

**EXTRACTION, CHARACTERIZATION AND
APPLICATION OF SELECTED NATURAL DYES
AND MORDANTS ON LEATHER.**

BY

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**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE AWARD OF THE DEGREE OF MASTER OF SCIENCE
(M.Sc.) IN TEXTILE SCIENCE AND TECHNOLOGY**

**DEPARTMENT OF TEXTILE SCIENCE AND TECHNOLOGY
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OCTOBER, 2006

DECLARATION

I declare that the work in the thesis entitled “EXTRACTION, CHARACTERIZATION AND APPLICATION OF SELECTED NATURAL DYES AND MORDANTS ON LEATHER” has been performed by me in the department of Textile Science and Technology under the supervision of Prof. Bello, K. A. and Prof. Nkeonye, P.O. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

.....

..... Name of student Signature

Date

.....

CERTIFICATION

This thesis entitled “EXTRACTION, CHARACTERIZATION AND APPLICATION OF SELECTED NATURAL DYES AND MORDANTS ON LEATHER” by OGBOSO OKWUCHI meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, and is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This research work is dedicated to my ever loving husband M.Y.N. Ishidi and my children Ruth, Eunice and Joy.

ACKNOWLEDGEMENT

I thank God who has made all things possible in spite of the many obstacles in the course of the studies.

I am indeed grateful to my supervisors Prof. Bello, K. A. and Prof. Nkeonye, P. O. whose patience and forbearance were tremendous and wonderful, without which, I would not have had much to show for all my efforts.

Many thanks go to all my lecturers, who have given their best to improve my knowledge and skills in the course of this study. Special thanks go to Prof. Kolawole, E. G., Dr. Yakubu, M. K., Mr. Giwa, A., Mr. Iliya, E. B., Mr. Lawal, A. S. and Mr. Danladi, B. I. Also, I appreciate all the non-academic staff whose moral supports have been highly valuable.

The numerous assistance from Mr Depo, O. of pharmacology department, Mr Fidelis, A. of biological sciences and Mrs. Toyela, H. of microbiology department of, Ahmadu Bello University Zaria are also highly appreciated.

Finally, I wish to thank my beloved, husband, Mr. M. Y. N. Ishidi for always being there for me. I say thanks to my lovely daughters, Ruth, Eunice and Joy for always being lovely and supportive to me in the course of my studies.

ABSTRACT

Extracts were obtained from Savanna mahogany (Khaya senegalensis), Annatto (Bixa Orellea), Red Onion (Allium cepa), Mango (Mangnifera indica), and Zobo (Hibiscus sabdariffa) in various solvents ranging from acetone, ethanol, methanol, water and chloroform. The results obtained showed that the extracts were found to possess different colour impacting chromophores and could be used for leather application. The shades of the colours can also be varied using plant mordants such as plantain and citrus peels.

The extracts are toxic free as none had LD₅₀ less or equal to 2 mg/kg. The least of the results obtained is that of zobo (Hibiscus sabdariffa) which showed LD₅₀ of 177.5mg/kg. The extracts could also be used in food and beverage industries. Most of the extracts showed clear zones of inhibition of microbial activities which is a clear indication that they could conveniently be used in an environment infested by such microbes.

Rub fastness, tensile strength, and percentage dye adsorption examination showed that the extracts of different solvents using plant mordants were good. The IR - spectra of the extracts confirmed the presence of colour imparting chromophores which are responsible for the individual colours of the extracts.

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CHAPTER ONE

1.0 Introduction

Extraction of colouring substances from common plants is not a new thing. In fact, that is the genesis of natural dyes. Our ancestors knew they could extract certain colours from certain plants, such as yellow from golden rod, onion skin, purple barriers or coreopsis, green colours from lily of the valley, Queen anne's lace or rhododendron and brown colour from acorns or marigold (Traci Sardis, 20002). Dyes are classified into synthetic and natural dye.

Growing demand for natural dyes in place of the synthetic ones is justified by the low toxicity of natural dyes due to the fact that synthetic dyes are mostly carcinogenic in nature as well as when released into the environment takes a long time to degrade; also the intermediates could still be more toxic (Versissimo et al 19912005). To minimize this impact effect, it is to substitute in a possible way the synthetic dyes which cause pollution in their manufacture

~~as well as~~ ~~can be substituted in its use~~ by natural dyes. The ~~importance~~ ~~application~~ of the natural dye in the industry diminished with the extensive use of synthetic dyes in different ~~fibers~~ ~~fibres~~ but still, in the last decade, the use of natural dyes gained ~~a~~ momentum in the world due to high demand by different industries, which was as a result of the new environmental law established by different countries.

Dyes from plants are widely ~~looked~~ ~~employed~~ ~~for~~ due to their biodegradability and low toxicity and can be employed in dyeing both natural and some synthetic ~~fibers~~ ~~fibres~~ (ALR2, 1999).

Every year international events are organized in ~~defense~~ ~~defence~~ of the environment in order to ~~reduce~~ ~~view~~ the different areas of ~~industrial~~ ~~production~~ and new laws are being put forward to use less polluting materials and processes. One of the United Nations reports published on the international conference held in Paris in 1998, called the attention on the danger that ~~the~~ lack of water threatens 2/3 of the world population. To process a ton of textile, one needs between 2.3×10^7 to 2.7×10^7 litres of water. The effluent generated during the process could pollute the environment as it contains quite a large quantity of the chemicals used in the finishing process. In fact, in the nearest future, the textile industry will have only two ways to follow, first is to construct big and highly effective water treatment plants which will be highly expensive or to adopt a process that could cause little or no pollution which the use of natural dye could be an important asset. (Mary ~~et la~~, 2004).

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1.1 Dyes

Dyes have been identified as intensely coloured substances which when applied to a substrate impart colour to that material by a process which at least temporarily destroys any crystalline structure of the coloured substance. (Verissimo et al., [2005](#)[1991](#)). Dyes can be ~~–natural~~[of natural](#) or synthetic origin.

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The art of applying colour to textile fabrics goes far back into antiquity. The unearthing of coloured fabrics in the course of excavations in Egypt and Asia has proved beyond questions that textile colouring was developed independently and practised by almost all primitive people. The earliest probably was made by men who observed the stains left by various parts of the plants. They learned that a great number of these dyes could be fixed on fabrics only by the use of auxiliary materials such as acid and metallic salts and there was often an improvement in the shade. This was the genesis of mordanting.

1.2 Chemical Constituents of ~~Dyes~~[Dyes \(Othmer, 1965\)](#).

Colours of dyes are due to electronic transition between various orbitals, the probability of these transitions determines the intensity of the colour. The energy differences between the orbitals determine whether the colour falls in the visible region of the electromagnetic spectrum (400 - 700 nm). Although all organic molecules absorb light to some extent, the majority absorbs light

in the ultra-violet region i.e. below 400nm; hence they appear colourless (Williams ~~at a~~and Flaming, 1980).

The wave-length of light absorbed is also affected by constituents on the dye molecule, both through their electron withdrawing ability or electron donating groups and also through the position they occupy (Vogel, 1978). Every dye or pigment therefore exhibits a characteristic colour arising from its chemical structure. However, the colour seen for a given coloured substance is the reflected (complementary) colour, the substance having absorbed particular wavelengths within the visible spectrum. Table 1.1 shows the pairs of complementary colours and wavelengths absorbed.

Table 1.1: Absorbed and Reflected Colours (Graham, 1972)

Wave-length (nm)	Colour absorbed	Complementary colours
400 - 435	Violet	Yellow - Green
435 - 480	Blue	Yellow
480 - 490	Greenish -Blue	Orange
490 - 500	Bluish-Green	Red
500 - 560	Green	Purple
560 - 580	Yellow- Green	Violet
580 - 595	Yellow	Blue

595 - 605	Orange	Green-Blue
605 - 750	Red	Blue-Green

If a substance absorbs all visible light except one band, which it reflects, the substance will have the colour of that reflected band. Thus, a substance can appear blue because it absorbs the yellow portion of the spectrum only or because it absorbs the entire visible spectrum except blue. The shades however, will be different, apparently no dye gives a pure shade i.e. does not reflect only one band of wavelength.

Many substances which appear to be colourless nevertheless have absorption spectra but in these cases, absorption takes place in the infra-red or ultra-violet and not in the region of the visible spectrum. (Vogel, 1978, 1978). The absorption spectrum ~~of the purity of the colour observed~~ depends on the ~~shape of the absorption spectrum~~ chemical structure of the dye. Bright colours are the result of narrow absorption bands with sharp peaks. Non - spectral colours such as brown are associated with absorption spread fairly evenly over a wide wavelength range and black is the result of absorption throughout the visible region of the spectrum (Evans and Stapleton, 1971).

1.3 Justification of the Present Study

- a. Most of the synthetic dyes used today are carcinogenic in nature as they, during enzymic decomposition releases carcinogenic amines.
- b. The raw materials: Mahogany bark, Annatto Seed, Red Onion Peels, Mango Leaf and Zobo are of little economic value.

- c. ~~This definitely will~~To create ~~a whole lot of~~ employment for Nigerians.
- d. ~~To~~~~his will~~ reduce exploitation, most times, because the major source of colorants presently is the imported synthetic dyes, the importers ~~sale~~ sell the dyes at exorbitant cost.
- e. To improve the local leather dyers who have always ~~have~~had a problem of low fast dyed leather.

1.4 Scope of the Research Study

- a. To study the anti-microbial activities of the dyes extracted from the plants used for the research.
- b. To assess the toxicity of the extracted dyes.
- c. The application of the extracted dyes on tanned leather.
- d. To study the effect of the dye on the physical properties of chrome and vegetable tanned leatherss.
- e. To assess the fastness properties of the dyed leatherss.
- f. To determine the percentage exhaustion of the extracts on leather.

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1.5 Objectives

- a. Extraction of dyes from different plants
- b. Characterization of the colorants using ultra-violet ~~Spectrophotometers~~spectrophotometer, infra-red spectrometer and nuclear magnetic resonance
- c. Actualization of the process for application on chrome and vegetable tanned leatherss using plantain or citrus peels.

- d. To study the toxicity and anti - microbial ~~activates~~ activities of the dyes.

1.6 Research Questions

- a. Since there are many synthetic dyes in the market, what is the need going to extract dye from plants?
- b. How would this research check the problem of toxicity associated with most synthetic dyes?
- c. Will massive harvesting of the flowers, leaves or barks for dye extraction, not have an ~~advance~~ adverse effect ~~in~~ on the ecological system of our plants?
- d. In what capacity will this research help the leather industries?
- e. What impact will this research have on the economy of the nation, especially on the area of poverty alleviation?
- f. What will be the major difference or similarity between the proposed extracted natural dyes and synthetic dyes?
- g. Are there materials and equipment on ground to enable the successful completion of this research?
- h. What are the possible major challenges that may be encountered in the course of this research work?

CHAPTER TWO

2.0 Literature Review

Up to the end of the 19th century, dyes from plants were the only textile colours used other than inorganic pigments and dyes of animal origin. With the development of the cheaper synthetic dyes, natural dyes were completely

replaced and the cultivation of dye plants ceased. Now interest in natural dyes has [been](#) revived not only in Europe but also in Japan and the United States. These are due in part to increasing case of allergic reaction against synthetic dyes and in part to changing environmental considerations [_](#) (ALRALP, 1999) [_](#).

There are three categories of natural dyes: natural dyes obtained from plants (indigo), those obtained from animals (cochineal) and those obtained from minerals (ocher) [_](#) (Suresh, 2005). Indeed, common plants we ~~found~~ [find](#) around our surroundings [s](#) can help cut down the textile and leather industry reliance on imported synthetic dyes and reduce the pollution they ~~cause~~ [cause](#) (Cody, 1937).

Today, the ~~Scientist~~ [scientists](#) in Philippine Textile Research Institute have identified twenty six ~~Species~~ [species](#) of ~~Plants~~ [plants](#) - including mangrove trees, a type of onions, guava and cashew-nut trees that could be used to produce high quality natural dyes. These species are widely distributed in Philippines and in other tropical countries in Africa, Asia and Latin America, and can easily be cultivated in [humidity](#) regions [s](#).

The PTRI - an Institute of The Philippians Department of Sciences and Technology has also developed techniques for efficient extraction of natural dyes (Mary, 2004) [_](#).

2.1 Natural Dyes

These are the dyestuff produced by some plants and animals living in nature without any chemical transformation. Root, stem, leaf and flowers of the plants are used fresh or dried. For insects containing dyestuff, the female species are dried and used after grinding (Recep, 2005).

2.1.1 Natural Dyestuff Used To Obtain Red Colour

This is divided into two groups: Those originated from plants and those originated from insects. Examples of those originated from plants are as enumerated below:

a. Madder (Rubia tinctorum L) (Madhila, 1999)

Rubia tinctorum L plant is a multi - year climbing plant of 50 - 80cm which belongs to rubia species of Rubiaceae family. The dyes are found in the roots of the plants and amount ranges between 1-4 % according to the condition of the regions. Old roots contain more dyestuff compared to the young ones. It gives Turkey red dyeing on cotton and with salts of various metals. With chromium, it gives bluish red and orange yellow with tin. Other plants of Rubiaceae family giving red color are as follows: Rubia Paregrina L, Rubia cordifala L, Gulium Varium L, Asperala tinctoria L and Rubia uismene.

b. Safflower (Carthamus tinctorial L) (Recep, 2005)

This is a plant belonging to the carthamus species and tubfloral sub- family of the compositions. The family of the safflower grown in various regions of Turkey as an oil plant was used for dyeing until the first half of the 20th

century. Safflower in several countries was used as red or yellow dyestuff resources. The red colour is given by the carthamus .

2.1.2 Natural Dyestuff for coloring violet- (Recep, 2005)

Xexapiex trunculus L and Bolus binndoris L have been known in old time as sources of natural dyes. They are found in seas and oceans but especially Mediterranean coast and Marmora Sea. Its collection is a hard task and the dyeing is very complicated. Another source for violet is the root of Alkanna tinctorium nefora. The dyestuff it contained is alkanin and is generally used in hand print

2.1.3 Natural Dyestuff used For Colouring Blue- (Recep, 2005)

This belongs to vat dyeing group with very complicated method of dyeing. Before 20th century the leaves of woad (Isatis tinctoria L) and some other plants containing indigo such as indigofera tinctoria L of indian-Indian origin were used for colouring blue. Blue dyes can be obtained from the following:

a. **Weld (Reseda luteola) (luteola) (Lobato, 2001)**

It is a multi- year plant living in Anatolia, which can grow up to 1.5meters5 metres. It is grown in Turkey, in the rocky region at 40 - 150 metersmetres height in eastern Anatolia and at the height near salt lake in central AnatliaAnatolia. AllThe parts above the ground isares used for dyeing. The dye it contains is lutcolin. Its flowers however contain apigeminapigenin along with the lutcolin. The use of weld in Anatolia dates back to 16th century.

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b. **Camomile (Anthemis tinctoria L)**

It is a two-year plant and it is grown on calcareous soil. It can be found in every part of Anatolia. The dyestuff it contains is Isorhmectin, a little miricetin and guervetin. It provides shiny~~ng~~ yellow colour by alum mordant.

c. **Daisy (Anthemus tinctoria L)**

It is a one year plant ~~ef_~~ which can grow up to 30cm. The dyestuff it contains is apigenin. Carpets in Southern Anatolia have been coloured yellow with daisy. Apigenin is found in the flowers of the daisy. The fresh flower gives better results than the dried one.

2.1.4 Natural Dyestuff Used for Colouring Black- (Recep, 2005)

Black colour is obtained by processing with metallic salts. Acorn, ~~Oak-oak~~ galls or sumac leaves are used to obtain black colour.

2.1.5 Natural Dyestuff Used for Colouring Orange (John, 2005).

Orange colours are generally obtained through the use of plants providing red or yellow dyestuff. Orange colour has also been achieved by using hema (Lawsonia inersis L) leaves or onions peels.

2.1.6 Natural Dyestuff Used for Colouring Green (Melissa, 1975).

There is no natural green dyestuff with high fastness level. They are [Chlorophyll-chlorophyll](#) obtained from many plants. But it does not give true dyeing.

2.1.7 Natural Dyestuff Used for Colouring Brown ([Melissa, 1975](#)).

The most available materials for colouring brown are walnut leaves. These are used fresh or dried. Red-brown is obtained through processing alizarin with metallic salt.

2.2 Dyeing ([Nkeonye, 1990](#))

Dyeing is a process of colouring material, whereby the colour becomes part of the [fibersubstrate](#). The fastness of the colour or its permanency depends upon the dye and the process of application. Real dyeing is a permanent colour change and the dye is absorbed by being chemically combined with the [fibersubstrate](#).

In the manufacture of the final piece of clothing, several colour variations are blended for different effects. The yarn can be treated before weaving to obtain a frosted effect; this is by controlling the penetration of the dye into the [fiberfibre](#).

2.2.1 Different Stages of Dyeing (Grabe and Liebermann, 1868).

2.2.1.1 As raw stock:

The dye is applied after the fiber-fibre has been cleaned, but before it is formed into thread. It gives best possible dye fastness and product uniformity, but tends to waste dye. It is also difficult to change colours as all the equipment must be cleaned before next dyeing.

2.2.1.2 As a sliver

After the fiber-fibre has been cleaned and treated, it is carded. In this process, the fibers-fibres are all laying in the same direction and form a short, loose rope called sliver. Different slivers can be dyed different hues or shades. The spinning process can then use the different colours to form attractive effects on the finished cloth piece or a blend of different fibers fibres could be used also for different effects.

2.2.1.3 As a yarn

This is the most common type of dyeing as the finished product has a better appearance, increased luster and good fastness. A quality of yarn or thread can be produced, then used as required to meet sales need. The product is of very high quality.

2.2.1.4 As a finished piece of cloth.

This is the most economical method as the waste of dye and labour is minimized. It is also convenient when there is a change in colour and style.

Uniformity of colour throughout the piece can be difficult and fastness would be of lesser quality.

2.3 Mordant _-(Doko,1984)

Most of the colouring matters of natural origin used in medieval times were not capable of producing permanent colours on textiles by themselves. The [fibers-fibres](#) had to be prepared for the reception of the dye by impregnation with metallic oxides such as those of aluminium, iron, or tin. These substances were known as mordants, derived from the French word "Mordre" which means to bite. The name was considered appropriate because it was believed that the oxide bit the dye and held it on to the [fiberfibre](#). Essentially they open the pores and combine with the [fiber-fibre](#) and this enables the dye to be chemically bonded.

It has been found that various mordants produced different colours from the same bath and this is due to the polygenetic character of the natural dye. This means that a single natural dye may produce a range of hues with different mordants as shown in Table 2.1.

Table 2.1: Colours obtained with different mordant-s (Doko, 1984)

Mordant	Madder (Alizarin)	Log wood (Hematein)	Weld (Chuteolin)	Fustic (Morin)	Cochineal (Carminic acid)
Aluminum	Red	Greenish Violet	Greenish Yellow	Bright Yellow	Crimson
Tin	Pink	Reddish Violet	Bright Yellow	Orange Yellow	Scarlet
Iron	Brown	Grey to Black	oliveOlive	Dark olive	Purple
Chrome	Purple- Brown	Navy-Blue	Olive-Yellow	Olive Yellow	Purple
Copper	Yellowish- Brown	Greenish- Blue	Yellow- Olive	Olive	Dark-red

With mordant, the colour gain more stability and durability on the fiberfibre.

Mordants are either vegetable or mineral. Vegetable mordants are from different plants while mineral mordants are soluble metallic compounds.

2.4 Description of the Plants Used for the Research (Noah, 1995).

2.4.1 Mango (Mangnifera indica)

Mango plant is one of the most important and widely cultivated fruits of the tropical world. The name Mango by which the fruit is known is English and is derived from man-gay which the Portuguese adopted as mange when they settle-settled in Western India. The Mango tree is evergreen, often reaching

large size of about 1.5 - 1.8 ~~meters~~metres and attaining great age. It is one of the favourite shade trees of the tropics. The leaves are up to 0.3 ~~meter~~metre long. The fruits vary greatly in size and character, as would be expected of a species that has been in cultivation for a long time. Mango has a botanical name of "Mangnifera indica" and belongs to the family "Anacardiaceae". Mango is widely grown in India, Malaya, America and Africa. It is one of the main fresh fruits available in Northern Nigeria and occupies a position of some importance in the diet of the people.

2.4.2 Savanna mahogany (Khaya senegalensis) (Scoth, 1999)

Savanna- mahogaeny is a plant with hard, red-brown bark. It is widely used in the furniture industry. It is a large evergreen tree with smooth pinnate leaves. Together with other species, it yields the world's most valuable cabinet wood varieties with ornamented figure in the grain and is highly priced. In United States, it occurs naturally only in the extreme Southern part of ~~the~~ Florida, but planted else where in the ~~state~~State as an ornamental and shade tree.

2.4.3 Red Onions (Alluim cepa)

This is a cool season biennial plant. Alluim cepa is of Asiatic origin, belonging to the plant order lilales. Onions are grown annually and propagated most frequently by seeds sown directly in the field. The field spacing varieties are generally grown 0.02 - 0.1 ~~meter~~metre apart in 14 - 16 m rows. Red onions varieties are classified mainly according to pungency and use. The bulbs may be white, red or yellow.

2.4.4 Zobo (Hibiscus sabdariffa)

The shrub is about 0.5 to 3.0 ~~meter~~metre high, branching near the base. These branches often grow vertically and parallel to the main stem, elongated and thin specimens tend to sprawl. The stem encloses greenish pith which is odourless. The leaves are alternate, stalked, and flexible petals. The petals are somehow creamy yellow with a central staminal column carrying a large number of stamens with kidney shape.

2.4.5 Annatto (Bixa orellana)

Bixa orellana is widely known as lipstick tree. It is a native of the new world tropics and the only species of the family Bixaceae. It grows up to 9 ~~meter~~metres with rose-pink flower. The leaves are ovals and brown pods that contain the seeds. In the matured stage of the plant, it looks more like a tree. The ripening period for the fruit is between December and July.

2.5 ~~Fiber~~Fibre Structures in Relation to Dyeing (RYS, 1972).

~~Fibers~~general are generally classified into the following: natural vegetable, animal hair, mineral matter, regenerated chemically from natural animal or vegetable ~~fibers~~fibres and synthesized wholly from chemicals. However, they are all polymers, i.e. giant molecules which are made up of repeat units of a particular monomer covalently joined together. Functional groups within the polymers retain their chemical properties and determine the type of dyestuff for which the ~~fiber~~fibre would have an affinity for.

Generally, [fibers-fibres](#) having many polar functional groups will have a greater affinity for the ionic dyestuff while those having very few polar groups or none at all will have greater affinity for non-ionic dyestuff. The absorption and penetration of water between the polymer molecules is necessary for the creation of voids for the dye molecules to diffuse into from an aqueous dye - bath.

Swelling of [fibers-fibres](#) on wetting is due to lateral separation of chains by infiltration of water molecules. [Fibers-Fibres](#) with many polar functional groups are hydrophilic in nature. This is because water is also a polar compound. Those [fibers-fibres](#) having little or no polar functional groups are described as being hydrophobic i.e. water repelling, since it would have a low affinity for polar water molecules. Chemical structure of polymer chain can also determine what chemical assistant may be added to the dye bath from which it is being dyed e.g. wool and silk have low resistance to alkali (Trotman, 1975).

The micro - molecular structure which has to do with arrangement of the polymer molecules within the [fibers-fibres](#) also have a greater role to play in the dyeing properties of any given type of [fiberfibre](#). When synthetic [fibers fibres](#) are freshly spun the molecules within the [fibers-fibres](#) are in a highly amorphous state and the [fibers-fibres](#) themselves are of low tenacity. Their qualities in terms of tenacity are therefore improved by drawing the [fibersfibres](#). The drawing causes the molecules to slip and slide over one another and become oriented. This can be compared to spinning of cotton

yarn from cotton slivers and the stretching out of the sliver with a twist to hold ~~in~~ the ~~fibers-fibres to~~ form ~~to~~ much stronger yarn.

A skin effect is observed with man-made ~~fibers-fibres~~ which ~~is-is~~ due to the resistance which the outer flow of molecules encounters with the walls of the orifice of the spinnerets. This results in a much higher degree of orientation on the outside of the yarn than those within. Crystallinity tends to impart hydrophobicity to ~~fibers-fibres~~ even having polar functional groups. This is due to the screening off of polar functional groups with possible intermolecular hydrogen bonds. Also, the closed arrangement of polymer molecules leaves little or no space for dye molecules to penetrate into it from the dye bath. Effective exhaustion of a dyestuff by crystalline man-made ~~fibers-fibres~~ is made possible by having knowledge of their glass transition temperature (T_g). This temperature of dyeing marks the onset of dyeing for the ~~fiber-fibre~~ being dyed because at temperatures below the T_g value, the polymer molecules are frozen into position relative to each other. As the ~~dyeing temperature~~ dyeing temperature approaches and exceeds T_g for the ~~fiber-fibre~~, the polymer molecules rotate about their bonds till free volumes (voids) are created for the dye molecules to diffuse into (Othmer, 1965).

~~Also the fiber mechanical properties plays an important role in determining the types of dyeing machine to be used, example loose wool can not be dyed on a jig machine where dyeing is done under high tension as this can disintegrate the tow.~~

2.6 Forces of Attraction Between Dye and ~~Fibers~~ Fibres during Dyeing(Nkeonye,1990)

In order to obtain a clear view of the mode of attraction of the dye to the ~~fiber~~fibres, knowledge of the forces which bind the dyes to the ~~fibers~~ fibres is of obvious importance in the present review. In most dyeing processes, the material to be dyed is brought into contact with a transfer medium containing the dye. The most common transfer medium is water, in which the dye may be dissolved or dispersed. During dyeing the dye passes from this solution or dispersion into the ~~fiber~~fibres. The transport of the dye from the solution into the ~~fiber~~ fibres may be regarded as entailing three steps viz. Transfer of dye from the bulk of the solution to the ~~fiber~~ fibres surface, sorption of dye at the ~~fiber~~ fibres surface, and penetration of the dye into the interior of the ~~fiber~~ fibres substance.

The ~~first~~ action in any dyeing operation is therefore the concentration of the dye molecules at the internal surface of the ~~fiber~~ fibres as the dye can reach. The concentration so produced ~~is~~ is however, not usually sufficient to give a usefully deep colouration and fastness properties required of a dyed material; ~~it~~ It is required that the dyed be associated strongly with the ~~fiber~~ fibres to make it resistant to such agents as water, detergents, perspiration, weather, solvent etc (Ugbolue and Alula,1980,1980).

For this to be achieved, other factors must be brought into play. These are the chemical forces which can operate between a dye molecule and a ~~fiber~~ fibres molecule, and also those between the dye molecules themselves which

can cause their association into larger units. These forces have been classified as ionic forces, hydrogen bonding, covalent bonding and [Van-van der Waals](#) forces (Derbyshire [and Peter](#), 1955) (~~and RattleeRattee, 1974, 1974~~).

2.6.1 Ionic Bonds (Ionic Forces) (Abrahart, 1977)

This is the mutual attractions between positives [centers-centres](#) in a [fiber fibre](#) and negative [centers-centres](#) in a dye molecule and between negative [fiber-fibre](#) sites and positive [center-centre](#) in a dye molecule. This is the case when an atom transfers its electron to another atom, [the one that lost the electron-in the effect](#) becoming positively charged [and the while the](#) atom that received [the electron](#) will become negatively charged. These types of forces play a large part in the dyeing of protein [fibers-fibres](#) with acid and direct dyes, nylon with acid dyes and polyacrylics with basic dyes.

2.6.2 Hydrogen Bonding

~~These-This~~ results from the acceptance by a covalently bound hydrogen atom of a lone pair of electrons from an electron donor atom. Hydrogen bonding can act in five different ways:

- intermolecularly extending over many molecules
- intermolecularly joining two molecules together

- intermolecularly where the electron donating is by ~~acetyinic or~~ double bond linkage
- intramolecularly forming a chelate ring.
- intramolecularly as ion in hydrogen fluoride (HF₂)

Hydrogen bonding has some properties of normal valency bonding. They interact when the atoms approach within very close distance to each other. They are relatively of the order of 8.4-49.4 ~~KJ/Mol~~ ~~KJ/Mol~~⁻¹. They are relatively easy to form and break. Hydrogen bonding is applied almost in all dyes in all systems.

2.6.3 Covalent Bonding

These are chemical bonds between dyes and substrate molecules. They are brought about by chemical reaction between a reactive dye molecule and the substrate ~~molecule-molecule~~, example hydroxyl group of a cotton ~~fiber~~ ~~fiber~~. In fact covalent bonding has to do with primary valency bonding where each of the participating atoms has to donate one electron to the common linkage. This is the strongest of all dye - ~~fiber~~ ~~fiber~~ bonds. They have the highest energy of about 84 ~~KJ~~ ~~KJ~~/Mol. Covalent bonding is the bond responsible in reactive dye bond on leather, wool and nylon.

2.6.4 Van Der Waals Forces

These are forces existing between atoms and molecules of all substances and are small compared with the other inter-atomic forces present in the dyeing process. They are the result of second order wave mechanical interaction of

the π -orbital of dye and fiber-fibre molecules. These forces are especially effective when the dye molecules are linear, i.e. long and flat and can approach close enough to the fiber-fibre molecules or molecular unit.

2.7 Classification of Dyes According to Method of Application **—(Abrahart, 1977)**

Dyes are classified by the dyer according to their method of application to textile fibers as enumerated below:

2.7.1 Sulphur Dyes

This type of dye is mainly used for cellulosic fiber, it gives green, blues, brown colours and have all round fastness. They are water insoluble dyes, containing sulphur both as an integral part of the chromophore and in attached polysulphide chains. They are normally applied from a sodium sulphide bath and the dye is reduced to water soluble form, reoxidation to shade occurring on the fiber-fibre by contact with atmospheric air (oxygen).

2.7.2 Azoic Dyes

Azoic dyes are insoluble azo dyes which are prepared insitu (i.e. within the fiber) giving rise to fast prints and dyeings on cotton mainly, giving shades of high standard of fastness to light and wet processing. They give bright, intense hues particularly in the yellow, orange and red ranges.

2.7.3 Reactive Dyes

These are characterized by the presence of a reactive group that combines chemically with a suitable group in the ~~fiber~~-fibre e.g. hydroxyl group in cotton, the amino group in protein and the polyamide. There are three chemical classes of reactive dyes: azo, anthraquinoid and phthalocyanine. Reactive dyes have extremely good wash fastness but are susceptible to chlorine.

2.7.4 Solvent Dyes

Solvent dyes are dyes containing no sulphur or other water solubilizing groups. ~~It is~~They are soluble in organic solvents, the nature of which varies according to application. They are insoluble in water but soluble in a range of organic solvents such as alcohols, esters, ethers, aliphatic and aromatic hydrocarbons. The type of application involved determines the choice of solvent. Applications include varnishes, printing inks, colouring candles, soaps, petrol and dope dyeing of synthetic polymers

2.7.5 Disperse Dyes

Disperse dyes are sparingly water ~~insoluble~~ dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous dispersion. Disperse dyes belongs to the three main classes: nitro~~oa~~arylamine, azo and anthraquinone dyes. Almost all contain amino or substituted amino groups, but do not contain solubilizing groups such as sulphonc groups. They are usually ground in a mill to fine particle sizes (1-4 μ) in an aqueous solution

containing a dispersing agent. The latter normally stabilizes the dye suspension and acts as restraining and retarding agent.

Disperse dyes are used in dyeing cellulose acetate, nylon, polyester and polyacrylonitrile [fibers/fibres](#). Dispersion of the dyes which are largely insoluble in water is achieved by using small quantity of wetting agents such as naphthalene sulphonic acid formaldehyde [condensate/condensate](#) - (Nkeonye, [1990](#), [1990](#)). Substituents are present in the dye molecules which help to make the dye molecule readily dispersible in water e.g. - N = N -, - OH, -NH₂, O-alkyl, -NH alkyl. They form weak hydrogen bonds with water.

2.7.6 Vat Dyes

They are so called because the early dyeing processes for the application group involved reducing the insoluble parent dye in large "vats" to form the soluble [Leuco-leuco](#) form. The [fibers-fibres](#) to be dyed having been saturated with the alkaline leuco solution were exposed to air for the subsequent oxidation and reformation of the insoluble parent dye within the [fiber/fibre](#).

These vats have however, in modern industries been replaced by the continuous feed methods where the fabric having passed through the alkaline leuco bath for a while is then passed on to an oxidation bath while more of the fabric is fed into the leuco dye bath. Sodium hydrosulphite is used to effect the reduction. Other types were developed for viscose, nylon, wool,

silk and acrylics. Their small size makes them give bright colour and is also easy to apply with ~~the~~ high leveling power on all ~~fibers~~fibres. The major application is the dyeing and printing of cotton.

2.7.7 Acid Dyes

These are water soluble dyes which are applied basically from acid solution onto ~~fibres~~fibers possessing basic nitrogen groups e.g. leather, wool, silk, nylon. The water solubility is as a result of the presence of sulphonic acid groups or in rare cases carboxylic acid group. Acid dyes are found in nitrophenols, azo compounds, triphenyl methane, anthraquinoids or indigoid compounds (Recep, 2005). There are three kinds of acid dyes which are in accordance to their molecular mass and ease of leveling. Those of higher molecular mass which do not level easily (groups 2 and 3) are known as acid milling and neutral milling ~~dyes~~dyes (Steven and Nunn, ~~2005~~1979).

2.7.8 Chrome Dyes

This is also known as mordant dyes. They are acid dyes which have been applied in conjunction with metallic mordant. Chrome presently is the most popular metallic mordant hence the generalized term "chrome dye". The resultant metal complex dye has a larger molecular size and gives dyeings of higher wash fastness than acid dyes without chrome treatment. On wools, they have improved light fastness and good fastness to dry-cleaning. The wool may be treated with the solution of chrome salt before or after dyeing or ~~simultaneously~~simultaneously (Stout, ~~1970~~, 1970).

2.7.9 Direct Dyes

They are also known as “substantive” dyes. They are commonly used for cotton and other cellulosic ~~fibers~~fibres. They are applied from an aqueous medium with the aid of an electrolyte to achieve dye fixation. The main chemical classes to which direct dyes belong are the dis, tris, tetrakis azo compounds. Other classes are stilbene, copper-phthalocyanine, oxazine, quinoline or thiazole compounds (Trotman, 1975) .They ~~has~~ve high light fastness values.

2.7.10 Basic Dyes

They are also referred to as cationic dyes and are salts of organic colour bases. They are characterized by the presence of a basic ammonium group. It may also be present as a part of a heterocyclic ring as a tetravalent atom, hence triphenyl methane dyes, ~~xan~~athenes, acridenes, oxazine and thiazine are considered or are used as basic dyes. Basic dyes are used on acrylic ~~fibers~~fibres

2.8 Hides and skins(Sarka, 1980)

Hides and skins are derived from human beings, a mammal, the size of an elephant or a mouse, a bird like, an ostrich or a sparrow, a small sardine or a huge shark, a lizard or a crocodile, ~~its~~with structure ~~having will be found to~~have certain features in common.

Hides or skins vary in thickness and have distinct patterns peculiar to the species. Hides normally are thicker than skin. Every hide or skin consists of three distinct layers:-

- the upper layer called epidermis or cutis
- the middle layer called corium or dermis
- the flesh layer called hypodermis.

2.8.1 Functions of a Hides or and Skins

- a. It provides a light, durable covering for the body.
- b. It helps to regulate the body temperature.
- c. It prevents or minimizes injury to vital organs and acts as a barrier to bacteria infection.
- d. It presents a waterproof surface to the outside, while allowing moisture (sweat) to reach its surface from inside.
- e. It is flexible, stretching and contracting with its wearer's movement.

During processing of hides and skins, it is desirable to retain all the above mentioned characteristics and to alter them as little as possible. Boots and shoes made from plastics or other synthetic compounds are more uncomfortable in wear as these substances do not permit the free passage of perspiration.

2.8.2 Tanning (Mann, 1969)

This is the process for converting hides or skins into leather, a form which makes them resistant to decay, while increasing their wearing qualities

inherent in the living hides or skin. The art of tanning started when man first killed animals for food and removed their hides as a covering for him and family. Experience taught him that untreated dry hides were hard, so he rubbed them with stones using the brains and marrow of the slain beasts. They also used smoke to preserve hides. Alum, gallnuts, tree barks, pods and leaves have all been used from very early times for producing leathers.

The footwear and other leather goods found in a well preserved state in ancient Egyptian tombs give an adequate illustration of the skill and craftsmanship achieved during the early period. The art of tanning advanced considerably during the middle ages. In those times, science and art of tanning were kept secret, such knowledge, usually were being passed from father to son. Today, tanning processes are not such close secrets. No matter what hide or skin is to be processed, the procedure is the same; the removal of the undesirable parts (epidermis and hypodermis) and the rendering of the dermis strong, flexible and resistant to putrefaction.

2.8.3 Tanning Procedure (Mann, 1969)

The hide or skin is soaked in vats to wash away adhering blood, dirt or dung, return the moisture removed during their drying or salting or to make certain parts easily removable and facilitate the penetration of chemicals. Soaking of hides takes up to 72 hours depending on the thickness. After soaking, liming proceeds. This process takes up to 14 days. Liming is done to separate the epidermis so that it and the hair may easily be removed from the dermis. It also breaks down and removes some of the fats and causes swelling and plumping of the [fibres](#). During liming, [hides](#) that are heavily damaged by

putrefaction as to render them unsuitable for leather are sorted out. The softened epidermis and the hair are removed by either machine equipment with revolving rollers or by hand. After this stage, it is washed thoroughly with running water in a revolving drum. The hide is then digested by a process called bathing in order to remove certain undesirable proteins. This takes about 30 minutes and leaves the hides or skin soft and silky.

In the past, droppings of domestic fowls or dogs were used as reagent for bating; presently pancreatic enzymes and ammonium chloride are used. The above enumerated process is only to prepare the true dermis for tanning- (Mann, 1969). Tanning can either be vegetable or mineral.

2.8.3.1 Vegetable Tanning (Tannins)

Tannins are bitter astringent principles found in root, bark, leaves or galls of various trees. They have the property of combining with the fibres of the hides or skins rendering them more resistant to decay. In the Northern Nigeria, the main source of vegetable tannin is from the pods of *Acacia arabica* (Bagaruwa H) and wattle bark is also commonly used (Mann, 1969). Vegetable tanning are divided chemically into two groups namely; pyrogallol and catechol (pyrocatechol). These classifications were made based on the substances obtained on dry distillation of vegetable tanning materials (Sarkar, 1980).

Tannin extracts are prepared by leaching the finely chopped plant material with water. The liquor is then concentrated in vacuo to yield a viscous semi-

solid mass, which hardened on cooling. Vegetable tanning is [a slow process if compared to chrome \(mineral\) tanned leather](#) requiring from 25 to 100 days depending on the thickness of the hides or skin. Tanning is carried out in vat containing tannins in various concentrations and with different degrees of acidity [depending on the substrate and the required shade](#). The hides or skins is immersed in the weakest solution and are moved to more concentrate one every few days. In the stronger solutions, the tannins penetrates deeper into the hide and is deposited between the fiber [bundles \(Muralidharan and Sandra, 2005\)](#).

2.8.3.2 Mineral Tannin (Chrome Tanning)

This is a [very](#) rapid tanning process, taking only few hours [for complete tanning](#). The process is simple. Chrome tanned leather is popular with the consumers because of its light weight, durability and its resistance to heat. It is also easily dyed and finished.

[The Chrome-chrome used for the tanning belongs to](#) a group of elements known as trivalent, usually representing one valency linkage. A typical salt of trivalent chrome is Cr_2O_3 . The hide or skin fiber [re](#) has the power of absorbing and permanently fixing only the basic salt whereby the fiber [re](#) is tanned or converted into leather (Sarkar, 1980).

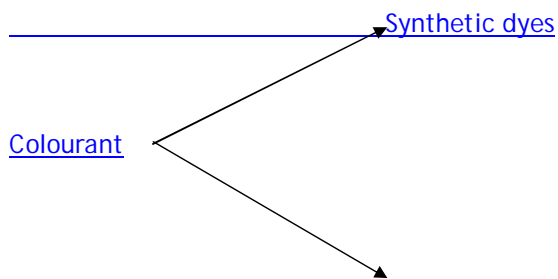
[The effluent generated via chrome tanning is difficult to manage.](#) Leathers produced by chrome tanning can be very hard [when compared with the vegetable tanned leather](#), but may be deficient in water proof qualities

unless filled with grease or wax, a process referred to as resin finishing- in other word the water resistance properties of vegetable tanned leather is preferred to that of chrome tanned leather. Water resistance is a very good property for leathers for shoe upper and military and paramilitary boot.

2.8.4 Dyestuffs Available for the leather Industries (Tysoe, 1994)

Just like in other substrate many of the available dyes could be used for leather application, but the most widely used dye class for the leather industry at present is the 'acid dye' category, which infact is contracting rapidly as a result of the protein present in hide and skin. Leather dyes do not have their own colour index generic name as obtained in other substrate but are either acid, direct, mordant or reactive types and appears in the colour-Colour index-Index where a leather usage has been suggested by a manufacturer-~~manufacturer~~. Figure 2.1 summarizes the colourants used for leather application.

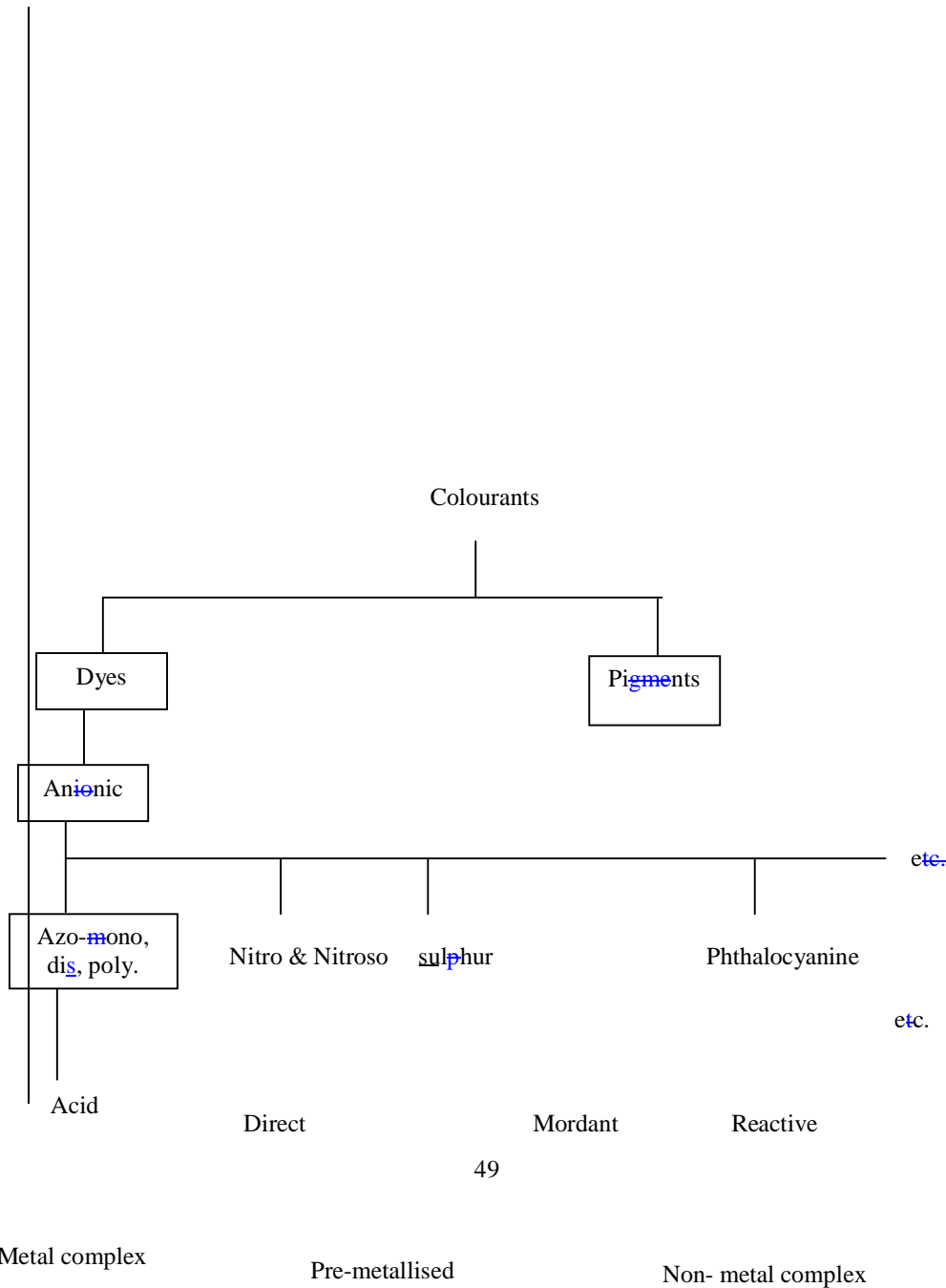
Figure 1 is the classification of colourants used for leather application.



Natural dyes

Figure 1: Classification of Leather Colourants

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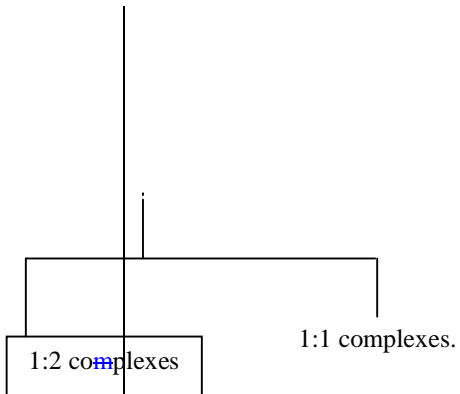


Figure 1: Colourants for leather application

The following criteria were used for the above classification: solubility, ionic charge, chromophore, dyeing behavior and metallization.

2.8.5 Natural Dyes ~~in~~ for Leather

Dyeing of leather is one of the important stages in post tanning operations in the leather production. This process enhances the aesthetic appearance of the leather. Dyes for leather dyeing are mostly chosen from textile dyes. The concern for use of synthetic dyes due to toxicological considerations gained momentum in the recent time. The increasing awareness of harmful effects of synthetic dye among consumers all over the world created the necessity to look for safer dyes.

The ~~search for attractive dye to~~ banned dyes based on the twenty listed aryl amines gave way for development of natural dyes. The use of natural dyes is

an age old process both in textile and leather industries. They produce innumerable shades on different leathers. Some of the known sources includes madder, quercitron, log-wood, henna, safflower, annatto etc.

Presently in USA and Germany, natural dyes are used in large scale ~~(Ganesan, 1999)~~. There is also a report on the use of Brazil wood, Orcein and cutch to get different colour shades on leather.

The basic principle to understand when leather is being dyed with natural dyes is its three dimensional structure and its charge characteristics after tanning with tanning materials. The changes brought about in the pelt during the pretanning and tanning operations are the major parameters considered before dyeing. The chemical reactivity of collagen gets altered during the above process due to the change in pH conditions and interaction with different chemicals. The resultant collagen/leather will have different surface charge characteristics. This determines the type of dyes to be used (Madhulatha et al, 1999).

2.8.6 Dyeing of Leather (Traubel and Eitel, 1977)

Leather is dyed to improve its appearance and make it saleable in a finished form. Leathers have inherent pigmentation and grain characteristics, which together with other factors make attainment of uniformity of shade throughout the piece difficult if not impossible ~~to attain~~; but this makes leather difficult to duplicate synthetically and this factor gives it psychological appeal. A variety of dyeing procedures are in commercial use, including drum, spray, paddle, brush, tray and solvent dyeing. The first two

~~being most~~ are the most applied techniques. Dyeing temperature is controlled within the range 25-60 °C and the pH is set in the range 3.8 - 5.5. Liquor ratio is generally low, example in drum dyeing, 2-8 times the weight of leather.

2.8.7 Dye Selection for Leather Application (Venkataraman, 1978)

Leather dyes are selected based on the hue of the dye, application, properties (solubility, levelness, and penetration), fastness properties and the tinctorial strength or cost factor. Brown and black shades remains the most important leather colours representing about 85 % of the total market. Because dyeing is done at low temperature, dyes must be soluble in the 40-65 °C range. Solubility ~~inte~~ weak acids is also important as dyes are applied at weakly acidic pH (3.8 -5.5)

CHAPTER THREE

3.0 Experimental

3.1 Materials

All the ~~materials~~ materials used for this ~~werere~~ research were collected in Zaria, and identified in the Department of Biological Sciences, Ahmadu Bello University, Zaria.

3.1.1 Plants

Common Name	Scientific Name	Family Name
Mango	<u>Mangnifera indica</u>	Anacardiaceae
Zobo	<u>Hibiscus <u>sabdariffa</u></u>	Malvaceae

Savanna mahogany	<u>Khaya senegalensis</u>	Meliaceae
Red onion	<u>Allium cepa</u>	Liliaceae
Annatto	<u>Bixa orellana</u>	Bixaceae

3.1.2 Chemicals

All chemicals used as solvent for extraction were of analytical grade and required no purification.

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Acetone

Ethanol

Methanol

Water (Distilled)

Chloroform

Silica gel

Hexane

Ethyl ether

Vegetable and chrome tanned leather.

3.2 Instruments:

Apparatus used for the experiments includes:-

Soxhlet apparatus

Heating mantle

Beakers of varying sizes

Distillation apparatus

Weighing balance

Vacuum pump

Melting point apparatus

Measuring cylinder

Clamp

Melting point apparatus

UV ~~–~~ spectrophotometer [- Winfirst-](#)

IR - spectrometer [- Thermo - TQ](#)

Thin-layer chromatography equipment

Tensometer (MT-LQ Model)

Wallace thickness guage

Kubelka apparatus

3.3 Extraction of the Crude [Dye](#) from the Plant

The crude [dye](#) was extracted from the plants by soxhlet extraction. 100g of the ground [ed](#) sample was packed and placed in the porous thimble and later placed in the inner tube of the soxhlet apparatus. The apparatus was then fitted to flat-bottom flask and a chosen solvent was introduced. The flask was boiled gently using heating mantle, the vapour passes up through the tube and ~~was condensed by the~~ condenser, the condensed solvents fall back into the thimble and gradually fills the body of the soxhlet.

When the solvents reached the top, it was automatically siphoned [ed](#) over into the flask with the extracted substance. The process automatically repeated itself. Depending on the sample, the extraction lasted for between 3 to 4 hours. When extraction ~~is~~ [was](#) completed, the solution was concentrated by distilling the solvent back and evaporating on a water bath. The extracted

crude [dye](#) was further dried in a desiccator bottle. The same procedure was applied for all the five different plants using all the five solvents [separately](#) for each of the plants.

3.4 Separation by Thin-layer Chromatography

A thin-layer glass was placed on a clear surface and a faint pencil line parallel to one of the edges at a distance of 2.5cm from the edge was drawn. The line was divided by marking with dots to serve as origins where sample spot will be placed. A clear capillary tube was dipped into the solution of the different [crudes](#) and was used to spot the thin - layer at the point marked. The spot was then allowed to dry and then placed into the chromatography tank to ensure that the developing solvent does not touch the spotted sample. The thin-layer glass was kept standing [—, Aa](#) after which the tank was covered. The separation was carried out for one hour and was then removed. The solvent front was marked with pencil and allowed to dry. The R_f value was then calculated. And each of the bands was collected as a pure sample in different sample bottles.

3.5. UV- visible Spectroscopy Analysis ([Dudley and Lan, 1980](#))

A solution of the sample of known concentration was made and introduced into a clean cell tube and a reference solvent was filled into another cell. The cells were then introduced into the [themo--](#)spectrophotometer and scanned through a range of [wavelengths](#) from 200 to 800nm and the absorbance of each wavelength recorded. The wavelength that gave the highest absorption was taken as the maximum absorption wavelength (λ_{max}) of each dye. The results are shown in [Table 4.6](#).

3.6 Anti - microbial Screening ([Rajni et la, 2004](#)) ([Ndukwe, 2005](#))

Clinical isolates of [Escheris](#)~~cheia~~[eoi](#)~~coli~~, [staphylococcus aureus](#), [Pseudomonas al](#)~~ruginosaaeruginosa~~, and [Proteus mirabilis](#) were obtained from Department of Microbiology—, A.B.U Zaria. The cultures were tested for purity. Each innoculum was prepared by inoculating the stock culture into freshly prepared blood agar and incubating aerobically at 38⁰C for some hours. Freshly prepared blood agar plates were inoculated by placing a loopful of the innoculum in the middle of each plate and cross- streaking with sterile wire loop. The paper discs were placed aseptically and pressed firmly on the surface of an inoculated agar plate control experiment set up using a paper disc soaked in pure [dimetyl sulphoxide \(DMSO\)](#). All the plates were incubated aerobically at 35 ⁰C for 24 hours after which they were examined for zones of inhibition of growth and were recorded. The results obtained are shown in Table 4.7.

3.7 Acute Toxicity ~~testing~~[Testing](#)—([Achunike, 1983](#))

Investigation of acute toxicity was carried out for the unknown substance using toxicity index, which is LD₅₀. ([Litere](#) dose that can kill 50% of the animals). The animal (mice) was weighed and then treated with the extracts via intravenous administration. They were observed frequently; nature and time of all advance effects were noted. Dead animals were autopsied and

examined macroscopically for any pathological changes and the surviving animals were weighed accordingly. If any animal recovered and regained weight again, this was taken as a sign of having survived the acute intoxication

Observation and weighting was carried ~~out-at~~ for 14 days and the experiment was then terminated. All the surviving animals were sacrificed at the end of each test and then autopsied and examined macroscopically for any pathological changes. LD₅₀ was calculated using the formula:

$$LD_{50} = \sqrt{A + B}$$

where:

A: is the maximum quantity of the substance that can kill the animal

B: is the minimum quantity of the substance that cannot kill the animal

The results obtained are shown in Table 4.8.

3.8 Tensile Strength Measurement

The tensile strength of each sample was determined using tensometer of MT - LQ Model. The thickness of each sample was determined using micrometer screw - gauge. The length and width of each sample ~~was~~ recorded to be 80mm by 20mm, correct beams ~~were~~ selected and the machine ~~was~~ was set at

zero after clamping the sample firmly and maximum force at break was recorded. Tensile strength was calculated using the formular:

$$\text{Tensile strength} = \frac{\text{Maximum breaking load (N)}}{\text{Cross sectional Area (M}^2\text{)}}$$

And the results obtained are recorded in Tables 4.9-4.13.

3.9 Measurement of Water Absorption in Leather, IUP/7

A disc of leather sample was cut using the pressing knife of 80mm. They were weighed and the thickness and diameter were measured. The Kubelka apparatus was rinsed with distilled water and was supported by a glass rod protruding the rubber band.

The leather samples were soaked in the water for some time, then the apparatus was turned at right angle and allowed to drain and the reading was taken on the volume of water absorbed. Such procedure was repeated under time interval of choice. The percentage water absorption was calculated using the expression

$$Q = 100 V/M$$

Where:

M = Mass of sample (g)

V = volume of water (cm³)

The results obtained are shown in Tables 4.14 - 4.18

3.10 Dyeing of Leather

The extracted dyes were used in dyeing vegetable and chrome tanned leathers. The standard method of dyeing leather was followed using the recipe.

- 120% of water (60°C)
- 2% of dye
- 0.1% of formic acid

A solution of the dye (2%) of each extract was made with distilled water. using heating mantle and, the temperature of the medium was raised to 60 °C. ~~Adjust~~ the pH of the bath was adjusted to 5.5 with formic acid. The samples were introduced into the bath and run for 45 minutes in a bottle shaker at a controlled speed. Formic acid (0.1%) and 20 ml of the mordant (plantain or citrus peel) in solution were added to the medium and run for additional one hour.

3.11 Percentage Dye Absorption

A dye bath of known concentration was made and the optical density/absorbance of the solution was taken using spectrophotometer. After dyeing the optical density /absorbance was taken again and the percentage absorbance was calculated using the formular :

$$\% \text{Exhaustion} = \frac{\text{Absorbance before dyeing} - \text{Absorbance after dyeing}}{\text{Absorbance before dyeing}} \times 100$$

3.12 Rub Fastness Test

Rub fastness tester (STM421) was used to assess the stability of the dye on the substrate. Both wet and dry rub fastness were assessed.

For dry fastness test:

Here a dry felt was run on the leather for series of cycles, ranging from 30, 60 and 120 cycles, after which it was assessed for staining and degree of change in colour using the grey - scales.

For wet fastness test:

Here the felt was wetted with warm water and then run on the leather for 30, 60 and 120 cycles respectively, and the same assessments for dry felt were made. The results obtained are summarized in Tables 4.24-4.28.

3.13 Infra -Red Spectroscopy Analysis

A small quantity of the dye extract was digested with paraffin oil. The dissolved sample was then spread on a transparent sodium chloride cell and placed back in the mountable holder and then scanned. The spectrograph of the percentage transmittance was obtained and the number of the various functioning groups present in the sample assessed. The results are shown in Table 4.29.

CHAPTER FOUR

4.0 Results

4.1 Percentage Dye Yield of the Plants in various Solvents

The results of the extraction using various solvents, the percentage yield and melting points are shown in Tables 4.1 - 4.5

Table 4.1: Ethanol Extracts of 100g of the Materials

Material	Yield (g)	% Yield	Melting Point (°C)	Nature of extract
S- <u>avanna</u> mahogany	6.8	6.8	400	Granules
Annatto	9.2	9.2	400	Sticky
Red onions	20.0	20.0	388	Granules
Dry mango leaf	12.3	12.3	389	Granules
Fresh mango leaf	40.0	40.0	388	Sticky
Zobo	31.6	31.06	400	Sticky

Table 4.2: Acetone Extracts of 100g of the Materials

Material	Yield (g)	% Yield	Melting Point (°C)	Nature of extract
<u>Savanna</u> mahoganyS- <u>mahogany</u>	6.2	6.2	400	Granules
Annatto	12.0	12.0	400	Sticky
Red onions	19.0	19.0	386	Granules
Dry mango leaf	13.2	13.2	375	Granules
Fresh mango leaf	32.0	32.0	386	Sticky
Zobo	11.02	11.02	400	Sticky

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Table 4.3: Methanol Extracts of 100g of the Materials

Material	Yield (g)	% Yield	Melting Point (°C)	Nature of extract
Savanna mahogany S- mahogany	7.0	7.0	400	Granules
Annatto	18.0	18.0	400	Sticky
Red onions	28.0	28.0	378	Granules
Dry mango leaf	41.0	41.0	388	Granules
Fresh mango leaf	38.0	38.0	378	Sticky
Zobo	42.0	42.0	400	Sticky

Table 4.4: Water Extracts of 100g of the Materials

Material	Yield (g)	% Yield	Melting Point (°C)	Nature of extract
Savanna mahogany S- mahogany	15.0	15.0	400	Granules
Annatto	8.6	8.6	400	Sticky
Red onions	16.0	16.0	377	Granules
Dry mango leaf	8.2	8.2	387	Granules
Fresh mango leaf	21.0	21.0	377	Sticky
Zobo	38.0	38.0	400	Sticky

Table 4.5: Chloroform Extract of 100g of the materials

Material	Yield (g)	% Yield	Melting Point (°C)	Nature of extract
Savanna mahogany ₹- mahogany	11.8	11.8	400	Granules
Annatto	10.2	10.2	400	Sticky
Red onions	8.2	8.2	385	Granules
Dry mango leaf	14.0	14.0	387	Granules
Fresh mango leaf	19.6	19.6	385	Sticky
Zobo	22.4	22.4	400	Sticky

4.2 UV - ABSORBANCE

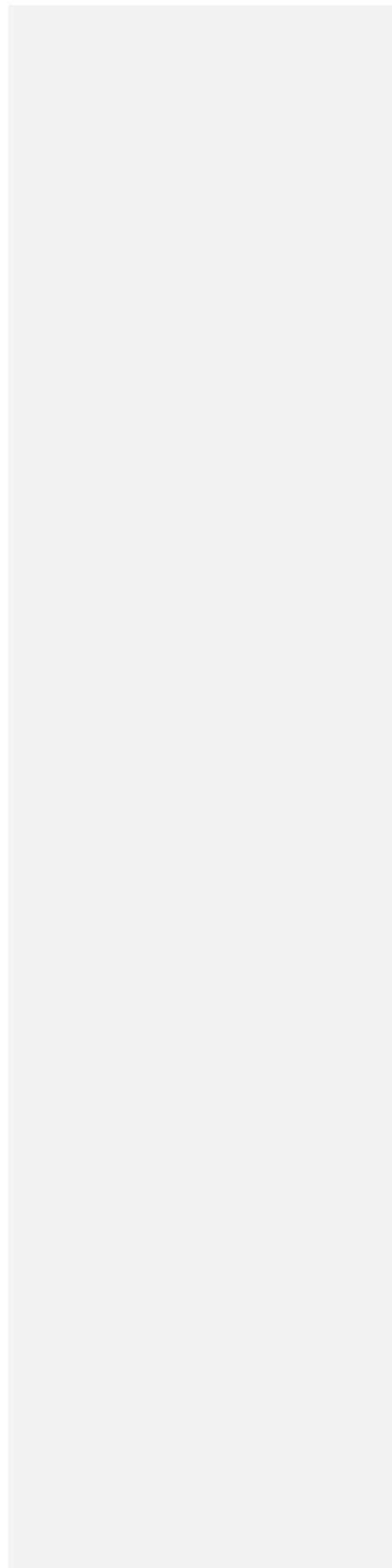
The results of the wavelength of maximum absorption (λ_{max}) of each extract in different solvents are shown in Table 4.6.

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Table 4.6: Visible Absorption spectra of the Extracts in various solvents

Materials	λ_{max} in Different solvents (nm)				
	Ethanol	Acetone	Methanol	Water	Chloroform
Savanna mahogany	495	490	495	500	485
Annatto	650	650	655	650	645
Red onion	390	395	395	390	390
Dry mango	595	595	595	590	605
Fresh mango	580	580	600	600	595
Zobo	650	650	650	645	650

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4.3 Results of the Anti-microbial Activities of the Extracts

The results of the anti - microbial activities of the extracts in various _____solvents are shown in Table 4.7.

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Table 4.7: Microbial Activities of the Extracts in various Solvents

Material	Microbial Activities of the Extracts in various Solvents			
	A	B	C	D
<u>Savanna mahogany</u>	Resistant	Resistant	Non resistant (+)	Resistant
Annatto	Resistant	Resistant	Non resistant (+)	Resistant
Red onions	Non resistant (+)	Non-resistant (+++)	Non-resistant (+++)	Non- resistant (++)
Dry mango	Resistant	Non-resistant (++)	Non-resistant (++)	Non- resistant (++)
Fresh mango	Resistant	Non resistant (+)	Non-resistant (++)	Non- resistant (+++)
Zobo	Non-resistant (++)	Non resistant (+)	Non resistant (+)	Resistant

Note:

A = *Staphylococcus*

B = *Pseudomonas aeruginosa*

C = *Proteus mirabilis*

D = ~~*Escherichia coli*~~ *Escherichia coli*.

+ = Slight growth
 ++ = Moderate growth
 +++ =severe growth

4.4 Acute Toxicity Investigation Result

The acute toxicity investigation results of the extracts in different solvents are shown in Table 4.8.

Table 4.8: Results of First and Second Acute Toxicity Investigation of the Extracts

Sample	First investigation			Second investigation			LD ₅₀
	Weight (g)	Dose (mg/kg)	No. of Mortality	Weight (g)	Dose (mg/kg)	No. of Mortality	
A	15	1000	3/3	14	1600	1/1	565.6
	18	"		19	800	1/1	
	13	"		20	400	1/1	
	16	100	0/3	18	200	0/1	
	15	"					
	14	"					
	14	10	0/3				
	13	"					
	14	"					
B	17	1000	2/3	15	600	1/1	244.9
	16	"		19	300	1/1	
	15	"		18	200	1/1	
	18	100	0/3	18	100	0/1	
	18	"					
	15	"					
	19	10	0/3				
	19	"					
	17	"					
C	15	1000	3/3	14	1000	1/1	632.5
	18	"		19	800	1/1	
	13	"		20	600	1/1	
	16	100	2/3	18	400	0/1	
	14	"					
	14	"					
	13	10	0/3				
	14	"					
	15	"					

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Table 4.8 continued

Sample	First investigation			Second investigation			
	Weight (g)	Dose (mg/kg)	No. of Mortality	Weight (g)	Dose (mg/kg)	No. of Mortality	
D	13	1000	3/3	16	800	1/1	400
	16	"		19	600	1/1	
	14	"		18	400	0/1	
	14	100	0/3	18	200	0/1	
	13	"					
	15	"					
	13	10	0/3				
	18	"					
	15	"					
E	16	1000	3/3	14	800	1/1	400
	19	"		19	600	1/1	
	15	"		20	400	0/1	
	15	100	0/3	18	200	0/1	
	14	"					
	13	"					
	48	10	0/3				
	16	"					
	14	"					
F	16	1000	3/3	14	600	1/1	177.5
	14	"		19	400	1/1	
	14	"		20	200	0/1	
	13	100	2/3	18	100	0/1	
	15	"					
	13	"					
	18	10	0/3				
	13	"					
	17	"					

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Where:

A = Savanna mahogany

B = Annatto

C = red onion

D = Dry mango

E = Fresh mango

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4.5 Tensile Strength and Percentage Elongation At Break Of Chrome Tanned Leather

The results of the tensile strength and percentage elongation of the dyed leathers are shown in Tables 4.9 - 4.13.

Table 4.9: Results of Tensile Strength and Percentage Elongation at break of Acetone Extracts of Dyed Leathers.

Sample	Chrome Tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.05	1.26	1.32	1.56	1.09	0.98	1.26	1.11	1.34	1.51		1.02
Load at break(N)	52.0	49.0	62.0	42.0	52.0	46.0	73.0	48.0	68.0	47.0	42.0	40.0
Tensile strength (10 ⁴ N/M ²)	3.0	6.2	3.9	2.6	3.3	2.8	4.4	3.1	4.4	3.1	2.6	2.5
% elongation at break	19	15	20	26	31	13	40	32	28	38	39	

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Table 4.10: Results of Tensile Strength and Percentage Elongation at break of Ethanol Extracts of Dyed Leathers.

Sample	Chrome Tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.25	1.09	1.27	1.35	1.10	1.04	1.29	1.09	1.30	1.52	1.10	1.04
Load at break(N)	85.0	46.0	97.0	63.0	58.0	49.0	59.0	41.0	62.0	46.0	40.0	41.0
Tensile strength (10^4N/M^2) (10^4N/M)	5.2	3.9	6.1	3.9	3.6	3.0	4.3	3.5	4.5	3.0	2.8	2.4
% elongation at break	19	15	20	26	31	13	35	36	30	39	37	32

Table 4.11: Results of Tensile Strength and Percentage Elongation at break of Methanol Extracts of Dyed Leathers.

Sample	Chrome Tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.22	1.10	1.26	1.30	1.07	1.02	1.24	1.13	1.36	1.48	1.19	0.99
Load at break(N)	80.0	57.0	47.0	85.0	44.0	50.0	55.0	52.0	65.0	43.0	44.0	42.0
Tensile strength (10^4N/M^2) (10^4N/M)	5.0	3.6	3.7	5.3	2.8	3.1	4.1	3.8	4.6	2.6	2.6	2.3
%	29	22	19	30	33	20	36	36	31	38	36	37

elongation at break												
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Table 4.12: Results of Tensile Strength and Percentage Elongation at break of Water Extracts of Dyed Leathers.

Sample	Chrome Tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.23	1.04	1.30	1.31	1.08	0.45	1.23	1.08	1.31	1.43	1.20	1.02
Load at break(N)	81.0	48.0	52	62.0	31.0	54.0	61.0	40.0	54.0	46.0	40.0	41.0
Tensile strength (10^4N/M^2) (10^4N/M)	5.1	3.0	6.8	3.9	1.9	3.4	4.5	3.4	3.8	2.9	2.6	2.3
% elongation at break	25	24	20	34	35	21	37	36	31	29	34	22

Table 4.13: Results of Tensile Strength and Percentage Elongation at break of Chloroform Extracts of Dyed Leathers.

Sample	Chrome Tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.26	1.08	1.29	1.34	1.05	0.99	1.28	1.06	1.30	1.52	1.17	1.04
Load at break(N)	70.0	52.0	88.0	62.0	38.0	56.0	66.0	42.0	44.0	50.0	41.0	41.0

Tensile strength (10^4N/M^2) (10^4N/M)	4.4	3.3	6.1	3.9	2.4	2.3	4.7	3.3	2.0	3.4	2.5	2.3
% elongation at break	24	19	13	21	29	14	30	29	31	22	35	29

Note: The tensile strength of undyed skin of chrome tanned leather has minimum load at break of 1500kg/cm^2 and that of vegetable tanned leather is 1450kg/cm^2 (SDC, 1978)

Where:

A = Savanna mahogany

B = Annatto

C = Red onion

D = Dry mango

E = Fresh mango

F = Zobo

4.6 Water Absorption of the dyed Leathers

The results of the water absorption of the dyed leathers with time are shown in Tables 4.14 - 4.18.

Table 4.14: Result of Water Absorption of the Acetone Extract Dyed Leather

Samples	Chrome tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.33	1.34	1.40	1.53	1.35	1.41	1.22	1.14	1.32	1.41	1.30	1.09
Weight (g)	1.39	1.42	1.54	1.52	1.53	1.41	1.34	1.26	1.41	1.50	1.39	1.20
Diameter (cm)	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Vol. of H ₂ O absorbed at 15 min.	2.8	3.4	3.6	3.6	3.5	3.3	2.8	3.0	3.0	2.9	3.1	3.0
30 min.	3.0	3.6	3.6	3.8	3.7	3.6	3.2	3.3	3.4	3.5	3.2	3.0
1hour	3.1	3.8	3.8	3.9	3.8	3.7	2.9	3.5	3.4	3.6	3.4	3.4
2hours	3.2	3.8	4.2	4.1	3.9	3.9	3.0	3.6	3.4	3.6	3.3	3.5

Table 4.15: Result of Water Absorption of the Ethanol Extract Dyed Leather

Samples	Chrome tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.40	1.36	1.41	1.46	1.38	1.42	1.43	1.36	1.18	1.09	1.52	1.48
Weight (g)	1.50	1.62	1.52	1.48	1.53	1.41	1.52	1.47	1.34	1.21	1.73	1.58
Diameter (cm)	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Vol. of H ₂ O absorbed at 15 min.	3.2	3.6	3.8	3.8	3.9	3.9	2.9	2.7	2.5	2.3	3.1	3.3
30 min.	3.4	3.9	4.0	3.9	4.1	4.1	3.2	2.9	2.8	2.8	3.4	3.5
1hour	3.5	4.1	4.3	4.4	4.4	4.5	3.2	3.0	3.0	3.2	3.7	3.7
2hours	3.8	4.3	4.4	4.7	4.6	4.7	3.4	3.2	3.3	3.4	3.9	4.0

Table4.16: Result of Water Absorption of the Methanol Extract Dyed Leather

Samples	Chrome tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.35	1.36	1.42	1.48	1.34	1.43	1.68	1.71	1.34	1.41	1.31	1.26
Weight (g)	1.4	1.46	1.57	1.50	1.54	1.44	1.82	1.88	1.62	1.67	1.59	1.48
Diameter (cm)	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Vol. of H ₂ O absorbed at 15 min.	3.2	3.6	3.8	3.9	3.5	3.4	3.3	3.4	3.1	3.0	3.0	2.7
30 min.	3.4	3.7	3.9	4.2	3.8	3.8	3.3	3.6	3.3	3.4	3.3	2.9
1hour	3.6	3.5	4.2	4.4	4.1	4.2	3.5	3.6	3.5	3.5	3.4	3.1
2hours	3.9	4.2	4.4	4.5	4.4	4.5	3.0	3.9	3.7	3.7	3.6	3.5

Table4.17: Result of Water Absorption of the Water Extract Dyed Leather

Samples	Chrome tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.40	1.44	1.46	1.47	1.38	1.48	1.28	1.37	1.51	1.39	1.20	1.17
Weight (g)	1.53	1.57	1.60	1.59	1.50	1.60	1.32	1.42	1.72	1.68	1.04	1.48
Diameter (cm)	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Vol. of H ₂ O absorbed at 15 min	3.7	3.9	4.0	4.0	3.5	4.1	2.8	3.0	3.3	2.7	2.9	2.7
30 min	3.8	4.2	4.3	4.2	3.7	4.4	3.0	3.0	3.4	2.9	3.0	2.9
1hour	4.0	4.4	4.6	4.5	4.0	4.7	3.3	3.4	3.4	3.3	3.4	3.1
2hours	4.2	4.6	4.8	4.8	4.3	5.0	3.8	3.6	3.6	3.5	3.5	3.3

Table 4.18: Result of Water Absorption of the Chloroform Extract Dyed Leather

Samples	Chrome tanned Leather						Vegetable Tanned Leather					
	A	B	C	D	E	F	A	B	C	D	E	F
Thickness (mm)	1.38	1.42	1.45	1.50	1.37	1.41	1.28	1.31	1.42	1.22	1.52	1.61
Weight (g)	1.41	1.47	1.49	1.53	1.41	1.44	1.38	1.50	1.62	1.48	1.69	1.4878
Diameter (cm)	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Vol. of H ₂ O absorbed at 15 min.	3.5	3.9	4.0	4.2	3.7	3.9	3.2	3.4	3.6	3.4	3.8	4.0
30 min.	3.8	4.1	4.3	4.5	3.9	4.2	3.3	3.6	3.6	3.7	3.9	4.1
1hour	4.0	4.3	4.5	4.7	4.3	4.5	3.3	3.8	3.8	3.8	4.0	4.2
2hours	4.4	4.7	4.8	5.1	4.6	4.7	3.4	3.6	3.9	3.9	4.2	4.4

Where:

A = Savanna Mahogany

B = Annatto

C = Red onion

D = Dry Mango

E = Fresh Mango

F = Zobo

4.7 Percentage Dye Adsorption

The results of the percentage dye absorption after application for chrome and vegetable tanned leathers are shown in Tables 4.19 - 4.23.

Table 4.19: Percentage Dye Adsorption of the Leathers using Ethanol Extracts

SAMPLE	A	B	C	D	E	F
CHROME + Plantain	15.87	19.33	21.12	23.09	24.72	20.45
Chrome+ Citrus	13.23	16.03	18.51	20.85	20.92	18.34
Veg. + Plantain	20.81	22.62	22.11	25.50	25.68	22.01
Veg. + Citrus	17.06	20.54	19.89	23.12	24.01	20.25

Table 4.20: Percentage Dye Adsorption of the Leathers using Acetone Extracts

SAMPLE	A	B	C	D	E	F
CHROME + Plantain	15.26	18.11	21.35	24.56	24.44	21.12
Chrome+ Citrus	14.01	16.22	19.96	22.31	22.63	20.88
Veg. + Plantain	20.06	22.04	21.35	24.10	24.69	23.15
Veg. + Citrus	18.72	19.87	19.98	20.11	21.05	20.69

Table 4.21: Percentage Dye Adsorption of the Leathers using Methanol Extracts

SAMPLE	A	B	C	D	E	F
CHROME + Plantain	15.09	18.62	21.32	23.22	24.32	21.08
Chrome+ Citrus	14.11	16.21	18.12	19.48	20.11	16.22
Veg. + Plantain	20.03	21.34	24.14	22.51	24.18	22.78
Veg. + Citrus	18.66	19.18	21.23	21.48	22.03	19.92

Table 4.22: Percentage Dye Adsorption of the Leathers using Water Extracts

SAMPLE	A	B	C	D	E	F
CHROME + Plantain	14.18	20.18	20.96	20.67	23.98	21.13
Chrome+ Citrus	13.26	16.74	15.84	18.87	20.22	17.56
Veg. + Plantain	21.79	22.56	23.47	24.18	24.65	22.35
Veg. + Citrus	22.35	18.76	18.05	19.24	20.14	20.24

Table4.23: Percentage Dye Adsorption of the Leathers using Chloroform Extracts

SAMPLE	A	B	C	D	E	F
CHROME + Plantain	15.32	19.24	20.62	23.44	24.03	20.66
Chrome+ Citrus	14.79	17.21	17.89	20.32	21.11	19.32
Veg. + Plantain	19.92	20.31	21.10	23.22	24.55	24.14
Veg. + Citrus	17.33	18.42	19.23	20.48	21.33	22.62

where:

- A = Savanna mahogany
- B = Annatto
- C = Red onion
- D = Dry mango leaf
- E = Fresh mango leaf
- F = Zobo

4.8: Rub Fastness Test of the dyed leather

The results of the rub fastness assessment of the dyed leathers are shown in

Tables 4.24 - 4.28.

Table 4.24: Results of Rub Fastness Test of Acetone Extracts on the Leathers

Sample	No. of cycle	Chrome Tanned				Vegetable Tanned			
		Dry		Wet		Dry		Wet	
		X	Y	X	Y	X	Y	X	Y
Acetone Extract									
S.—avanna mahogany	30	5	5	4/5	5	4/5	4	4/5	4
	60	4/5	5	4/5	5	¾	3	¾	3
	120	4/5	5	3	4	¾	3	¾	3
Annatto	30	4/5	5	4/5	4	¾	4	¾	4
	60	4/5	4	3	4	¾	3	2/3	3
	120	4/5	4	¾	4	2/3	3	2/3	3
Red onions	30	5	5	4/5	5	4/5	5	4/5	4
	60	5	5	4/5	5	4/5	5	3/4	4
	120	4/5	4	4/5	4	4/5	4	¾	4
Dry mango leaf	30	4/5	4	4/5	4	4/5	4	¾	4
	60	¾	3	3	4	2/4	3	2/3	3
	120	2/3	3	2/3	3	2/3	3	2/3	3
Fresh mango leaf	30	4/5	4	4/5	4	4/5	4	¾	4
	60	2/3	3	2/3	3	2/3	3	2/3	3
	120	3	3	2/3	3	2/3	3	2	2
Zobo	30	4	5	4	5	¾	4	¾	4
	60	3/4	4	3	4	3	3	2/3	3
	120	3	4	2/3	4	2/3	3	2	2

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Table 4.25: Results of Rub Fastness Test of Ethanol Extracts on the Leathers

Sample	No. of cycle	Chrome Tanned				Vegetable Tanned			
		Dry		Wet		Dry		Wet	
		X	Y	X	Y	X	Y	X	Y
Savanna mahoganyS-mahogany	30	5	5	5	5	4/5	5	4	5
	60	4/5	4	4/5	5	4/5	5	4	5
	120	3/4	4	4	4	3	4	3/4	4
Annatto	30	5	5	5	5	5	5	5	5
	60	5	5	5	5	5	5	5	5
	120	4/5	5	4/5	5	4	5	3/4	3
Red onions	30	5	5	5	5	4/5	5	4	4
	60	4/5	5	4	5	4	5	3	2
	120	4	5	3/4	4	3	4	3/4	5
Dry mango leaf	30	4	5	4	5	3/4	5	3/4	5
	60	3	4	3/4	4	3	4	2/3	5
	120	2/3	2	3	4	2	3	2	2
Fresh mango leaf	30	4	5	4	5	3/4	4	3/4	4
	60	3/4	5	3	5	2/4	3	3	3
	120	3/4	5	2/3	4	2/3	3	2/3	2
Zobo	30	4	5	4	5	4	5	4	5
	60	4/5	4	4	5	3/4	4	2/3	3
	120	3/4	3	2/3	4	2	2	2	2

Table 4.26: Results of Rub Fastness Test of Methanol Extracts on the Leathers

Sample	No. of cycle	Chrome Tanned				Vegetable Tanned			
		Dry		Wet		Dry		Wet	
		X	Y	X	Y	X	Y	X	Y
Savanna mahogany	30	5	5	5	5	5	5	5	5
	60	5	5	5	5	4/5	5	4/5	4
	120	4/5	5	4/5	5	4/5	4	4	4
Annatto	30	5	5	5	5	5	5	5	5
	60	5	5	5	5	4/5	5	4	4
	120	4/5	5	4/5	5	4	4/5	¾	4
Red Onions	30	5	5	5	5	5	5	4/5	5
	60	5	5	5	5	4	4	4	4
	120	4/5	4	4/5	4	¾	4	¾	4
Dry mango leaf	30	4/5	5	4/5	5	4	5	¾	4
	60	4	5	4	5	¾	4	3	3
	120	4	4	3	4	2	3	2	3
Fresh mango leaf	30	4/5	5	4	5	¾	4	¾	4
	60	4/5	5	3/4	4	3/4	4	3	3
	120	¾	4	3	3	3	3	2	2
Zobo	30	4	5	4/5	4	4/5	4	¾	4
	60	3	4	4	4	¾	3	2/3	2
	120	2/3	4	¾	3	2	2	2	2

Table 4.27: Results of Rub Fastness Test of Water Extracts on the Leathers

Sample	No. of cycle	Chrome Tanned				Vegetable Tanned			
		Dry		Wet		Dry		Wet	
		X	Y	X	Y	X	Y	X	Y
Savanna mahogany	30	5	5	5	5	4	5	4	5
	60	4/5	5	4	5	4	5	4	5
	120	4/5	5	4	5	¾	4	3	4
Annatto	30	5	5	5	5	4/5	5	4/5	5
	60	4/5	5	4/5	5	4	4	4	4
	120	4/5	5	4/5	5	3/4	4	¾	4
Red onions	30	5	5	5	5	4	5	4	5
	60	5	5	5	5	3	4	3	4
	120	4/5	5	4/5	5	3	4	2	3
Dry mango leaf	30	4/5	5	4	5	3	4	3	4
	60	3	4	¾	4	2/3	3	2/3	4
	120	3	4	2	3	2	3	2	3
Fresh mango leaf	30	4/5	5	4	5	4	5	4	4
	60	3	4	3/4	4	2/3	3	2/3	3
	120	3	4	3	3	2	3	2	3
Zobo	30	4	5	4	5	4	5	3	4
	60	4	5	4	5	¾	4	3	4
	120	3	4	2	4	3	4	2	3

Table 4.28 Results of Rub Fastness Test of Chloroform Extracts on the Leathers

Sample	No. of cycle	Chrome Tanned				Vegetable Tanned			
		Dry		Wet		Dry		Wet	
		X	Y	X	Y	X	Y	X	Y
Savanna mahogany Mahogany	30	5	5	5	5	4	5	4	5
	60	5	5	5	5	4	4	3/4	4
	120	4/5	5	4	4	3/4	3	3/4	3
Annatto	30	5	5	5	5	4	5	4	5
	60	5	5	5	5	3/4	4	3/4	4
	120	4	5	4	5	3	4	3	4
Red onions	30	5	5	5	5	4	5	4	5
	60	5	5	5	5	3/4	4	3/4	3
	120	4	5	4/5	5	3	4	2	2
Dry mango leaf	30	4/5	5	4	5	4	5	4	5
	60	4	5	4	5	3/4	4	3/4	4
	120	3/4	4	3	4	2	2	2	3
Fresh mango leaf	30	4	5	3/4	5	4	5	4	5
	60	4	5	3	4	3	4	3/4	4
	120	3	4	2	2	2	3	2	3
Zobo	30	4/5	5	4	4	4	4	4	4
	60	3	4	3	4	2/3	3	3	3
	120	2/3	2	2	2	2	2	2	3

- X - Degree of Staining
- Y - Degree of Color Change
- 5 - No Stain or Color Change
- 4/5 - Slight Stain
- 4 - Minor Stain and Color Change
- 3/4 - Moderate Stain
- 3 - Moderate Stain and Color Change
- 2/3 - High Stain
- 2 - High Stain and Color Change
- 1/2 - Very High Stain
- 1 - Very High Stain and Color Change

4.9 Infra - Red Spectroscopy

The results of the infra - red spectroscopy of the various extracts shown in

Table 4.29.

Table 4.29: Results of the IR - Spectrum of the Extracts

Sample	Wave-Number	Groups found	Comment
S. avanna mahogany	3000 - 2900 2800 1700 - 1500 1300	-COOH -C-H -C - C	Carboxylic (Broad) Alkynes Aromatic ring (vibration) Finger prints
Annatto	3000 1500 - 1400	-C-H -C-C	Alkynes (M) Aromatic ring
Red onions	2900 1800 1500	-C-H, -COOH =C=O -C-C, -C-NH	Carboxylic, Alkynes Carboxylic group Aromatic ring
Mango leaf	3500 2900 - 2800 1800 1500 1300	-N-H -COOH =C=O -C-NH, C-C Finger print	Amine (Broad) and Phenolic group (Broad) Carboxylic Acid Carbonyl group Amide group Finger print
Zobo	2900 2700 1900-1700 1300	-C-H -NH ₂ -ONH ₂ -, C-C -	Alkanes Broad due to the presence of overtone band Amide Finger Print

CHAPTER FIVE

5.0 Discussion of the Results

5.1 Nature of the Extracts and Percentage Yield of the extracts:

The dyes extracted were crystalline (Granular form) except for the Fresh mango (mangnifera indica) and Zobo (Hibiscus sabdariffa) leave extracts which appeared to be jelly-like (sticky). The percentage yields of the extracts in various solvents varied and were reasonably encouraging when compared with the economic value of the raw materials. The average percentage yield for all the plants in various solvents is less than 50%, which seems low when compared to the normal synthetic dyes which percentage yield above 80%.

Savanna mahogamy (Khaya senegalensis) had the least yield except for water and chloroform extraction, followed by annatto (Bixa orelllea) which recorded methanol as the best solvent for extraction with percentage yield of 18.0 % and water has the least with percentage yield of 8.6 %. Red onion (Alluim cepa) showed an average percentage yield of 18 % in all the various solvents.

From the results obtained the best solvent for extracting dyes from Red onion (Alluim cepa) is methanol, which had percentage yield of 28.0% and chloroform should not be used in the extraction of the dyes as it produced the least yield of 8.2%. Fresh mango (Mangnifera indica) generally in all the

solvents produced more than 20% yield except for chloroform which had 19.6 % yields. Dry Mango had an average percentage yield of 15% but showed an excellent percentage yield of 41.0% in methanol. Zobo (Hibiscus sabdaniffa) ~~in~~ on average produced a good yield ranging from 22.4% to 42.0% but had a poor yield for acetone extraction. In general, the results obtained showed that, solvent selection is an important factor in dye extraction from plants. As a result, solvent for extraction should be chosen based on the type of plant to be extracted from. Since the period of extraction was not made constant for each plant, the complete extraction was taken as the time the extraction solvent ~~of extraction to being~~ siphoned ~~becomes~~ became clear.

5.2 Ultra - Violet Absorbance

Table 4.6 shows the λ_{max} - (~~Wavelength-wavelength~~ of maximum absorption) of the different extracts obtained from the individual plants. All the dyes extracted showed strong and broad absorption in the visible region, which shows the presence of colour imparting ~~chloro~~ chromophores which ~~is~~ are responsible for the hues. Hue is the predominant colour transmitted by an organic compound when the complementary colour contained in the light passing it has been absorbed (Griffith, 1984). The wavelength of the extracts ranges from 345 to 650nm which from literature corresponds to the complementary colours of yellows, green, purple, violet, and blue as recorded by (Griffiths, 1984)-

From the results ~~obtained as~~ shown in Table 4.6, Savanna mahogany (Khaya senegalensis) had a λ_{max} - ranging from 485nm to 500nm in the various

solvents, ~~which from~~ literature indicates it absorbs violet colour of light to show yellow -green colour. Annatto (Bixa orella) extracts had λ_{max} ranging from 645 to 655 nm depending on the solvent and absorbs red light colour to show blue-green colour. Annatto extract of methanol ~~showed-gave~~ the highest λ_{max} of 655 nm ~~as-which indicates that it is it to be -result-is~~ more polar than the Annatto of the other four different ~~four~~ solvents. Chloroform showed the least λ_{max} of 645nm. Red onion (Allium cepa) extracts had λ_{max} near uv, ranging from 390nm to 395nm, and show yellow colour. Dry and Fresh mango (Mangnifera indica) extracts had λ_{max} ranging between 580 to 605 nm and absorbs orange colour light to show green -blue colour. Zobo (Hibiscus sabderiffa) extracts had λ_{max} of between 645 nm to 650 nm depending on the solvent. All the solvents showed λ_{max} of 650nm except water extract which showed λ_{max} of 645 nm. From the uv-~~-~~ absorbance, the visible colours of individual extracts could be established, though they- may be altered in application to produce ~~a-~~ different colours all-together by the use of mordants. The differences in the λ_{max} of the individual plants in various solvents is an indication that the colour can be shifted bathochromically or hypsochromically depending on the polarity of the solvent used. The colour can be shifted bathochromically which is referred to as red shift by attaching an electron- withdrawing group of increasing strength to the ring. This addition of electron withdrawing group will caouse an increase in the λ_{max} of the extract. Also the colour of the extract can be shifted hypsochromically by attaching to the ring an electron donating group which will caouse a decrease in the λ_{max} of the extract, thereby resulting to a blue shift.

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5.3 Anti-microbial activities of the extracts

From the assessment conducted, the extract though biodegradable showed a very good ~~resistant~~ resistance to some microbial activities when screened for their anti-microbial activity against, selected microbes such as: staphylococcus, ~~Pseudomonas pseudomonas aeruginosaaeruginosa~~, proteus mirabilis and ~~Escherichia escherichia coli, -Aas~~ recorded in Table 4.7. There was a clear ~~zoneszone~~ of ~~inhabitation~~ inhibition by ~~savanna~~ Savanna mahogany (Khaya senegalensis) for Staphylococcus, ~~Pseudomonas pseudomonas aeruginosa aeruginosa~~ and ~~Escherichia escherichia coli~~. Which This is a good indication that when leather is dyed with Savanna mahogany (Khaya senegalensis), such leather can not be attacked by any of the three mentioned microbes, but under certain condition, ~~Proteus proteus~~ mirabilis may attack the leather, because Savanna mahogany (Khaya senegalensis) showed weak resistance to ~~Proteus proteus~~ mirabilis. Also savanna mahogany extracts dyed leather could be used in an environment infested with any of the above mentioned microbes without any fear of the microbes growing on the leather. Annatto (Bixa orellaea) extracts showed ~~resistant~~ resistance to Staphylococcus, ~~pseudomonasP- aeruginosaaeruginosa~~, and ~~escherichia coli E.coli and but only~~ slight ~~resistant~~ resistance to microbes such as Proteus mirabilis.

From the results obtained in Table 4.7, Savanah mahogany (Khaya senegalensis) and ~~annatto~~ Annatto (Bixa orellaea) showed almost the same degree of resistance to microbes used for the assessment. Red onion (Allium cepa) extract when treated with the microbes were non - resistant. There was

no inhibition of microbial growth. When Red onion (*Allium cepa*) was treated with *Pseudomonas aeruginosa* or *Proteus mirabilis*, there was severe growth of the microbe in the medium unlike when the same extract was treated with *Staphylococcus* or *E. coli* which show slight and moderate growth. In general Red onion (*Allium cepa*) shows different degrees of microbial activities; as such it should not be used to dye leather that would be used in an environment infested by any of the four microbes unless special treatment is given to the leather in addition, in order to prevent the microbial activity.

Dry Mango (*Mangnifera indica*) extract showed clear zone of inhibition when treated with *staphylococcus*, so can be used to dye leather that would be used in *staphylococcus* infested environment. The same Dry mango (*Mangnifera indica*) extract when treated with *pseudomonas aeruginosa*, *Proteus mirabilis* or *escherichia coli* showed the same degree of activities of microbes as a result cannot be employed in dyeing leathers that will be used in an environment infested by these microbes except if additional treatment is given to prevent the growth of these microbes. Fresh mango (*Mangnifera indica*) showed clear zone of inhibition when treated with *Staphylococcus*. There was no activity. The same extract when treated with *pseudomonas aeruginosa*, *Proteus mirabilis* or *escherichia coli* showed different degrees of microbial activities ranging from slight growth, moderate and severe growth respectively. From these results, leather that is dyed with Fresh mango (*Mangnifera indica*) extract cannot be used in an environment infected by these three microbes as there would be microbial activity on the leather.

When Zobo (Hibiscus sabdariffa) extract was treated with E. coli there was clear zone of inhibition of the microbial activity. The same degree of microbial activity (moderate growth) was obtained when the extract was treated with pseudomonasP. aeruginosa-aeruginosa or Proteus mirabilis, and severe growth when treated with Staphylococcus.

In general Savanna mahogany (Khaya senegalense) and Annatto (Bixa orellana) extract showed an outstanding resistance to all the microbes used for the research work, as a result they can be used for leather dyeing irrespective of the application (end use). Extracts such as from Red onions (Allium cepa), Dry and Fresh mango (Mangifera indica) and Zobo (Hibiscus sabdariffa) should be used with caution in leather dyeing as most of them showed clear microbial activities except for Dry and Fresh Mango (Mangifera indica) extract which showed clear zone of inhibition when treated with Staphylococcus and also Zobo (Hibiscus sabdariffa) when treated with E. Coli

5.4 Acute Toxicity.

Table 4.8 shows the acute toxicity investigation results conducted on each of the extracts. The assessments which were based on the litre dose of the extract that will kill 50 percent of the animals used for the investigation (LD₅₀) confirmed all the extracts to be toxic free. Savanna mahogany (Khaya senegalensis) extract which from the results obtained had 1000 mg/kg of the extract destroying all the animals employed in the first investigation and showed LD₅₀ of 565.5mg/kg which shows that Savanna mahogany (Khaya

~~senegalensisit~~ is toxic free. From literature, for any substance to be toxic, the LD₅₀ must be less than or equal to 2 mg/Kg (Achunike, 1983). Annatto (Bixa orellaea) also had 1000 mg/kg of the extract destroying all the animals and 100 mg/kg did not kill any of the animals, and had LD₅₀ of 244.9 mg/kg which falls within the safe limit. As a result, the extract is toxic free. Dry and Fresh Mango (Mangnifera indica) had 1000 mg/kg of the extract killing only two out of the three animals used for the first investigation, and had the value of 400 mg/kg LD₅₀ for both of the extracts. Both extracts show the same result in the second investigation. Zobo (Hibiscus sabdariffa) extracts in the first investigation destroyed all three animals used and shows LD₅₀ of 177.5 mg/kg after the second investigation.

In general, when the individual plant extract LD₅₀ was compared, it was clear ~~that Zobo~~ that Zobo (Hibicus sabdadariffa) showed the least LD₅₀ value of 177.5mg/kg, while red onion (Alluim cepa) showed the highest LD₅₀ value of 632.5mg/kg. When the results of the LD₅₀ of the various plant extracts were related to the acceptable value of LD₅₀ in literature, ~~it~~ it was observed that all the plants used for the research work ~~had their~~ extracts toxic free, as a result can conveniently be used not only in leather dyeing but also for food coloration.

5.5 Tensile Strength and Percentage Elongation at Break for Chrome and Vegetable Tanned Leathers.

After the application of the different extracts on the chrome and vegetables tanned leathers, some physical testing of the mechanical properties of

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finished leathers were conducted. Tables 4.9 - 4.13 generally show that natural dyes does not have any negative effect on the tensile property of the dyed leather, for both chrome and vegetable tanned. Table 4.9 shows that red onions (Allium cepa) has the highest load at break of 62.0N for chrome tanned leather with tensile strength of $3.9 \times 10^4 \text{ N/m}^2$ for acetone extraction and ~~savanna-Savanna~~ mahogany (Khaya senegalensis) showed a maximum load at break of 73.0 N with tensile strength of $4.4 \times 10^4 \text{ N/m}^2$ for acetone extraction.

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From literature, there is an indication that the extracts did not reduce the strength of the leathers after dyeing. Table 4.10 shows ~~red-Red~~ onions (Allium cepa) to have the highest load at break of 97.0 N and 62.0 N respectively for both chrome and vegetable tanned leathers. Also having tensile strength of $6.1 \times 10^4 \text{ N/m}^2$ and $4.5 \times 10^4 \text{ N/m}^2$ respectively.

In general for ethanol extract, none of the extracts has tensile strength that is below the acceptable value of 1500 N/m^2 and 1450 N/m^2 for chrome and vegetable tanned leathers respectively (SDC, 1978).

Table 4.11 shows Dry mango (Mangnifera indica) methanol extracts as the best ~~having-with~~ maximum load at break of 85.0 N for chrome ~~tamed-tanned~~ leather and Red onion (Alluim cepa) extract with 65.0 N for vegetable tanned leather. Both ~~having-showed~~ tensile strength of $5.3 \times 10^4 \text{ N/m}^2$ and $4.6 \times 10^4 \text{ N/m}^2$ respectively. Table 4.12 has ~~savanna-Savanna~~ mahogany (Khaya senegalensis) water extract as the best with maximum load at break of 81.0 N for chrome ~~tamed-tanned~~ leather and 61.0 N for vegetable tanned leather.

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Both ~~having showed~~ tensile strength of $5.1 \times 10^4 \text{ N/m}^2$ and $4.5 \times 10^4 \text{ N/m}^2$ respectively.

Table 4.13 shows Red onion (Allium cepa) chloroform extract as the best with 98.0 N maximum load at break and Savanna mahogany (Khaya senegalensis) with 70.0N and 66.0 N for chrome and vegetable tanned leathers respectively.

Both have tensile strength of $6.1 \times 10^4 \text{ N/m}^2$ and $4.7 \times 10^4 \text{ N/m}^2$ respectively.

In general Red onion (Allium cepa) showed outstanding maximum load at break in chloroform extraction for chrome tanned leather with tensile strength of $6.1 \times 10^4 \text{ N/m}^2$ and Savanna mahogany (Khaya senegalensis)—Methanol extract showed the maximum load at break of 66.0 N with tensile strength of $4.7 \times 10^4 \text{ N/m}^2$ for vegetable tanned leather. Therefore, methanol Red onion (Allium cepa) extract should be preferred where tensile strength and maximum load at break is an important factor. The least ~~being is~~ Fresh mango (Mangnifera indica) extracts. Ethanol and water extracts, ~~s~~ showed maximum load at break of 40.0 N with tensile strength of $2.8 \times 10^4 \text{ N/m}^2$ and $2.6 \times 10^4 \text{ N/m}^2$ respectively. So caution should be applied in using the extracts s for leather dyeing where good tensile strength is needed.

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5.6 Water Absorption of the Dyed Leathers.

The results of water absorption of the dyed leathers in Tables 4.14 to 4.18 ~~showshows~~ that all the leathers treated with the different extracts of various solvents have fairly good resistance to water absorption. From Table 4.14, all the acetone extracts of different plants hasve percentage water absorption of less than 5.2% which is the standard value acceptable in leather manufacture. Table 4.14, shows Savanna mahogany (Khaya senegalensis) as the best with

maximum water absorption of 3.2% after 2 hours and ~~red-Red~~ onions (Allium capa) as the least with 4.2% after 2 hours for chrome tanned leathers. For vegetable tanned leather, Savanna mahogany (Khaya senegalensis) also had the best result with 3.0% water adsorption after 2 hours.

Table 4.15 shows Savanna mahogany (Khaya senegalensis) ethanol extract as the best with percentage water absorption of 3.8% for chrome tanned leather and Annatto (Bixa orellana) with 3.2% for vegetable tanned leather. Table 4.16 shows Savanna mahogany (Khaya senegalensis) to have percentage water absorption of 3.9% for chrome tanned leather and vegetable tanned leather had Zobo (Hibiscus sabdariffa) as the best with 3.5% water absorption. Table 4.17 shows the water absorption of the different extracts and Zobo (Hibiscus sabdariffa) had the best water absorption resistance of 3.3% after 2 hours for vegetable tanned leather and Savanna mahogany (Khaya senegalensis) has 4.2% after 2 hours for chrome tanned leathers. Table 4.18 has Savanna mahogany (Khaya senegalensis) as the best with percentage water resistance of 4.4% and 3.4% for both chrome and vegetable tanned leathers. In general acetone extracts of all the plants ~~has showed~~ the best water resistance property when compared with the extracts of the other solvents and can be freely used ~~d-~~ to finish leather for shoe upper that can be used during rainy ~~rainy~~ ~~g-~~ season. The more water a leather absorbs the lower the value of the leather as water retention ~~inace~~ in leather is a disadvantage.

5.7 Percentage Dye Absorption during Dyeing

Tables 4.19 - 4.23 shows the results of the percentage dye absorption of the individual extracts of various solvents. The results obtained showed by calculation the percentage dye absorption to range from 15-25% for all the extracts. From the results obtained, all the plants extracts of ethanol have the highest dye absorption with vegetable tanned leather using plantain peel as the mordant. They ~~has anshowed~~ absorption of 20.81%, 22.62%, 22.11%, 25.50%, 25.68% and 26.81% ~~and~~ the least being chrome tanned leather with citrus as mordant.

Tables 4.20-4.23 show highest dye absorption on vegetable tanned leathers with plantain peels as mordant. Acetone extracts have vegetable tanned leather with 24.1% dye absorption as the highest while methanol recorded red onions (*Alluim cepa*) extracts as the highest with 27.23% dye absorption. Water extracts has Fresh mango (*Mangnifera indica*) as the highest with 24.65% dye absorption when treated with plantain peels. Chloroform extracts had Fresh mango (*Mangnifera indica*) extract with plantain peel mordant as the highest with 24.55% dye absorption.

Rates of penetration of dyestuff from theoretical point of view are known to be determined by such factors as nature of the substrate, pH of the collagen, pH of the dye bath, charge on the substrate, temperature, dye molecular size, mechanical agitation and duration of the dyeing. ~~Form-From~~ the results obtained, it is evident that the use of plantain peels which ~~contained~~ contains potassium for mordanting gave a better shade on both the chrome and vegetable tanned leathers than the citrus peel mordant, which in some extracts had a burning effect on vegetable tanned leather and so cannot be

recommended for mordanting vegetable tanned leather. Comparing the plant mordant (plantain and citrus peels) with the standardized metallic mordant such as alum etc., it is observed that alum is preferred for industrial application irrespective of the [cost, cost](#); because the fixing of the dye on the substrate is better with metallic alum mordant. [\(ArmiyaOthmer, 20041965\)](#).

5.8 Rub Fastness of Dyed Chrome and Vegetable Tanned Leathers.

The results of rub fastness of vegetable and chrome tanned leather using different extracts of various solvents are shown in Tables 4.24 - 4.28. The acetone extracts, have Savanna [maehogaony](#) (*Khaya senegalensis*) extract as the best extract for dyeing chrome tanned leather, followed by Red onion (*Alluim cepa*) which exhibited an excellent result for 30 and 60 cycles. Generally, vegetable tanned leathers showed poor rub fastness for all the plant extracts, as the colour change after rubbing was mainly below average. Annatto (*Bixa orrellea*) ethanol extracts had a very good rub fastness both for chrome and vegetable tanned leathers.

Table 4.26 shows the results of the rub fastness of methanol extracts; from the results obtained, almost all the extracts have good rub fastness as the degree of staining and colour change is above 3 in average number of cycles of 70. ~~Except~~ [The exception Zobeis Zobo](#) extract which showed a very poor rub fastness of 2 on vegetable tanned leather. Table 4.27, shows the rub fastness results of water extracts on chrome and vegetable tanned leathers. From the results obtained Red onion (*Alluim cepa*) showed ~~a very~~ outstanding good rub fastness for both leathers in dry and wet rub fastness. The degree of

colour change with Savanna mahogany (Khaya senegalensis) is also very good for both leathers. Table 4.28 shows the results of the rub fastness of chloroform extracts in the chrome and vegetable tanned leathers for both dry and wet assessment. From the result, Savanna mahogany (Khaya senegalensis), Annatto (Bixa orellaea), and Red onion (Allium cepa) showed a very good rub fastness ~~on the~~ both leathers. In general, all the extracts of different solvents on the average showed the same degree of rub fastness, for plants such as Savanna mahogany (Khaya senegalensis), Annatto (Bixa orellaea) and red onion (Allium cepa).

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5.9 The Spectra of the Extracts

The results of the infra-red analysis carried out for all the extracts are shown in Table 4.29. From the results, the extracts contained series of functional groups, which are chromophores that produce light absorbance in the visible region (Pointing, 1980). During application of the extract to leather, when a mordant is applied, it will result to a shift of λ_{max} depending on the mordant used. From the results, all the extracts had absorbance on different wave number which is an indication of different colours each extract is capable of producing. Savanna mahogany (Khaya senegalensis) from the results obtained has functional groups such as -COOH, ~~-C-H,~~ and OH as well as -C-H and C-C aromatic ring and finger prints, with wave numbers 2900 - 3000, 2800, 1500 - 1700 and 1300 cm^{-1} respectively.

This is a confirmation that ~~these~~ this extracts on its own has a colour imparting characteristics, which qualifies it as a dye and when ~~some kind~~

of certain mordants are added to the dyeing medium will improve the fixing of the colour on the substrate as well may cause a bathochromic or hypsochromic shift based on the charge in the mordants. Annatto (Bixa orellia) in addition showed the presence of exhibited some functional groups such as -C-H [alkyne(M)] and -C-C (aromatic ring vibration) with wave numbers 3000 and 1500 - 1400 cm^{-1} respectively, which are also chromophores form part of aromatic chromogens for colour imparting characteristic. R, Red onion (Allium cepa) showed the following functional groups such as -C-H, COOH, =C=O, -C-C, and -C-NH with wave-numbers 2900, 1800 and 1500 cm^{-1} respectively, while Mango (Mangifera indica) extracts from the results obtained showed the presence of amine with broad peak (-N-H), carboxylic acid group (-COOH), carboxylic-carboxylic group (= C= C) and amide group such as - C- NH with wave-numbers 3500, 2900 - 2800, 1800, 1500 and 1300 cm^{-1} respectively. Zobo extracts (Hibiscus sabdariffa) extracts showed the presence of - C- H (alkynes), -N-H₂ which is broad due to the presence of overtone band, -NH₂ (amide) and finger prints which is due to the presence of some groups such as sulphur and others with wave-numbers 2900, 2700, 1900 - 1700 and 1300 cm^{-1} respectively.

CHAPTER SIX

6.0 Conclusions ~~And~~ and Recommendations.

6.1 Conclusions

This research has to a ~~reasonable~~ recommendable extent demonstrated the use of plants such as Savanna mahogany (Khaya senegalensis), Annatto (Bixa orellaea), Red onion (Allium cepa), Mango (Mangnifera indica) and Zobo (Hibiscus sabdariffa) as sources of dyes for leather application, especially ~~the~~

on chrome and vegetable tanned leathers using plantain or citrus peel as mordant for dye fixation on the substrate. Extraction and purification of the dyes were by soxlet extraction and thin layer chromatography respectively. The percentage dye yield of the plants and percentage dye exhaustion were also below average. ~~From~~ Therefore from these results obtained, it is very obvious that the leather industries cannot absolutely rely on natural dyes for finishing, this is as a result of the poor percentage yield of these dyes. But can complement the available synthetic dyes with natural dyes.

From the UV-visible spectra results of the extract obtained, the extracts absorbed strongly in the UV-region. In other words, the extracts are organic compounds. The possible colours that could be obtained ~~form~~ from the individual plant extracts are yellow-green from Savanna mahogany (Khaya senegalensis), blueish -green from Annatto (Bixa orellana), yellow from Red onion (Allium cepa) and greenish - blue from Mango (Mangifera indica). Although these extracts have the above mentioned visible colours, these colours can also be altered during application (dyeing) by the use of different mordants (Patterson and Piling, 1991).

Anti - microbial screening of the extracts of different plants showed an indication of clear zone of inhibition for some extracts such as Savanna mahogany and Annatto on some particular microbes such as Staphylococcus, P. aeruginosa and E. coli ~~as a result some of the extracts~~ to a every good extent ~~can will~~ stop the growth of ~~certain these~~ microbes when used for leather dyeing, while extracts such as Red onion and Fresh mango, has ~~some~~

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~~had~~ very poor resistance to certain microbes such as P. aeruginosa, P. mirabilis and E. coli too. So caution should be exercised in selecting natural dyes for leather application for certain end uses, especially leathers that are supposed-meant to be used in hospital environment and some certain unkept environments.

Also life can easily be affected by substances that are toxic. The degree of the effect depends on the LD₅₀ of the substance. Man can come in contact with such toxic substances through clothing, foot-wares, food or water; as a result this research work was extended to cover the acute toxicity assessment of the extracts of different plants and the results obtained confirmed all the extracts to be toxic free. ~~Asince~~ since none of the extracts had LD₅₀ less or equal to 2 mg/kg, the limit of toxicity to animal life –as established by literature, ~~that any substance that has LD₅₀ (liter dose of the substance that can destroy 50% of the test animal) less or equal to 2 mg/kg is taken as a toxic substance as a result is harmful to life.~~ From the results obtained, Zobo (Hibiscus sabdariffa) had the least LD₅₀ of 177.5 mg/kg and the highest of the extract extracts is Red onion (Allium cepa) with LD₅₀ of 632.5 mg/kg.

The research also established that the natural dyes extracted from the plants did not depreciate-reduce the tensile strength property of the leathers, irrespective of the tanning process used for the leather processing. ~~Each of the processed leather maintains values above the required tensile strength for~~

~~both chrome and vegetable tanned leathers.~~ The tensile strength for all the treated samples varies from 2.8×10^4 - 6.8×10^4 N/M²

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The results of the water absorbance resistance of the leathers showed that on the average, chrome and vegetable tanned leathers processed, with plant extracts ~~in on~~ average ~~has showed~~ good water ~~resistant~~ resistance property. Vegetable tanned leather showed moderate percentage of dye absorption after application, especially with ethanol extracts of Zobo (Hibiscus sabdariffa).

Most of the extracts of the various plants after application showed a very good rub fastness. The best ~~being are~~ Savanna mahogany (Khaya senegalensis) extracts, ~~5, Red onions (Alluim cepa) extract 5 and Annatto (Bixa orellia) extract 4.5 and Red onions (Alluim cepa) extract~~. The three extracts showed excellent degree of resistance to staining and colour change in both chrome and vegetable tanned leathers as a result possess high rub fastness.

The infra-red spectra of the extracts confirmed the presence of chromophores such as COOH, CO, NH₂, -C-H, C-C and -C-NH in the extracted dyes, which ~~is the colour impacting component of any colouring matter account for the coloured nature of the extracts~~. In other words, the extracts are not just tannins but dyes that could be used in the leather, textile and food industries. The results obtained showed that the extracts ~~have are~~ aromatic ~~constitution and in nature with groups such as~~ hydroxyl group (OH) in the phenolic group,

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but the number and the position of the hydroxyl groups present in each of the extracts could not be established. ~~In general, plants extract possesses the above mentioned properties and is highly encouraged in leather dyeing, following the above mentioned procedures in selecting the extracts.~~

6.2 Recommendations:

From the results of the various assessments conducted, it is established that dyes from Savanna mahogany (*Khaya senegalensis*), Annatto (*Bixa orellana*), Red onion (*Allium cepa*), Mango (*Mangnifera indica*) and Zobo (*Hibiscus sabdariffa*) are 100 percent toxic free and can highly inhibit some microbial activities and therefore can be recommended for both food and beverages colouration.

More research work should be encouraged in the following areas:

- The effect of concentration of dye on anti - microbial activity. So that it will be known whether increase or decrease in concentration of dyes will affect inhibition of microbes.
- The anti-microbial activity of the dyes on dyed leather substrate. Even on textile substrates such as cotton, wool silk fibers e.t.c.

- Study should be done on the particle size reduction of extracts such as Mango (*Mangnifera indica*) and Zobo (*Hibiscus sabdariffa*) extracts, as this imposed some how-problem during application (dyeing).
- The low level of percentage dye exhaustion by the leather can also be investigated by varying the pH, time and temperature of dyeing.

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APPENDIX A

Percentage Yield of Different Plants in Various Solvent

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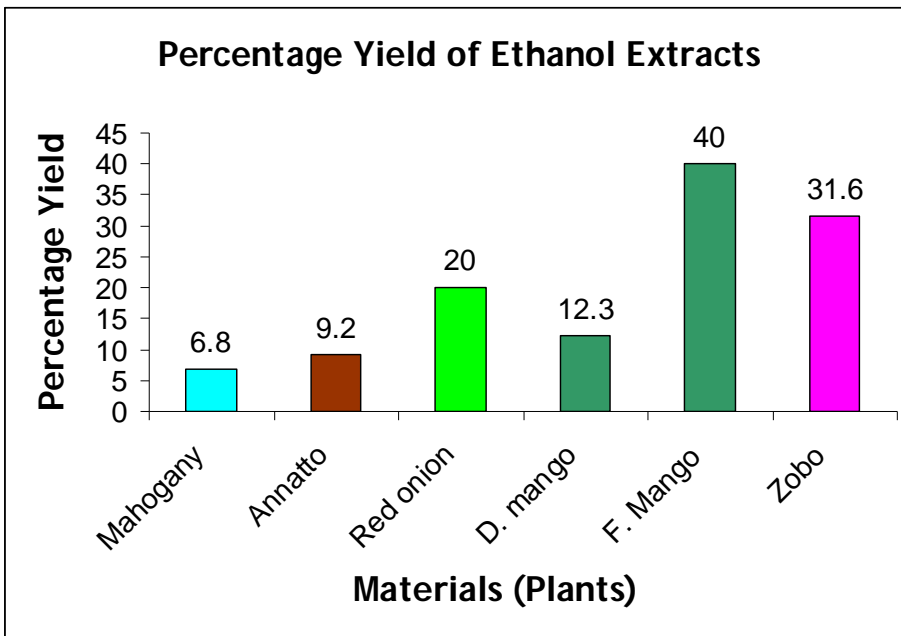


Fig 1: Percentage Yield of Ethanol Extracts.

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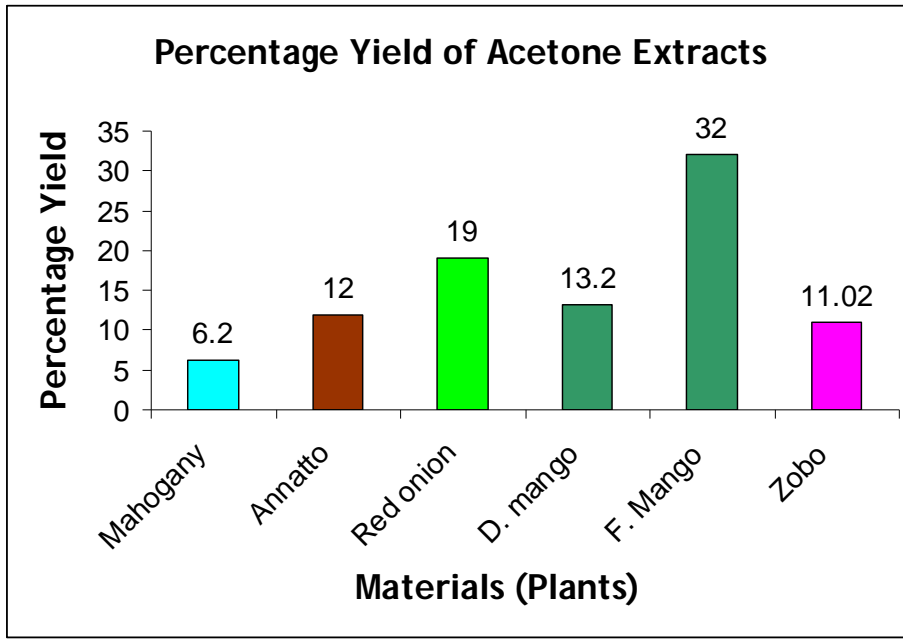


Fig 2: Percentage Yield of Acetone Extracts

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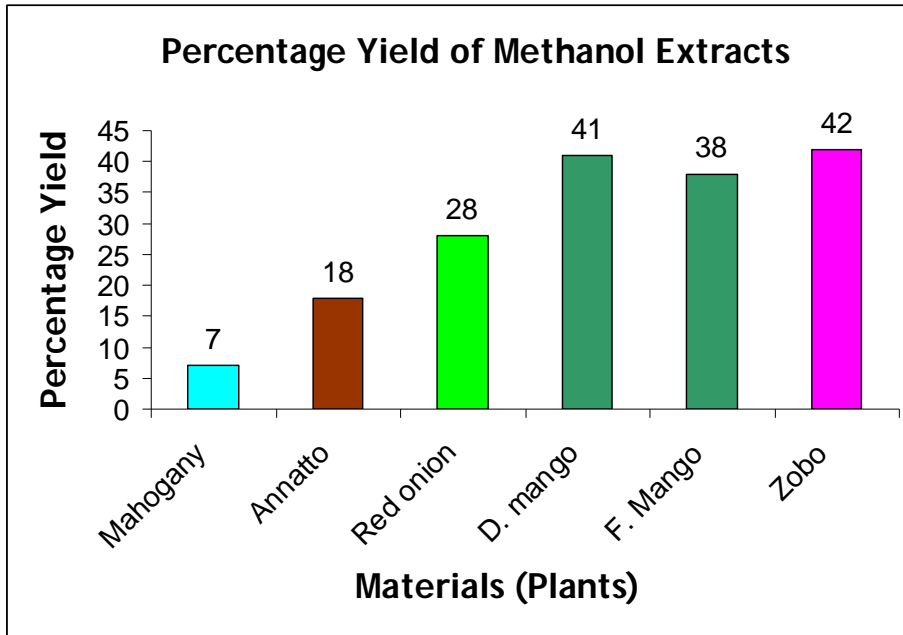


Fig 3: Percentage Yield of Methanol Extracts

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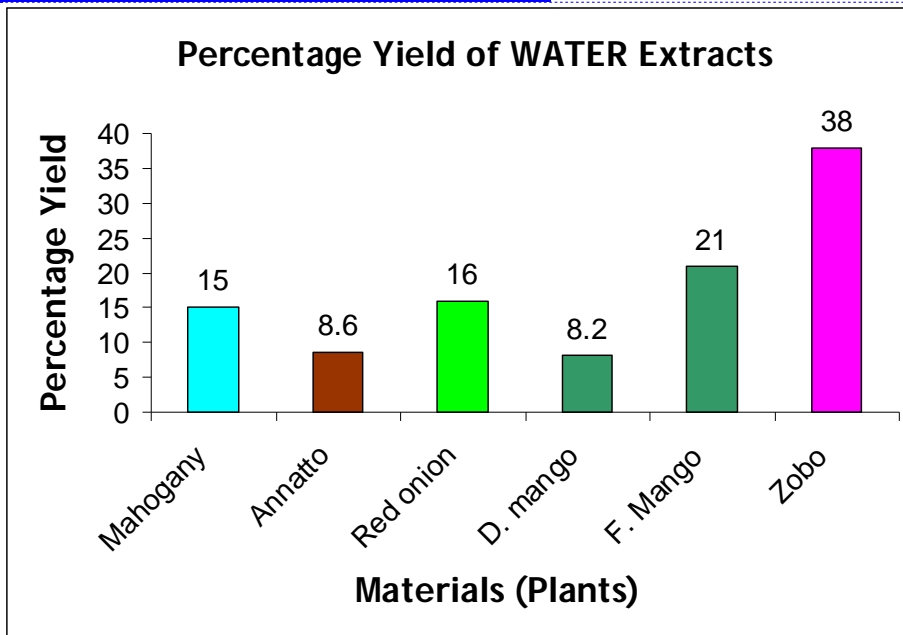


Fig 4: Percentage Yield of Water Extracts

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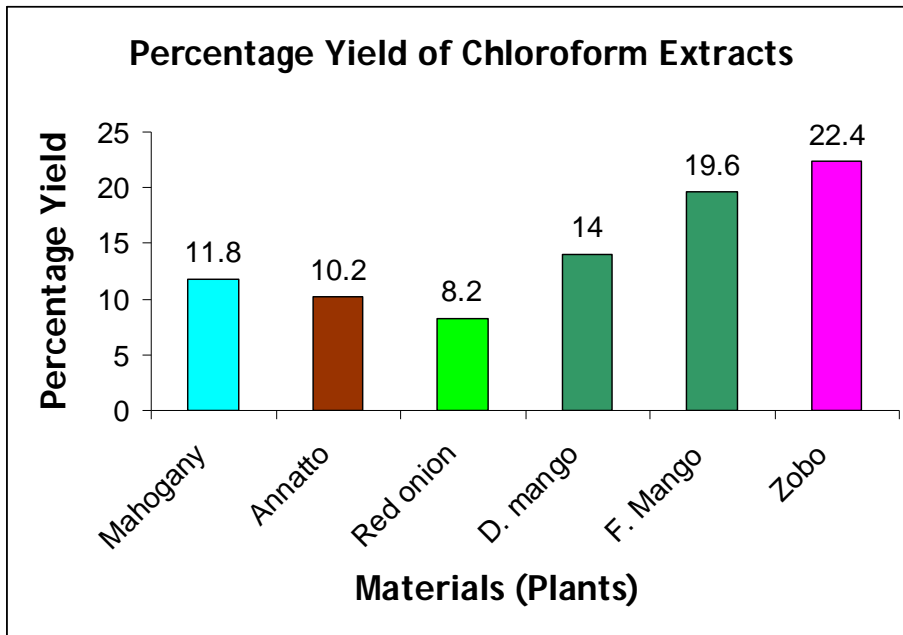


Fig 5: Percentage Yield of Chloroform Extracts

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APPENDIX B

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Visible absorption Spectra of the Extracts in various Solvents

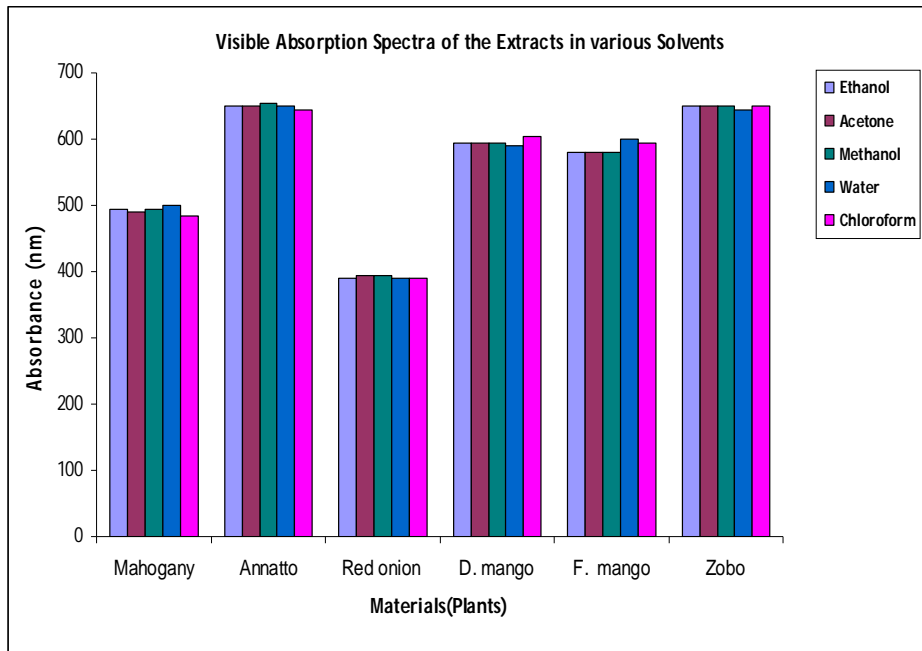


Fig 6: Visible Absorption Spectra of the Extracts in Various Solvents

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APPENDIX C

Toxicity Investigation Results

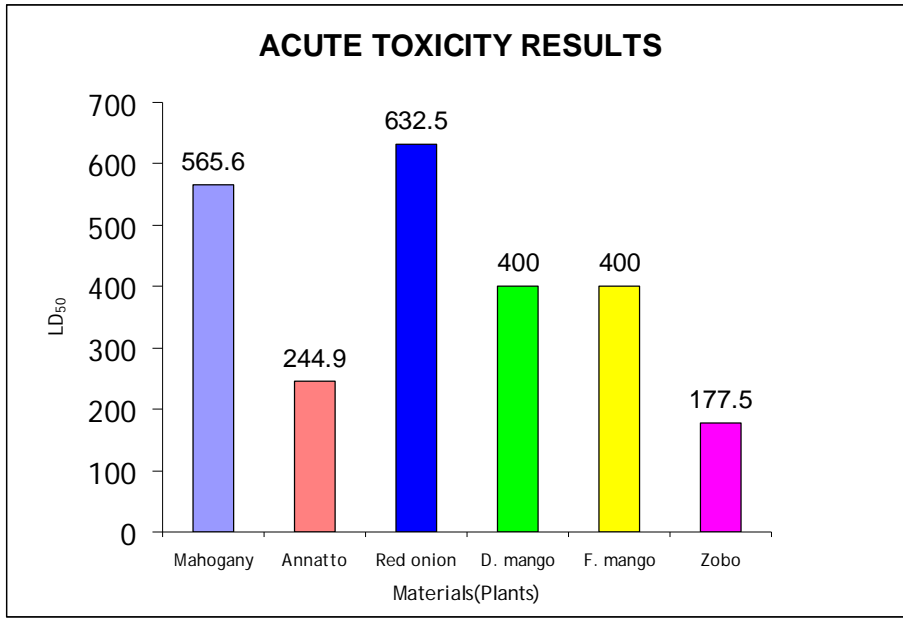


Fig 7: Acute Toxicity Investigation Results

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APPENDIX D

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Percentage Dye Adsorption of the Leathers using Ethanol Extracts

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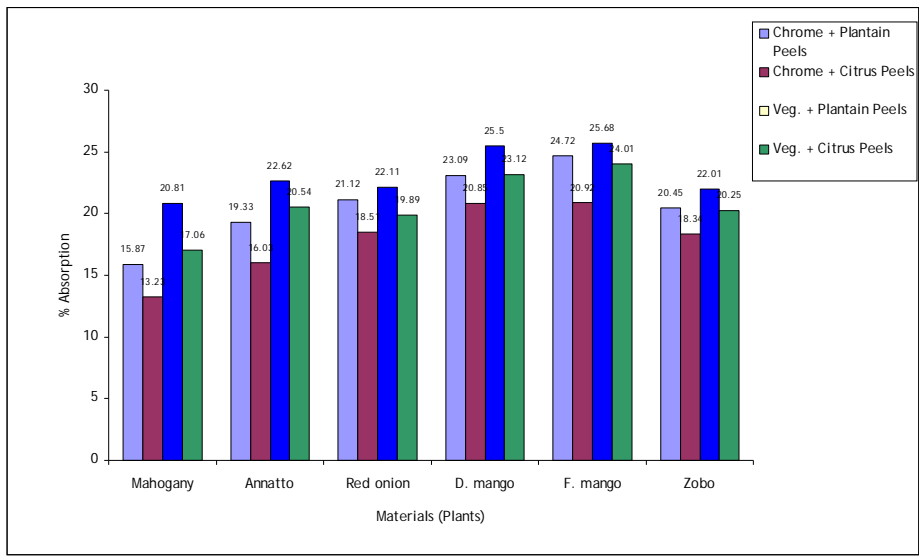


Fig 8: Percentages Dye Adsorption of the Leather using Ethanol Extracts

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Percentage Dye Adsorption of the Leathers using Acetone Extracts

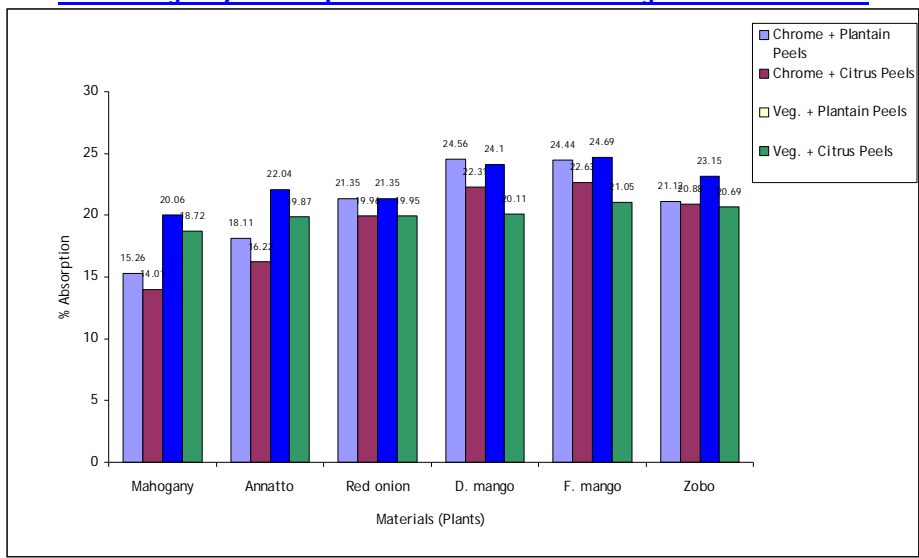


Fig 9: Percentages dye Adsorption of the Leather using Acetone Extracts

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Percentage Dye Adsorption of the Leathers using Methanol Extracts

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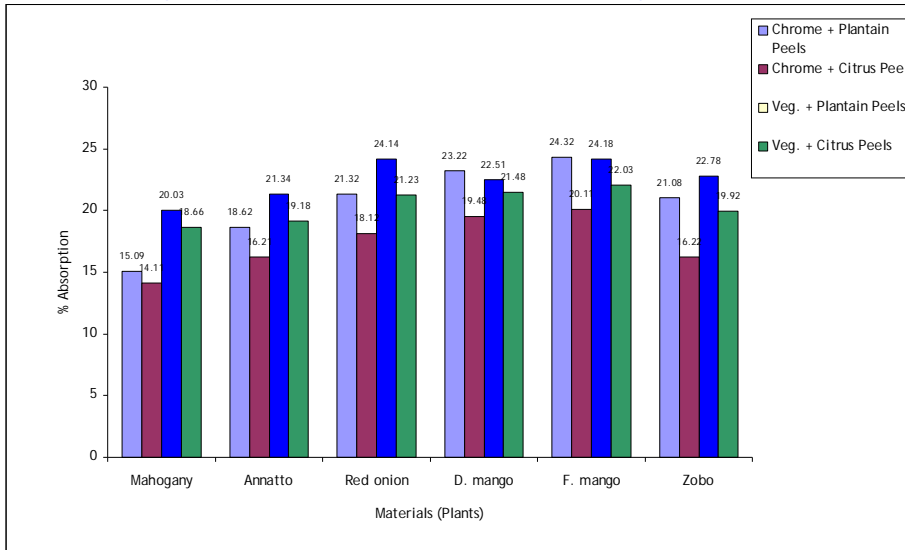


Fig 10: Percentages Dye Adsorption of the Leather using Methanol Extracts

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Percentage Dye Adsorption of the Leathers using Water Extracts

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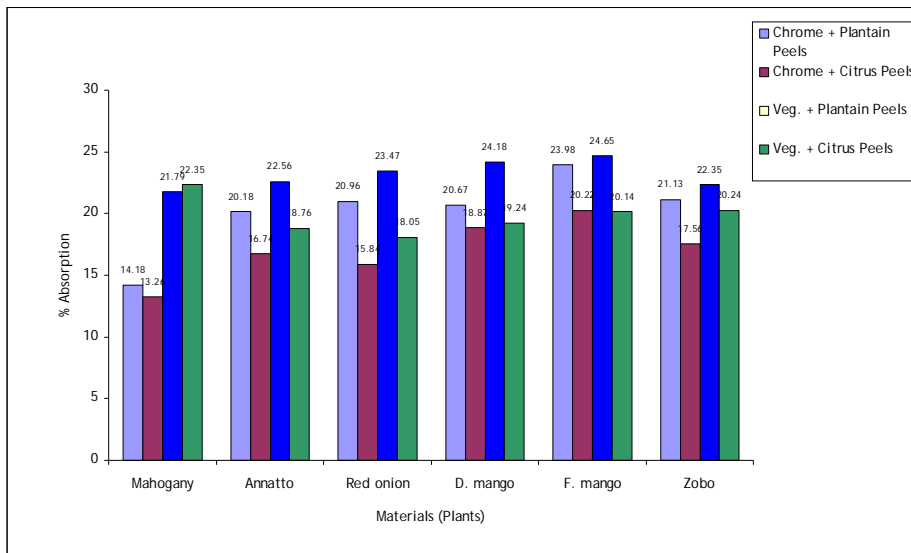
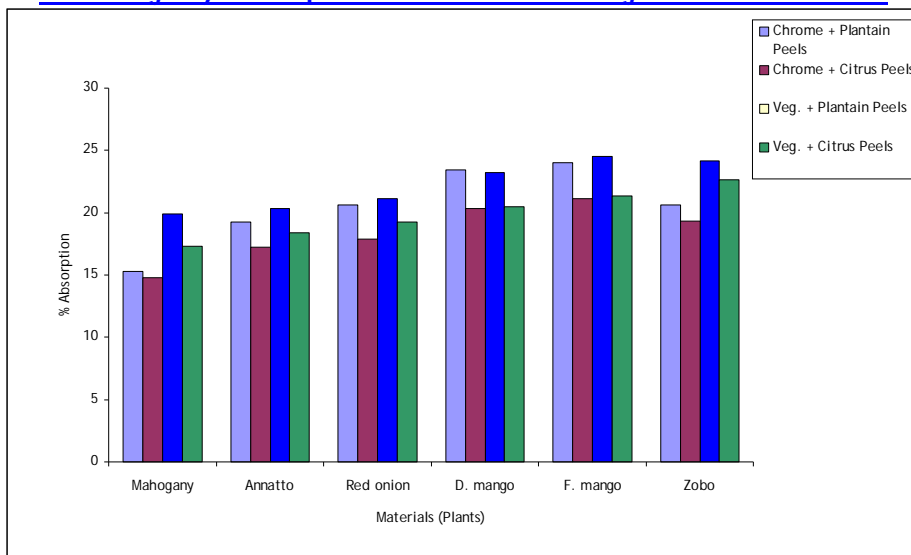


Fig 11: Percentages Dye Adsorption of the Leather using Water Extracts

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Percentage Dye Adsorption of the Leathers using Chloroform Extracts



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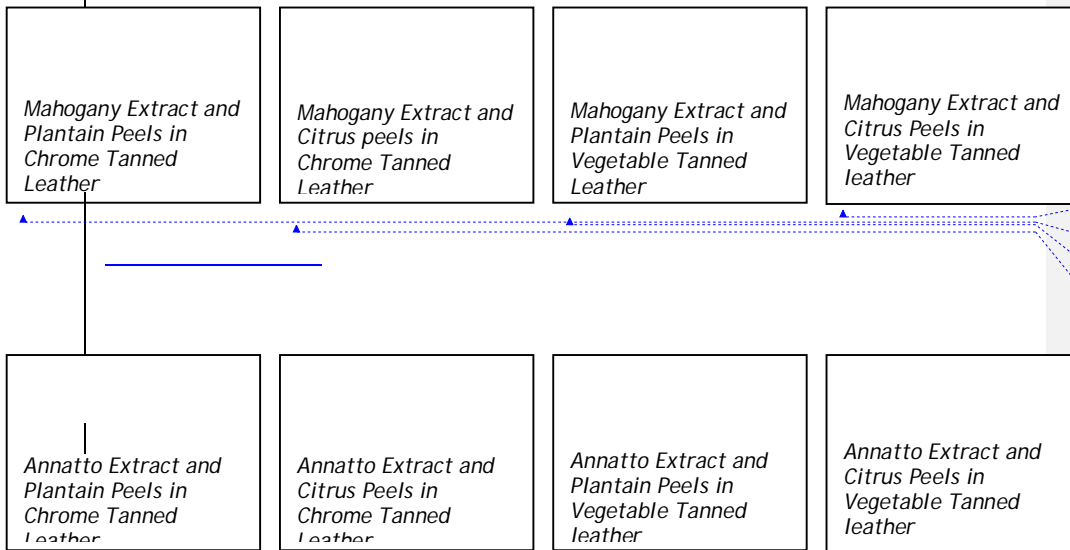
Fig 12: Percentages dye Adsorption of the Leather using Chloroforms

Extracts

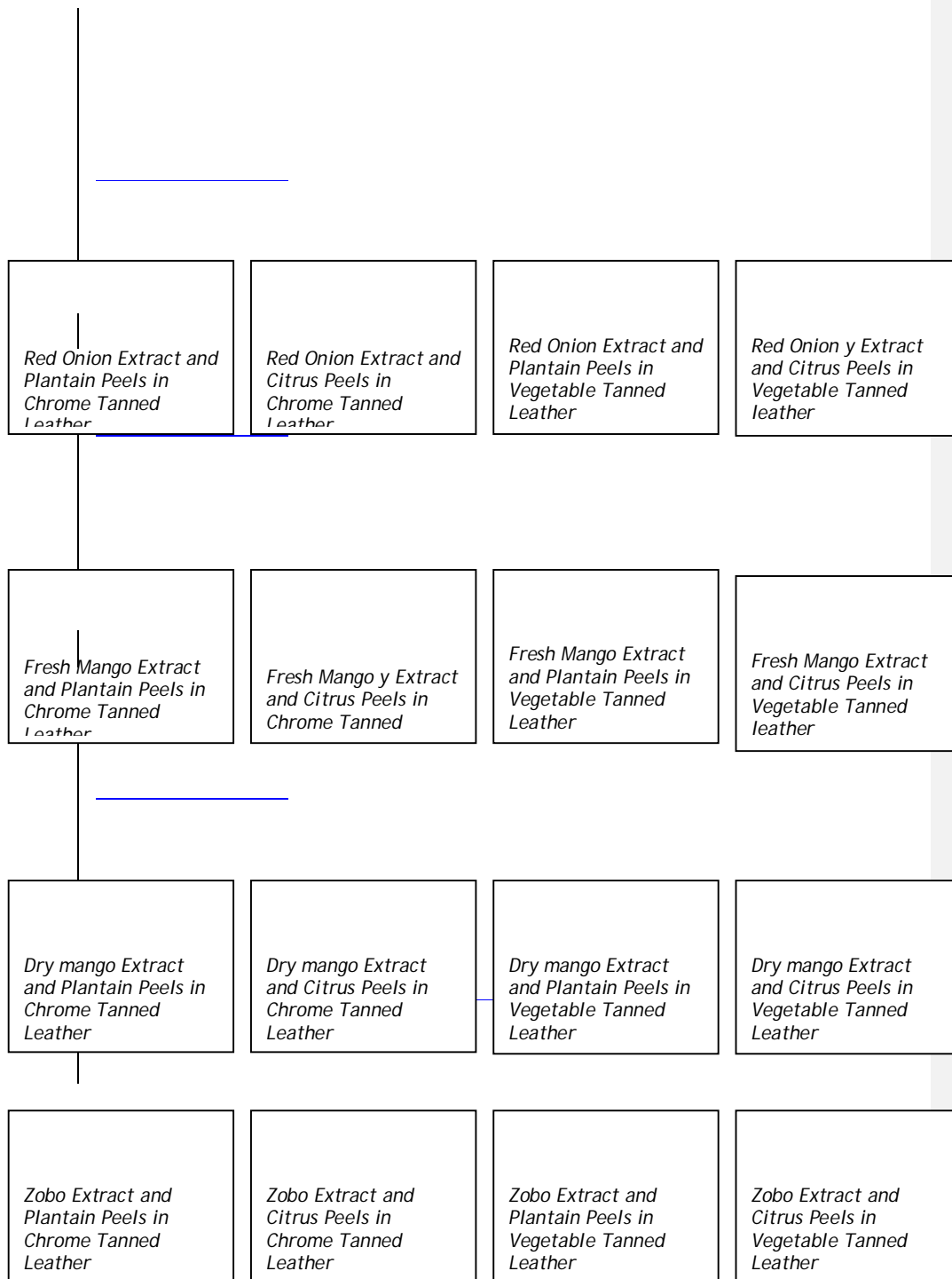
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APPENDIX E

Samples of Acetone Extracts on Leathers

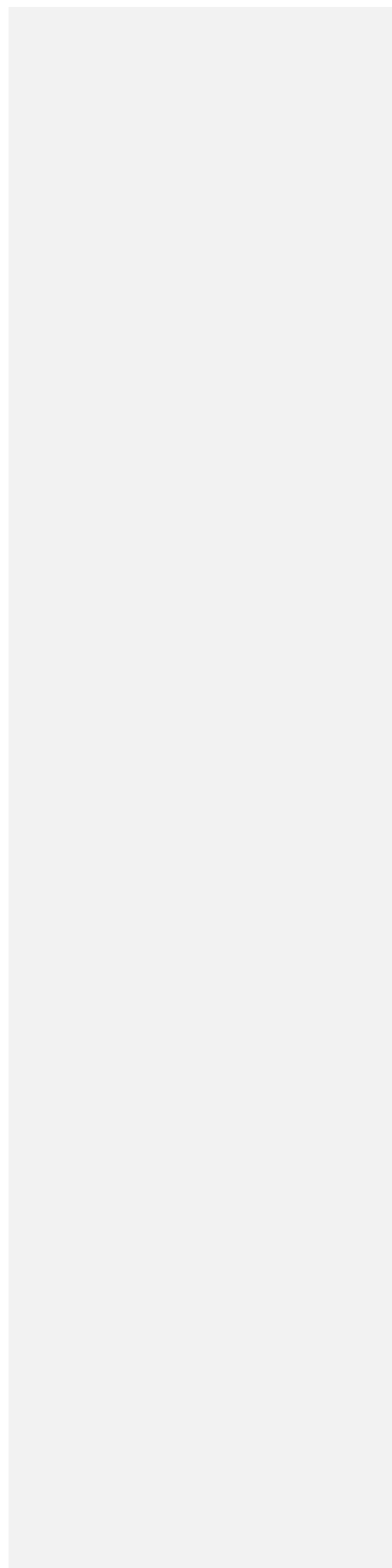


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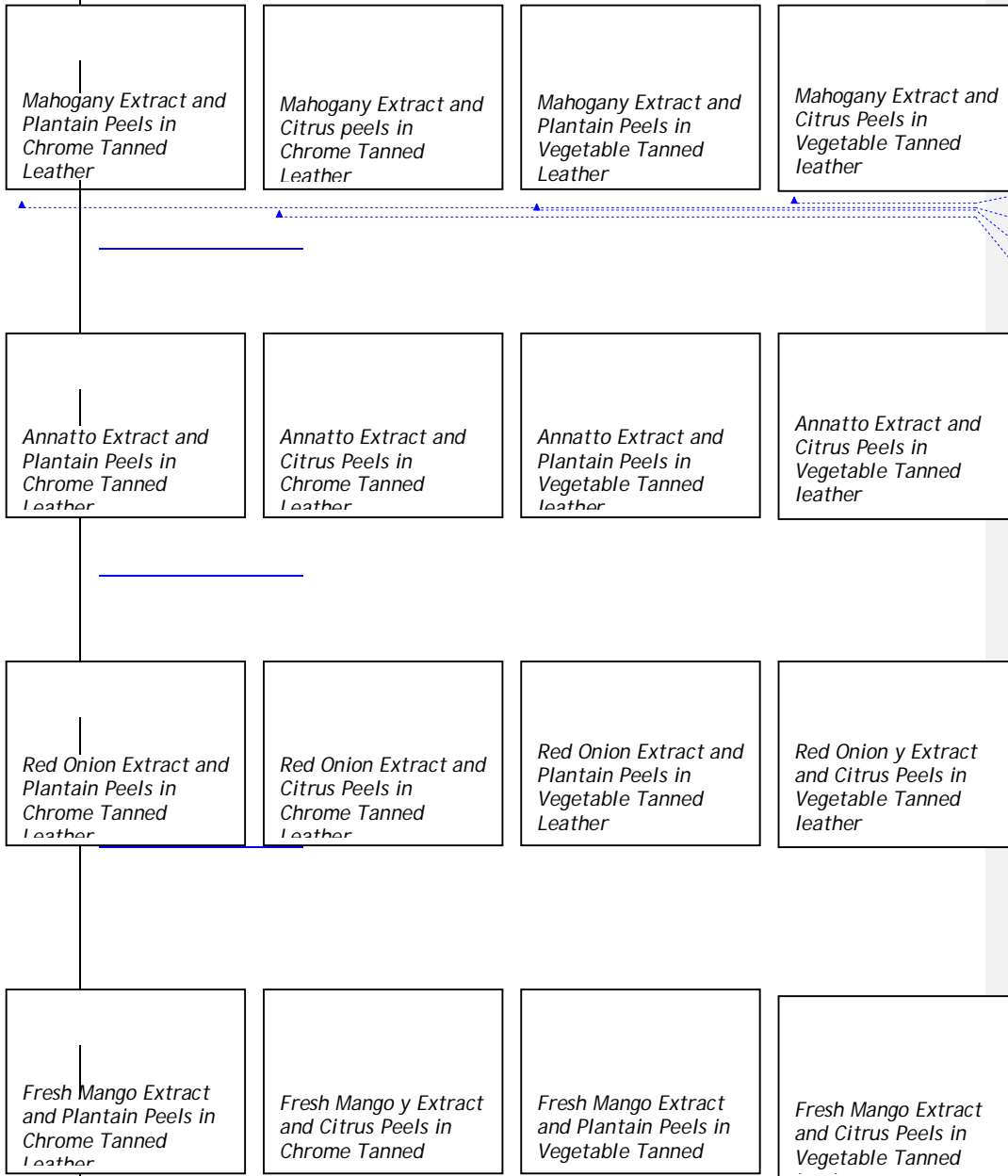


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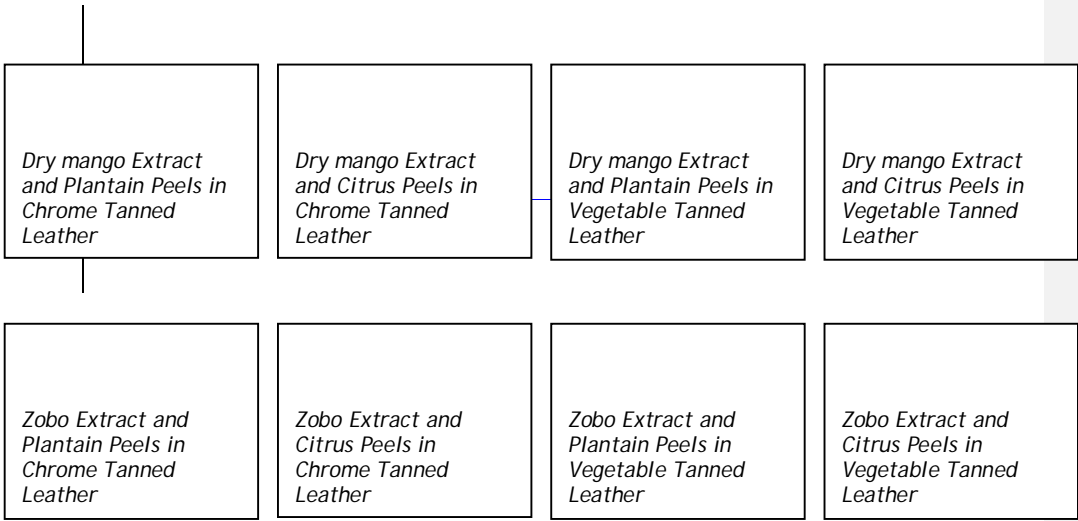
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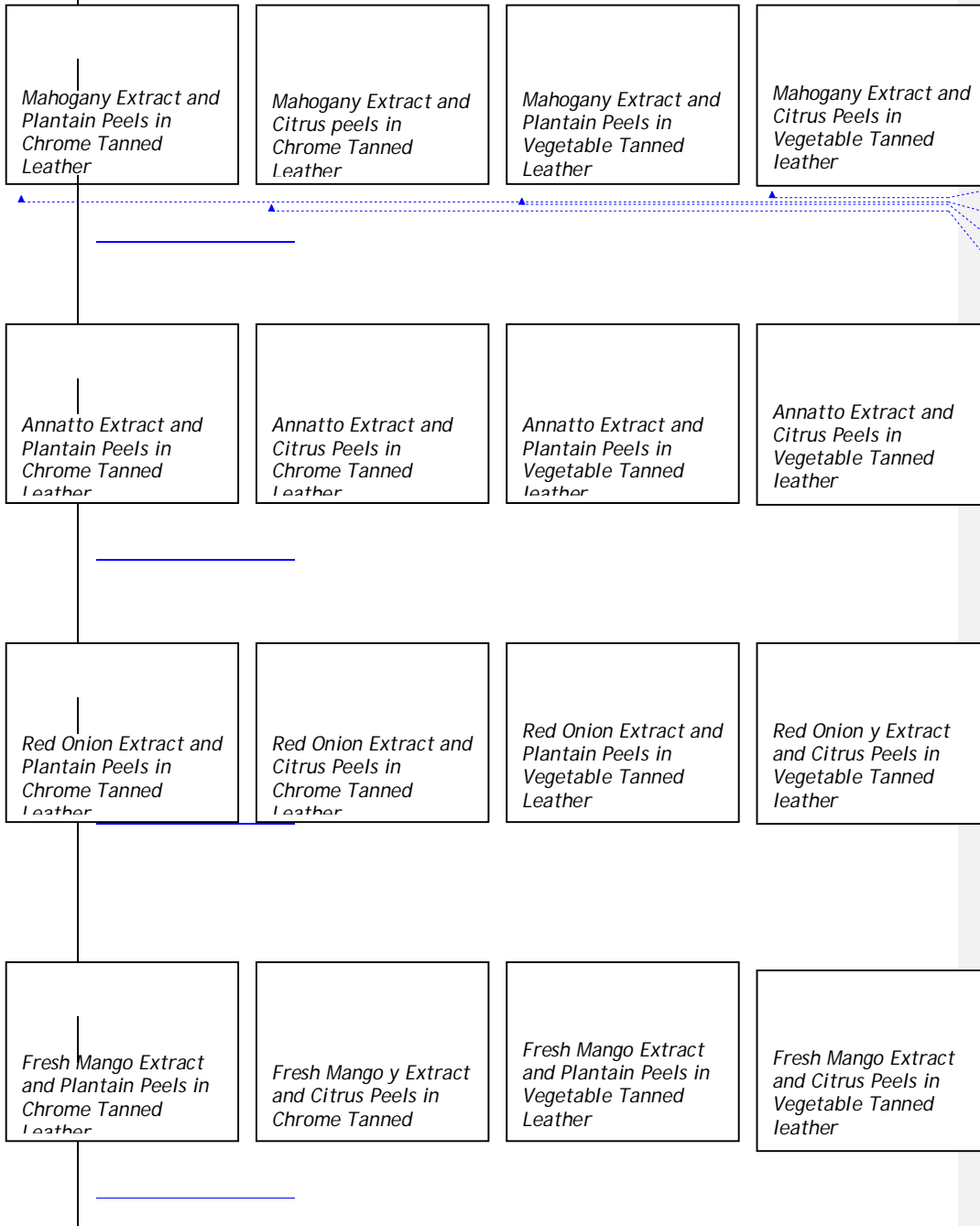
Samples of Ethanol Extracts on Leathers



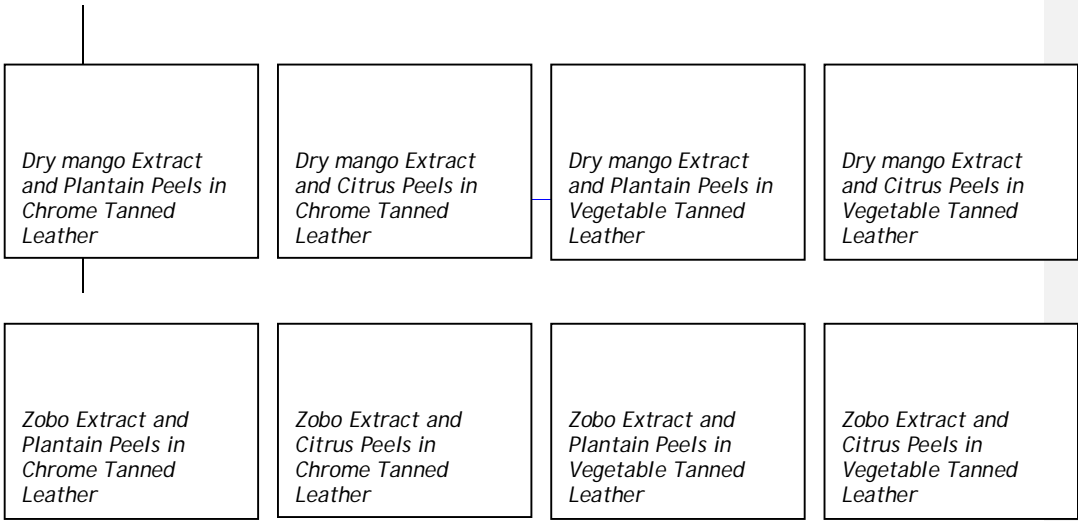
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Samples of Methanol Extracts on Leathers



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Samples of Water Extracts on Leathers

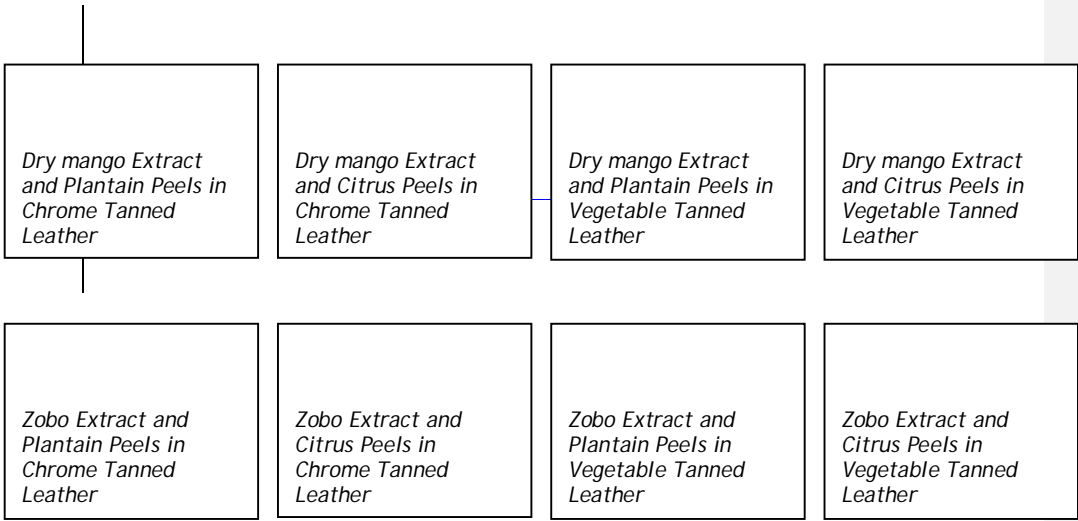
<i>Mahogany Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Mahogany Extract and Citrus peels in Chrome Tanned Leather</i>	<i>Mahogany Extract and Plantain Peels in Vegetable Tanned Leather</i>	<i>Mahogany Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Annatto Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Annatto Extract and Citrus Peels in Chrome Tanned Leather</i>	<i>Annatto Extract and Plantain Peels in Vegetable Tanned leather</i>	<i>Annatto Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Red Onion Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Red Onion Extract and Citrus Peels in Chrome Tanned Leather</i>	<i>Red Onion Extract and Plantain Peels in Vegetable Tanned Leather</i>	<i>Red Onion y Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Fresh Mango Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Fresh Mango y Extract and Citrus Peels in Chrome Tanned</i>	<i>Fresh Mango Extract and Plantain Peels in Vegetable Tanned Leather</i>	<i>Fresh Mango Extract and Citrus Peels in Vegetable Tanned leather</i>
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Samples of Chloroform Extracts on Leathers

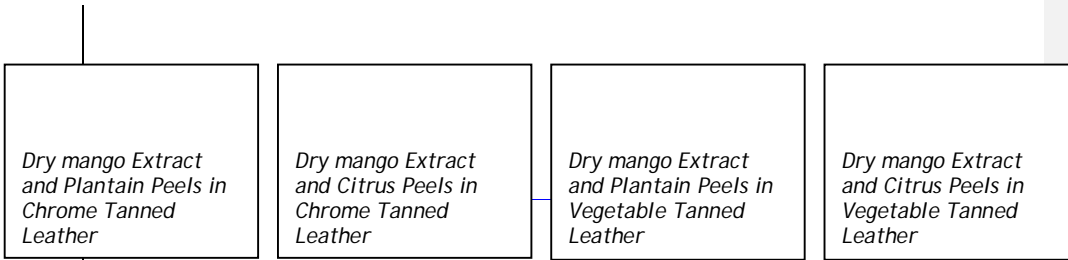
<i>Mahogany Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Mahogany Extract and Citrus peels in Chrome Tanned Leather</i>	<i>Mahogany Extract and Plantain Peels in Vegetable Tanned Leather</i>	<i>Mahogany Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Annatto Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Annatto Extract and Citrus Peels in Chrome Tanned Leather</i>	<i>Annatto Extract and Plantain Peels in Vegetable Tanned leather</i>	<i>Annatto Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Red Onion Extract and Plantain Peels in Chrome Tanned</i>	<i>Red Onion Extract and Citrus Peels in Chrome Tanned Leather</i>	<i>Red Onion Extract and Plantain Peels in Vegetable Tanned Leather</i>	<i>Red Onion y Extract and Citrus Peels in Vegetable Tanned leather</i>
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<i>Fresh Mango Extract and Plantain Peels in Chrome Tanned Leather</i>	<i>Fresh Mango y Extract and Citrus Peels in Chrome Tanned</i>	<i>Fresh Mango Extract and Plantain Peels in Vegetable Tanned</i>	<i>Fresh Mango Extract and Citrus Peels in Vegetable Tanned leather</i>
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APPENDIX F

IR-Spectra of the various Extracts

Savanna mahogany Extract Spectra

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Annatto Extract Spectra

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Red onion Extract Spectra

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Mango Extract Spectra

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Zobo Extract Spectra

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