determined as 65. Standard iodine value of the egg yolk (egg oil) lies between 64 – 82 (Sevim and Liu 2007). The iodine value of *Moringa oleifera* oil places it in the semi-drying group. The value of the refractive index was in line with those of cotton seed, palm and mango kernels respectively (Rossell,1991).

Peroxide value of *Moringa oleifera* seed oil which is a measure of the peroxides contained in the oil and secondary oxidative product, showed a low value (as crude seed oil) of 1.89, proving the oxidative stabilities of the

seed oil relatively. The high iodine value and oxidative stability shows that the seed oil upholds the good qualities of semi-drying oil purposes (Eromosele *et al.*, 1997).

Saponification value of the studied oil is 183.4. High saponification value indicated that the seed oils are normal triglycerides and very useful in the production of fatliquors. Also with the % FFA as oleic acid of 2.25 is good in the vulcanized shoe production which usually contain no more than 3 % free fatty acids (Tuck, 1981).

Viscosity defined as resistance of liquid to flow. Viscosity increased with molecular weight but decreased with increasing unsaturated level and temperature (Nouredini *et.al.*, 1992). Viscosity of oil is one of the factors governing its ability to penetrate into the fibre structure. *Moringa oleifera* seed oil with a value 43.13 cp has a good penetrating power and penetrates well into the leather because of its moderate viscosity and will not make the leather greasy on the surface. Tuck, (1981).

The unsaponifiable matter (%), which is similar to those of cotton seed oil, liver oil and sardine oil respectively used as fatliquoring agents. The density obtained at 30^{o}C was 0.9032 g/cm^{3} which shows that it is similar to that of the cod liver oil, groundnut oil, soybean oil which are good fatliquoring agents also (Sevim and Liu, 2007).

Table 4.1 Physico-Chemical Properties of *Moringa oleifera* Oil

PARAMETER	VALUE
Colour	Yellow
Oil content (%)	38
Oil density at 30°C (g/cm^3)	0.9032
Free fatty acid (as % oleic acid)	2.25
Iodine value (g/100g)	65.0
Saponification value (mg KOH/g)	183.4
Peroxide value (mEq/kg)	1.89
Refractive index	1.4650
Viscosity at room temperature in centipoises (cp)	43.13
Unsaponifiable matter (mg KOH/g)	2.6

4.2 DEVELOPMENT AND EVALUATION OF FATLIQUOR FROM THE OIL

Sulphuric acid was the sulphated agent used in the fatliqouring process. Of the sulphated fatliquor samples produced, only the sulphated samples with 30 % sulphating agent tended to solidify after washing. The products obtained with 10 and 15 % sulphating agents lacked adequate emulsion stability in water. Table 4.2 showed that the degree of sulphation as

measured by the organically combined sulphuric ester values increased with the proportion of the sulphating agent used. A comparison in Table 4.2 suggests generally that sulphating *moringa oleifera* oil resulted in higher degree of sulphation under the condition of this work.

Of the twelve fatliquor samples produced as shown in Table 4.2 below, only the sulphated samples with 30 % sulphated agent tended to solidify after washing. The products obtained with 10 and 15 % sulphating agents at 2 h reaction time and that from 10 % sulphating agent at 1h reaction time could not give adequate stability in water. Burton *et al.* (1963) obtained similar results with other oils. Works already carried out by Olawale *et al.* (2001) on neatsfoot oil and beniseed oil gave similar results as well as given in Table 4.3. The ash values also increased with the proportion of the sulphating agent added to the oil. A comparison of rate in Table 4.2 suggests generally that sulphating *Moringa* oil for 1h resulted in higher degree of sulphation than doing it for 2 h under the conditions carried out in this work. This might be due to increase in occurrence of side reaction at 2 h reaction time.

The oil-water emulsions of the sulphated samples were milky and the duration of stability of the 10 % emulsions increased with proportion of sulphuric acid added to the oil in Table 4.2. By relating the stability duration of the emulsion to the $-OSO_3^{2-}$ (emulsifying group) values of the oil (Table 4.2), it is observed that sulphated *Moringa* oils with values above

5 % are stable for more than four days. Those with the emulsifier values between 3.5 % and 5.0 % are only stable for between 5 and 30 minutes. This is expected since every other thing being equal, emulsion stability should increase with the emulsifier values.

The results in Table 4.2 relating appearance of the oil-water emulsion appearance to their stability are similar to the one credited to Jean Pore (1967). The appearance of the emulsion of products from experiments B (at 60 minutes reaction time) C, D and E could possibly be explained by relating this to the size of the particles (micelles) in the emulsions. The lighter colour is an indication of smaller particles in emulsions formed by products of experiment D (at 60 minutes reaction time and E (both times) according to Jean Pore (1967). The case of products from experiments A and B (at 120 minutes reaction time) cannot be explained on the same basis. The softest leather sheepskins were obtained when 5 % of the fatliquor was added to the leather though addition of 3 and 4 % of the fatliquor also produced leathers that are soft enough for some application.

Table 4. 2: Characteristic of the Sulphated *Moringa oleifera* Oil

Expt. label	% acid added	Time h	SO_3 %	Moisture %	Ash %	10 % oil/ water Emulsion	
						Colour	Time
A	10	1	0.85	3.4	3.01	Slightly milky	< 5 min
		2	1.05	2.50	2.09	Slightly milky	< 5min
B	15	1	3.22	7.52	6.23	Milky	< 5 min
		2	3.30	5.52	4.43	Slightly milky	< 3 min
C	20	1	4.65	12.77	30.08	Milky	32 min
		2	4.80	7.90	6.90	Milky	< 5 min
D	25	1	5.09	16.79	11.40	Slightly milky	102 h
		2	4.90	13.80	10.20	Milky	108 h
E	30	1	5.41	12.30	13.90	Slightly milky	120 h
		2	5.50	12.20	12.85	Slightly milky	180 h

Table 4. 3: Some Characteristics of The Sulphated Groundnut Oil [a]

Sample	Acid Added %	Time H	SO_3^{2-}	Moisture %	Ash %	10 % Oil Emulsion	
						Colour	Stability
A	10	2	0.93±0.02	3.60±0.01	3.00±0.01	Slightly milky	< 5min
B	15	2	3.44±0.10	7.50±0.01	6.21±0.05	Milky	30 min
C	20	2.	4.75±0.03	13.79±0.02	29.48±1.08	Milky	18h
D	25	2	5.14±0.03	17.67±0.11	11.30±0.13	Slightly milky	104h
E	30	2	5.40±0.04	12.23±0.10	14.20±0.02	Slightly milky	120h

[a]:Olawale *et al.,* (2001)

4.4 ANALYSIS OF TREATED LEATHER

4.4.1 Physical Characteristics

The results for lastometer, tensiometer, tear, flexometer and shrinkage temperature tests show the tensile strength value. The fatliquor from *Moringa oleifera* oil seem to impart greater strength properties on chrome leathers. This result is comparable to leathers treated with groundnut fatliquor (Olawale *et.al.*, 2001). The greater strength that the sulphated *Moringa oleifera* oil confer on the chrome leather is an indication of an excellent lubricating property of the oil. Hence the moringa fatliquor may have changed the pores of the leather, enhanced the rate of surface adsorption and encourage better fatliquor processes. This obviously shows the high quality of the developed fatliquor and its suitability for use in leather tanning industry.

The average thickness, the grain crack and bursting strengths give good property to the leather. Distension at crack and burst values compare fairly with groundnut fatliquor. The burst values compare favorably with groundnut fatliquor fatted leather obtained by Olawale *et al.*(2001). The shrinkage test was found to be good.

Table 4. 4: Characteristics of Fatliquored Leathers.

Characteristics	Leather fatted with The *Moringa* fatliqour	Leather fatted with groundnut fatliqour[a]
Lastometer tests		
Average thickness mm	1.47	1.57 ± 0.13
Grain crack strength N/mm	230.11	231.21 ± 1.32
Distension at crack mm	8.43	9.43 ± 0.12
Bursting strength, N/mm^2	284.62	286.62 ± 2.13
Distension at burst, mm	10.33	10.83 ± 0.52
Tensometer tests		
Tension strength, N/mm^2	36.28	36 ± 1
Percentage elongation %	110	90 ± 2
Double hole stitch tear test		
Force at tear, N	137	139 ± 3
Stitch tear strength, N/mm	90.89	92.87 ± 1.52
Flexometer test		
Damage at 100,000 flexes	None	None
Shrinkage temperature test		
Shrinkage test at 100°c for 2 min	Good	Good

[a]Olawale *et al.,* (2001)

4.4.2 Chemical Characteristics

The result of chemical analysis in Table 4. 5 below shows the ash, moisture, $Cr_2O_7^{2-}$ and fat contents of the leather. Fats are removed to prevent side reactions,

as well as increase the reaction sites for tanning. However, the operation disadvantage is that the fibres stick together and become stiff at too low fat content. The value of the extracted fat obtained is not high. Therefore the application of moringa fatliquor could give a good leather product. The amount of chromium is moderate and the moisture content which allows microbial activity on leather, is less. Hence there may be less effect of bacterial attack on the leather product.

Table 4. 5:Chemical Characteristic of Fatliquored Leathers.

Properties	Leather fatted with *moringa* fatliqour	Leather fatted with groundnut fatliqour[a]
Ash %	7.51	7.81±0.18
Moisture %	5.23	5.53±0.13
$Cr_2O_7^{2-}$	4.30	4.70±0.11
Extracted Fat %	3.80	4.08±0.15

[a]Olawale *et al.*, (2001)

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

The *Moringa* oil has good attributes in terms of its physico-chemical properties. This work has shown that the degree of sulphation of *Moringa oleifera* oil increased with the percentage of the sulphating agent at 1h and 2h reaction times. Stable oil-in-water emulsions were given by fatliquored samples produced with 20-30% sulphating agents. The fatliquoring characteristics of the oil was comparable with that of groundnut oil. The sulphated fatliquor prepared from locally available *Moringa oleifera* oil should serve as a suitable substitute for groundnut oil. However, the oil will require trace amount of stabilizers to satisfy some of the qualities required of a lubricant in the tanning process.

5.2 CONCLUSION

A fatliquor was successfully produced from m*oringa* oil using different concentrations of sulphating agents. The fatliquor emulsion formed was stable indicating that fatliquors produced in this work will have good shelf lives. The strength property of fatliquored leather is good as shown by properties such as tensile strength (36.28 N/mm^2), tear strength (137 N), grain crack (230.11 N/mm) and distention at crack (8.43 mm). Perhaps

the fatliquor process may be due to changes in the pore size in the leather, diffusion rate enhancement among other factors.

5.3 RECOMMENDATIONS.

The following recommendations will be useful for further research on *Moringa oleifera* oil:

- Study the effect of temperature, reaction time and the means of improving fixation of oil on leather.
- To develop a comprehensive recipes for the use of fatliquors to produce different types of leather.
- Government should formulate policies that may provide opportunities for soft loan to farmers for large scale production of the plant for greater yield of the oil.
- There should be formulation of policies that would promote plantation for tanning industries.
- Development of efficient and cost- effective management and utilization of fatliquors.
- Establish Processing industries such as food and seed oil processing for processing of seeds.
- Organise workshops and seminars for transfer of technology in the areas of cultivation of *Moringa oleifera* trees and harvesting of dried seeds as well as better processing techniques.

- Source alternate methods of green technology so as to eliminate sulphonation method used in this work which is not environmentally-friendly.

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