CHAPTER II

THEORETICAL CONSIDERATIONS

<u>Fats and Oils</u> [1-3]

Fats and oils are water-insoluble substances of plant or animal origin which consist mainly of glyceryl esters of long-chain fatty acids. Depending on the composition of the fatty acid components, they may be liquid at room temperature (oils) or solid (fats). All become liquid at higher temperature.
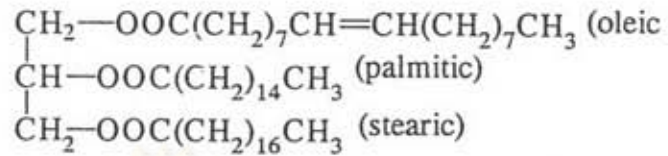
The main uses for fats and oils are: (a) for food, (b) for soaps and detergents, (c) for paints and other protective coatings, and (d) for other industrial purposes.

1. Composition and Properties

Fats and oils are essentially esters and, in the great majority of commercial oils, the alcohol component is glycerol. The nonester portion is usually less than 2 % of the total oil, and may contain sterols, hydrocarbons, aliphatic alcohols, and other organic compounds. Ordinarily, it consists mostly of sterols. A few oils contain ether component as part of the glyceride molecule, e.g., certain fish liver oils.

Triglycerides of a single fatty acid do occur in natural oils, e.g., glycerol trioleate (triolein), but by far the greater proportion of oils consists of "mixed" glycerides. Mixed glycerides contain either two or three different fatty

acids esterified to glycerol, for example,

$$
\begin{array}{l}
CH_2-OOC(CH_2)_7CH=CH(CH_2)_7CH_3 \text{ (oleic} \\
CH-OOC(CH_2)_{14}CH_3 \text{ (palmitic)} \\
CH_2-OOC(CH_2)_{16}CH_3 \text{ (stearic)}
\end{array}
$$

Scheme 2.1

Ordinary fats and oils consist of a complex mixture of such glycerides, containing several different major fatty acids and others in lesser amounts. The body fats of land animals are relatively simple in composition, in terms of the number of component acids. Vegetable oils are generally more complex, and fish oils appear to have the greatest number of components. There are about 150 different fatty acids that are known to occur in natural glycerides. A complete analysis of an oil is seldom required except for consists of the identification and estimation of the four to six major fatty acids.

Natural fats and oils have the general properties of esters of high molecular weight, ie, they are essentially neutral, relatively inert chemically, and of very low volatility. They are soluble in most organic solvents but insoluble in water. Some characteristics of common fats and oils are given in Table 2.1.

Long-chain fatty acids are commonly sold as mixtures with one or more major components. Properties of some pure individual acids are shown in Table 2.2.

Table 2.1 The properties of Common Fats and Oils

Fat or oil	Iodine value	Saponification value	Titer of fatty acids, °C
coconut	7-10	255-260	20-22
palm	51-58	196-210	36-45
olive	79-88	188-195	17-21
peanut	82-99	188-196	23-29
castor	82-90	177-187	3
rape	97-107	168-178	12-18
cottonseed	103-113	192-196	33-38
corn	103-125	188-193	21-24
sunflower	120-140	186-194	17-20
soybean	125-145	189-195	22-27
linseed	175-195	189-196	15-21
tung	not available	189-195	31-37
beef tallow	32-47	190-200	41-47
herring	123-146	183-190	27-30

Since the alcohol moiety is glycerol in all common oils and fats, the differences in chemical and physical properties of the glycerides are dependent on the nature of the fatty acid moiety. Fatty acids are classified mainly by chain length and degree of unsaturation. Thus the common acids are short-chain (about C_4-C_8), medium-chain (about C_{10}-C_{14}), and long-chain (C_{16} and longer). The melting point of the acids and their glycerol esters rises with chain length. The boiling point of the acids also rises but solubility in water and in organic

Table 2.2 The properties of pure fatty acids

Acid	Formula	Molecular weight	Melting point mp, °C	Iodine value
lauric	$C_{12}H_{24}O_2$	200.3	43.5	0
palmitic	$C_{16}H_{32}O_2$	256.4	62.9	0
stearic	$C_{18}H_{36}O_2$	284.5	69.6	0
oleic	$C_{18}H_{34}O_2$	282.5	16	89.9
eicosenoic	$C_{20}H_{38}O_2$	310.5	24	81.8
erucic	$C_{22}H_{42}O_2$	338.6	33.5	75.0
linoleic	$C_{18}H_{32}O_2$	280.4	-5	181.0
linolenic	$C_{18}H_{30}O_2$	278.4	-11	273.5
arachidonic	$C_{20}H_{32}O_2$	304.5	-	33.5
α-eleostearic	$C_{18}H_{30}O_2$	278.4	49	[a]
ricinoleic	$C_{18}H_{34}O_2$	298.5	5.5	85.2

[a] Varies with conditions of test.

solvents decreases. Thus the short-chain acids have appreciable volatility and solubility in water whereas the long-chain acids are, for all practical purposes, nonvolatile at ordinary temperature and pressure, and are practically insoluble in water.

Fatty acids are classified as saturated types (no double bonds), monosaturated types (one double bond), and polyunsaturated types (two or more double bonds). The melting point of the acids and their glycerol esters decreases from saturated to polyunsaturated, solubility increases, but volatility

and boiling point change only slightly. Special classes of unsaturated acids are those with one or more acetylenic (triple) bonds, and those with conjugated double or triple bonds. Less common types of fatty acids have a branched chain, an epoxy, cyclopropyl, or cyclopropenyl group, or other variation in structure.

2. Extraction and Refining

Extraction of oils from the vegetable materials in which they occur is accomplished by pressing or by solvent extraction. Both processes are widely used. Prior to extraction by pressing, vegetable seeds must be finely ground. The ground material is adjusted to a certain moisture content and warmed or cooked in a steam-jacketed vessel. It is then fed to the press. For solvent extraction the seeds are ground in such a way as to produce the flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low-boiling point solvent, usually a petroleum fraction.

The crude oil from either process is allowed to settle and is then filtered to remove solid material such as phospholipids. Refining of the oil is carried out or to remove other colloidal matter, free fatty acids, and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and absorbent materials. A further process, known as deodorization, may be applied to edible oils. It consists of treatment with steam at high temperatures and under low pressure to remove volatile material such as residual solvent, certain free acids, and other substances which would give undesirable tastes or odors. A final treatment for edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product of the desired characteristics.

Animal fats and fish oils are extracted from the tissues by rendering, that is, by heating in the presence of moisture or steam. Solvent extraction is also employed to some extent. Most of the extracted fats and oils require some degree of refining.

In this study, free fatty acids of soybean oil are used as raw material for synthesis. The composition of free fatty acids of soybean oil has shown in Table 2.3

Table 2.3 Nomenclature and formulas of the common fatty acids found in soybean oil [4]

Common name	Systematic name	Formula	% found
Saturated			
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	11
Stearic	Octadecanoic	$CH_3(CH_2)_{16}COOH$	4
Unsaturated			
Oleic	cis-9-Octadecenoic	$CH_3(CH_2)_7 \overset{H}{C}=\overset{H}{C} (CH_2)_7COOH$	25
Linoleic	cis-9,cis-12-octadec-dienoic	$CH_3(CH_2)_5 \left[CH_2 \overset{H}{C}=\overset{H}{C} \right]_2 (CH_2)_7CO$	51
Linolenic	cis-9,cis-12,cis-15-octadecatrienoic	$CH_3 \left[CH_2 \overset{H}{C}=\overset{H}{C} \right]_3 (CH_2)_7COOH$	9

Surfactant [2,5-6]

The term surfactant is a contraction of the longer, more awkward term surface-active agent. Coined in 1950, surfactant has become universally

accepted to describe organic substances with certain characteristic features in structure and properties. The term detergent is often used interchangeably with surfactant. As a designation for a substance capable of cleaning, detergent can also encompass inorganic substances when these do in fact perform a cleaning chore. More often, detergent refers to a combination of surfactants with other substances, organic or inorganic, formulated to enhance functional performance, specifically cleaning, over that of the surfactant alone.

Surfactants are characterized by the following features :

1) Amphiphatic structure

Surfactant molecules are composed of groups of opposing solubility tendencies, typically an oil-soluble hydrocarbon chain and a water-soluble ionic group.

2) Solubility

A surfactant is soluble in at least one phase of a liquid system.

3) Adsorption at interfaces

At equilibrium, the concentration of a surfactant solute at a phase interface is greater than its concentration in the bulk of the solution.

4) Orientation at interfaces

Surfactant molecules and ions form oriented monolayer at phase interfaces.

5) Micelle formation

Surfactants form aggregates of molecules or ions called micelles when the concentration of the surfactant solute in the bulk of the solution

exceeds a limiting value, the so-called critical micelle concentration (CMC), which is a fundamental characteristic of each solute-solvent system.

6) <u>Functional properties</u>

Surfactant solutions exhibit combinations of cleaning (detergency), foaming, wetting, emulsifying, solubilizing, and dispersing properties.

The presence of two structurally dissimilar groups within a single molecule is the most fundamental characteristic of surfactants. The surface behavior, ie, the surface activity, of the surfactant molecule is determined by the make-up of the individual groups, their solubility properties, their relative size and their location within the surfactant molecule. The term amphiphaty was proposed as "the occurrence in a single molecule or ion, with a suitable degree of separation, of one or more groups which gave affinity (sympathy) for the phase in which the molecule or ion is dissolved, together with one or more groups which are antipathic to the medium (ie, which tend to be expelled by it".

1. <u>Types of Surfactant</u>

Surfactants classification depends on the charge of the surface-active moiety, usually the larger part of the molecule. In anionic surfactants, this moiety carries a negative charge. In cationic surfactants, the charge is positive. In nonionic surfactants there is no charge on the molecule. Finally, in amphoteric surfactants, solubilization is provided by the presence of positive and negative charges in the molecule.

In general, the hydrophobic group consists of a hydrocarbon chain containing about 10-20 carbon atoms. The chain may be interrupted by oxygen atoms, a benzene ring, amide, ester, and other functional groups, and double bonds. A propylene oxide hydrophobe can be considered as a hydrocarbon

chain in which every third methylene group is replaced by an oxygen atom. In some cases, the chain may carry substituents, most often halogens. Siloxane chains have also served as the hydrophobe in some surfactants developed in recent years.

Hydrophilic, solubilizing groups for anionic surfactants include carboxylates, sulfonates, sulfates, and phosphates. Cationics are solubilized by amine and ammonium groups. Ethylene oxide chains and hydroxyl groups are the solubilizing groups in nonionic surfactants. Amphoteric surfactants are solubilized by combinations of anionic and cationic solubilizing groups.

The molecular weight of surfactants ranges from a low of about 200 to high in the thousands for polymeric structures. A surfactant with a straight-chain C_{12} hydrophobe and a solubilizing group is generally a very effective structure. The optimum can be higher by several carbon atoms or even slightly lower than 12 depending on the nature of the polar group.

In the application of surfactants, physical and use properties, precisely specified, are of primary concern.

1.1 Anionic Surfactants

Anionic surfactants may contain carboxylate, sulfonate, sulfate or phosphate in the surface-active moiety which are combined with a C_{12}-chain hydrophobe for best surfactant properties.

1.2 Nonionic Surfactants

Unlike anionic and cationic surfactants, nonionic surfactants carry no discrete charge when dissolved in aqueous media. Hydrophilicity in nonionic surfactants is provided by hydrogen bonding with water molecules. Nonionic surfactants are compatible with ionic and amphoteric surfactants.

Since a polyoxyethylene group can easily be introduced by the reaction of ethylene oxide with any organic molecule containing an active hydrogen atom, a wide variety of structures can be solubilized by ethoxylation.

1.3 Cationic Surfactants

As the name implies, the solubilizing group of a cationic surfactant carries a positive charge when dissolved in an aqueous medium. The positive charge resides on an amino or quaternary nitrogen. A single amino nitrogen is sufficiently hydrophilic to solubilize a detergent-range hydrophobe in dilute acidic solution. For increased water solubility, additional primary, secondary, or tertiary amino groups can be introduced or the amino nitrogen can be quaternized with low molecular weight alkyl groups such as methyl or hydroxyethyl. Polyoxyethylated cationic surfactants behave like nonionic surfactants in alkaline solutions and like cationic surfactants in acid solutions.

1.4 Amphoteric Surfactants

Amphoteric surfactants contain both an acidic and a basic hydrophillic group. Ether or hydroxyl groups may also be present to enhance the hydrophilicity of the surfactant molecule. Amphoteric surfactants are generally considered specialty surfactants. They do not irritate skin or eyes; they exhibit good surfactants properties over a wide pH range; and they are compatible with anionic and cationic surfactants.

2. Application of surfactants [2,7]

Surfactants are very versatile material which can be used in both household products and industrial processes. In household products, surfactants

are used as detergency which is the primary function. In recent years, a secondary function, such as softening in combination with detergency in laundry detergents or conditioning in combination with detergent in shampoos, has been offered as an additional product benefit. In general, products have tended toward functional specialization. In industrial uses, surfactants are widely used outside the household for a variety of cleaning and other proposes. They are used in many processes of petroleum industries, both the preparation and application of synthetic polymeric materials, and many processes of both fur and leather industries, etc.

Leather Industry

In the leather industry, the most important basic processes in the conversion of hides to leather include curing, soaking, fleshing, liming and depilation, degreasing, bating, pickling, fatliquoring or oiling, and finishing. These operation are usually carried out in the order named, but not all of them are necessary for any single type of leather.

1. Surfactant in leather industry [7-9]

In at least two of several processes of leather industry, degreasing and fatliquoring, surface active agents are of considerable importance. They find more of less limited use in most of the other processes with the exception of curing.

The fleshly flayed skins are usually cured at the slaughterhouse by salting and are received by the tannery in the raw salted state. Goat skins and some other hides from foreign sources are merely dried instead of being salted. Whether the hides are dried or salt-cured the first stage in processing is a

soaking operation. This serves to remove salt, if present, as well as water-soluble substances such as serum, etc. Wetting agents are sometimes added in the soaking of dried skins to speed up the penetration and aid in the removal or solution of encrusted material. They are not normally used, however, in the soaking of salt cured hides.

After the soaking operation of heavier skins, such as cow hide, horsehide and calf skin, are fleshed. This is a mechanical operation in which the adherent adipose and connective tissue on the inner or flesh side of the skin are removed by rotating knives. Thick hides of this type are sufficiently cleaned of fatty matter in this operation and do not require any subsequent degreasing. After fleshing they are ready to be unhaired. The lime and alkalis used in unhairing remove any residual fatty matter from the skins.

Sheep skins, pig skins, reptile skins, and furs are usually degreased by washing rather than by fleshing. The degreasing process is ordinarily carried out just after unhairing, but may be carried out in other stages before bating and tanning. The skins may be degreased in aqueous baths containing a relatively high percentage of detergent. Another method of treatment is the application of fat solvents to the skin and the subsequent washing out of solvent and dissolved grease with the detergent solution. In either event, the detergents should be good emulsifying agent, should function well in the presence of lime, or salts, and should be effective over a wide pH range. The fatty alkyl sulfates, the alkyl aryl sulfonates, and, more recently, the water-soluble polyethyleneoxide non-ionic agents have proved satisfactory in this connection.

Hair is removed from the hides by treating with alkaline reagents such as lime, methylamines and/or sodium or calcium sulfide solutions. Wetting agents are usually not considered necessary.

Bating is essentially a process of treating the leather with a mildly proteolytic enzyme. In modern practice clean, purified enzyme preparations are used almost exclusively. Wetting agents such as the sulfated fatty esters and

sulfated fatty alcohols are sometimes used to promote penetration of the bating compositions, but are apparently not of primary importance in this process.

The tanning process itself may be carried out in a number of different ways, and with reagents so apparently unrelated as chromium sulfate, formaldehyde, vegetable tannins, etc. Although, tanning is a highly complex physicochemical process it involves essentially a physical change in the nature of the skin protein (coagulation and denaturation) plus a physical or chemical combination of the protein with the tanning agent. There is a whole group of tanning agents, generally called "the synthetic tanning agents" or "syntans", which have become increasingly important in the past two decades and which resemble the aqueous surface active agents in many superficial respects. It is fairly well established, however, that whatever surface activity the syntans may possess is purely incidental to their tanning power. The synthetic tanning agents are complex aromatic sulfonates in which several aromatic rings may be linked together with methylene bridges or sulfide links. Such products invariably contain phenolic hydroxyl groups and/or naphthalene nuclei, and are generally made by combining a phenol (complex phenolic compound such as lignins may be used) with formaldehyde and a sulfonating agent. Sulfur or sulfur chloride may be used in place of formaldehyde to link the aromatic nuclei and increase the molecular weight. Many of the aqueous detergents containing sulfate or sulfonate groups, particularly the alkyl phenol and alkyl naphthalene sulfonates, have a certain degree tanning action but it does not approach that of the better synthetic tanning agents. The syntans and speed the tanning process, functioning both as surface active agents and tanning agents. The syntans and the alkyl aryl sulfonate detergents accordingly overlap in function as well as in molecular structure.

The sulfate and sulfonate wetting agents are often used as an adjunct in vegetable tanning liquors to promote their penetration. Wetting agents also exert a dispersing, solubilizing, action on the tannins, thus counteracting the

latter's tendency to precipitate and sediment out during the long course of the tanning process. Wetting agents are often used as assistants in chrome and alum tannages, particularly in the production of white leather with alum and formaldehyde.

After the hide is tanned, oils must be worked into it in order to impart flexibility, fullness, and softness. If the oil is applied in the form of an aqueous emulsion the process is called fatliquoring. Otherwise, it is called oiling or stuffing. In fatliquoring the choice of both oil and emulsifying agent has an important bearing on the quality of leather produced. The oils most generally used are cod liver oil, neat's-foot oil, and tallow. Moellon and degras (spent cod oils from the oil tannage process,not to be confused with wool grease which is also called degras) as well as some synthetic higher esters are also used. Mineral oil, in spite of their low cost, are not used, since they do not impart the desired properties to the leather.

The emulsifying agents used in fatliquoring are typical water-soluble surface active products which yield O/W emulsions. The soaps which were formerly extensively used have largely been supplanted by the sulfated fatty oils. The petroleum mahogany sulfonates and the alkyl aromatic sulfonates are also widely used in fatliquoring.

Fatliquoring, although it is a simple technical process , involves a rather complicated physicochemical mechanism. The emulsifying agent and part of the oil apparently combine with the leather and are held by fairly strong adsorption or chemical forces. The main portion of the raw oil is mechanically held in the interfibrillar spaces and is responsible for the actual lubrication. The combined oil is stated to contribute to the stretch and elastivity of the leather.

Surface active agents are extensively used in the dyeing of leather. The sulfates and sulfonates of high surface activity and also the syntans are effective in increasing the penetration and evenness of dyeing. The action is apparently similar to that which occurs in the case of wool, the surface active

agent competing with the dye for positions on the protein molecule. The quaternary ammonium, phosphonium, and sulfonium salts have also been used as leather dyeing assistants.

Leather goods may be washed effectively with the same type of detergents used for emulsifying fatliquors. If the washing is carried out in acid medium and in the presence of a tanning substance such as trivalent chromium ions, no loss of tanning substance is said to occur. Emulsions of oils in the usual sulfated oil or alcohol type detergent are also used as dressings for leather and patent leather.

In this study, the anionic surfactants which was synthesized in the laboratory, was used in the fatliquoring process.

2. Mechanism of fat treatment [10-13]

In the treatment of leather with an oil, several phenomena are involved. It is the balance between these phenomena and the conditions of application of the oil, the nature of the oil, and the nature of the leather which determines the type and extent of lubrication of the leather fibers. Three common methods have used to treat the leather as see below.

2.1. Practical fatliqouring

Fatliquoring has been the most widely used technique of fat application since about 1900. It was developed after the introduction of chrome tanning. In a fatliquoring system commonly using an anionic oil such as a soap or a sulfated oil, the oil droplet is introduced into the drum as an emulsion at a pH value where the emulsion is reasonnably stable. This technique allows uniform distribution of quantities of fat as low as about 5-8 % based on the weight of the leather. The emulsion breakes after comming nto contact with

chromed leather fiber. Then, it saturates the surface and penetrate the inner layers. Acidification completes the process. The attraction of the anionic oil group to the leather fiber brings about a stable bond upon drying, and the leather may have fixed oil. This will not be removed by a solvent, and when later extracts the leather may show some softness even through the fiber has been completely stripped of the free oil. Cationic oils have found limited application in the fatliquoring of most leather. They can be combined with anionic oils to form neutral emulsion which readily penetrate the leather. Fatliquoring compound, have varying emulsifying capacities and can be mixed with an appropriate proportion of a neutral oil.

2.2 Solvent fatliquoring

The principle of chemical bonding in the presence of an organic solvent is used in the so-called "solvent fatliquors". Solvent fatliquoring as proposed by Von Fuchs, is based on introducing the oil into the leather in a high-boiling solvent such as benzene, etc. This solvent will displace the water in the leather, leaving a solution of the solvent and the lubricant. Upon slow evaporation of the high boiling solvent, the lubricant remains absorbed on the fiber.

2.3 Stuffing

The treatment of leather with oils using a melt system rather than an emulsification system is known as stuffing. This technique is closely related to the old currying method and is one of the simplest forms of leather lubrication, used mainly for heavier vegetable-tanned leather. The wet leather is treated in a drum with a warm mixture of molten natural fat which contain some free fatty acids and other component which give them an anionic charge.

The anionic portions are attacked to the leather fiber due to their polar nature. The other components are then deposited on the leather fiber by physical absorption. Uniform distribution is attained by using about 20 % fat. This process take several hours at 40-50°C. The resulting fat content of 20-30 confers a greasy feel and dark color. The leather that has been treated can only be finished after degreasing of the surface.

3. Function of fatliquors [12]

The function of fatliquors are as follows

3.1 Lubrication

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

3.2 Adjustment of physical properties

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

3.3 Regularization of physical properties

By increasing the oil content of the leather in winter and reducing it in summer, the effects of seasonal temperature changes in the liming and tanning precesses can be nullifies. In the ideal air-conditiones factory such

changes would not occur, but in the average factory, where seasonal temperature fluctuations occur, fatliquoring plays an important part in keeping the production at a uniform condition through out the year.

3.4 Waterproofing

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

3.5 Filling effects

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

3.6 Protection

The presence of a film of fat in the leather structure gives protection to the leather against all harmful chemicals. It will protect the fibers

against acids, alkalis, water, and many other chemicals to which the leather may be exposed.

4. Types of fatliquor

The fatliquors may be divided into non-ionic type, cationic type, and anionic type.

4.1 Non-ionic fatliquors

Non-ionic fatliquors are made from raw oil and a non-ionic emulsifying agent. The latter is hardly affected by acids, alkalis or mineral tannages and therefore gives fatliquors of good penetration under most conditions.

4.2 Cationic fatliquors

Cationic fatliquors are made by mixing raw oil and a cationic emulsifying agent. In these emulsions the oil droplets gave a positive electrical charge. Cationic fatliquors gave excellent stability to acids and mineral salts and give good penetration on suede and chrome leathers. They tend to make the leather wet-back easily. They do not readily mix with other fatliquors, vegetable tans and acid dyes, which then tend to precipitate.

4.3 Anionic fatliquors

Anionic fatliquors, such as soap, sulfated and sulfited oils, have a negative electrical charge.

5. Fatliquor formulation [10,12]

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

5.1 Chemically treated oils

5.1.1 Sulfated oils

Sulfated oils which have greater stability at low pH, are desired for most application. The addition of the SO_4H group into the oil modifies the emulsion characteristics in that the dispersive power of the sulfated group is much greater than the carboxyl group of the soap. The manufacture of a sulfated oil is discussed in the following general procedure.

The oil is received in tank car quantities, then chilled and filtered. This pressing of the oil removes some of the high melting point components and gives the oil a lower cold test. The higher melting materials are useful in the making of other products. The pressed oil is checked for quality and then sulfated. The sulfation, shown in figure 2.1, is by the addition of sulfuric acid. The reaction is exothermic and proper temperature is maintained. When sulfated to the desired level the oil is put in a wash tank. In the wash tank sodium hydroxide solution is added to neutralize the excess sulfuric acid. The salt formed breaks the emulsion and the water-salt layer can be removed. The oil may then be blended with other oils. The product is shipped in wooden barrels or lined steel containers. Tank cars may be used in shipping some fatliquor oils.

The degree of sulfation is expressed by the combined sulfate (SO_4^{2-}) factor. The effect of increasing the combined sulfate is to reduce the filling properties and increase the fineness of emulsion giving better penetration.

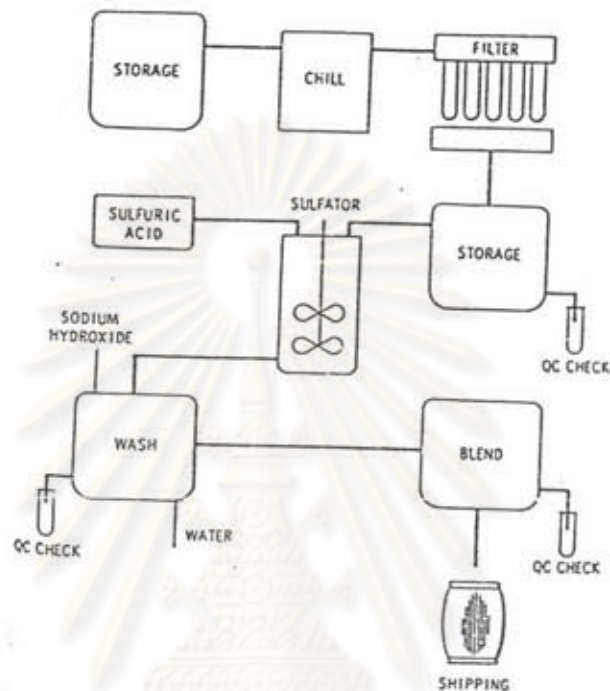These oils give negatively charged emulsions, and are therefore called anion oils.

Figure 2.1 The manufacture of a sulfated oil

5.1.2 Sulfited oils

Sulfited oils are used as one of the most popular of the modern fatliquoring system. They have application in the manufacture of chrome tanned leather. For lightweight, soft leather such as garment leathers or glove leathers, the penetration of the oil well into the leather is needed.

The reaction of the sodium bisulfite will take place at the double bond of an unsaturated fatty acid. The bond between the carbon and the sulfur of bisulfite results in oils of broad stability to salt and pH variations.The bisulfited addition reaction is shown in scheme 2.2 [10]

$$R{-}CH{=}CH{-}R' \ + \ NaHSO_3 \ \longrightarrow \ R{-}\underset{\underset{SO_3Na}{|}}{CH}{-}CH_2{-}R'$$
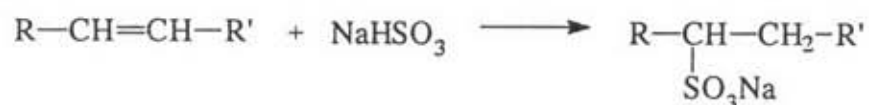
<div align="center">Scheme 2.2</div>

The reaction of sulfur trioxide by the reaction of oleum (sulfuric acid contains sulfur trioxide) will also result in carbon sulfur linkage and true sulfonates as shown in scheme 2.3

$$R{-}CH_2{-}COOH \ + \ SO_3 \ \longrightarrow \ R{-}\underset{\underset{SO_3H}{|}}{CH}{-}COOH$$
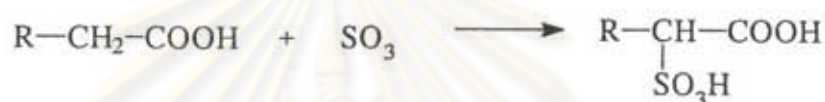
<div align="center">Scheme 2.3</div>

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

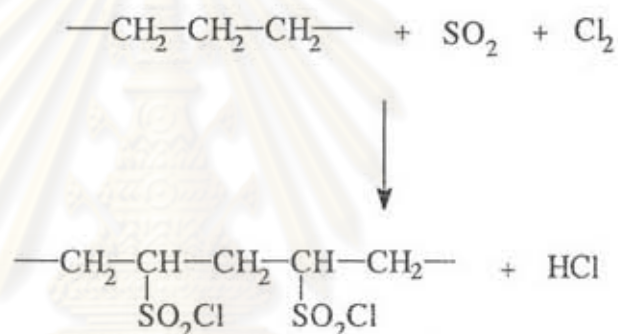### 5.1.3 Sulfunyl chlorides

Sulfunyl chlorides are one class of fatliquors that have gained popularity because of their versatility. The synthesis takes place in several steps.

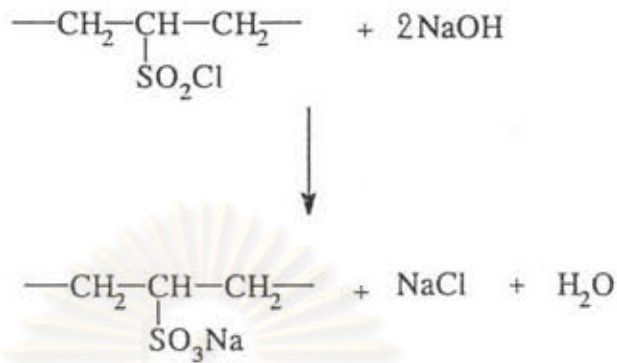(1) A linear aliphatic hydrocarbon is made by Fischer tropsch process.

$$CO + H_2$$

$$\downarrow$$

$$-CH_2-CH_2-CH_2-$$
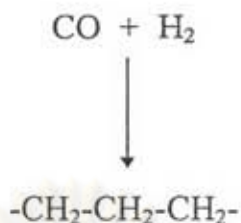
Scheme 2.4

(2) To this is reacted sulfur dioxide and chlorine.

$$-CH_2-CH_2-CH_2- \quad + \quad SO_2 \quad + \quad Cl_2$$

$$\downarrow$$

$$-CH_2-CH-CH_2-CH-CH_2- \quad + \quad HCl$$
$$\qquad\quad SO_2Cl \qquad\; SO_2Cl$$

Scheme 2.5

The length of the hydrocarbon chain can be controlled as well the degree of chlorosulfonation.

(3) Upon neutralization with sodium hydroxide, the chloride hydrolizes and a sulfonated hydrocarbon results.

$$-CH_2-CH-CH_2- \quad + \quad 2\,NaOH$$
$$\underset{SO_2Cl}{|}$$

$$\downarrow$$

$$-CH_2-CH-CH_2- \quad + \quad NaCl \quad + \quad H_2O$$
$$\underset{SO_3Na}{|}$$

Scheme 2.6

Because of the broad variation in the properties of these products, they are competitive with the bisulfited oils for soft leathers in the production fo garment, glove, and soft shoe types.

5.2 Raw oils

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

5.2.1 Types of oils

In addition to the method of application and the emulsion formation characteristics of oils, the ultimate lubrication properties and the physical characteristics of the resulting leather depend upon the types of oil used. Fats and oils use in leather manufacture fall into three broad classifications: (1) the triglycerides, (2) the fatty esters, and (3) the mineral oils. These simple classification cover almost all the leather-lubricating materials.

The most important are the triglycerides of the fatty acids. These include fish, plant, and mineral oils. They are similar in that they are esters of glycerol and are different in that they are made up of different fatty acids.

5.1.2 Chemical nature of the natural fats

Since the natural fats which are of interest to us are primarily triglycerides, their nature is determined by the fatty acids occurring in them. Practically all naturally occurring fatty acids have an even number of carbon atoms. The shorter chain saturated fatty acids, C-6, C-8 and C-10, are found in coconut and palm oils, milk fat, and other soft oils. C-12 fatty acid, lauric acid, is found in sperm oil. The saturated fatty acids of the C-16 and C-18 category are common to the animal fats and many of the vegetable fats. The fatty acids in the C-24 and C-25 category are found in the hard natural waxes such as carnauba wax and beeswax. The unsaturated fatty acids, primarily of the C-18 type, are quite common in the animal and vegetable oils. Those fatty acids having more than one double bond are classified as drying oils, such as linseed oil and cottonseed oil. Some fatty acids may contain additional hydroxyl groups such as lanopalmic (C-16 hydroxy saturated) found in wool fat and ricinoleic (C-18 hydroxy unsaturated) found in castor oil. Both wool fat (lanolin) or wool grease and castor oil are common fatliquoring materials when sulfated. The makeup of the natural fats would be evident on consideration of a few specific cases that are typical of their classes.

5.3 Emulsifying agents

5.3.1 Soaps

A number of soaps are used in fatliquoring upper leathers. The most popular soaps are soft and medium soaps, e.g. Marseilles soap (a green olive oil soap and triethanolamine oleate). They are sensitive to acid and hard water and are precipitated by chromium and aluminium ions. They give some filling effect and a less greasy surface.

5.3.2 Synthetic emulsifying agents

A very wide range exists and for general purposes is divided into three main groups which are anionic, cationic and non-ionic.

1) Anionic This is the most important group of emulsifying agents. The earliest members were the sulfonates primary fatty alcohols, and the range now includes secondary alkyl sulfonates, aryl sulfonates, and petroleum sulfonates. They are extremely useful as emulsifying agents and can be used either to emulsify oils or they can be added in small amounts to increase the stability of emulsion produce by other means, eg sulfated oils. If used in excessive amounts they may make the leather soft and loose grained, as well as making it permanently very hydrophilic. This latter effect increases the suitability of the leather for paste drying and aqueous finishing, but may cause trouble to the wearer.

2) Cationic The most common group of materials in this class are the quaternary ammonium compounds. They are expensive and their use is restricted to special effects, such as emulsifying oils used in mineral

tanning, as secondary fatliquors for leathers pasted to dry, and as mordants for leathers subsequently dyed with anionic dyestuffs.

3) <u>Non-ionic</u> The most common group of materials in this class are the polyethylene oxide-based materials. They produce very stable emulsions for general use over a wide range of leather making processes.

5.4 <u>Auxilliary materials</u>

There is a number of materials occasionally found in fatliquor emulsions to give special effects. These materials include :

5.4.1 <u>Weak alkalis</u>

The addition of small amounts of borax, sodium bicarbonate, and ammonia will increase the stability of the emulsion to acids and neutralise free fatty acids in the oils.

5.4.2 <u>Colloidal fillers</u>

A number of finely dispersed earths, e.g. china clay, carbohydrates like flour, vegetable gums, and soluble celluloses are added to increase the filling of the flanks or to increase the suitability of the leather for grain correction or sueding.

5.4.3 <u>Humectants</u>

The addition of humectants, e.g. glucose, glycerine, sorbitol and mannitol, will produce increased softness and mellowness in the

finished leather. They are very useful for producing softies, leathers for use in the tropics, and for sueding. Their use will reduce the tendency for grain crack in dry hot conditions and assist generally in shoe forming operations.

6. Theory of emulsion

To consider the forces acting on the molecule of liquid in a small droplet. If a molecule is located within the droplet, it will be attracted by other molecules of the same material by forces of attraction that are equal on all sides. At the surface of the liquid, however, the forces of attraction will be toward the center of the droplet and toward the molecules adjacent to it at the surface. The forces of attraction for the air, or media in the other phase, will be very small. The net result is that the surface of the droplet will have a tendency to pull inward and decrease its size as much as possible. This phenomena is known as surface tension. When the droplet is a surface between two immiscible (mutually insoluble) liquids, this tension is referred to as interfacial tension.
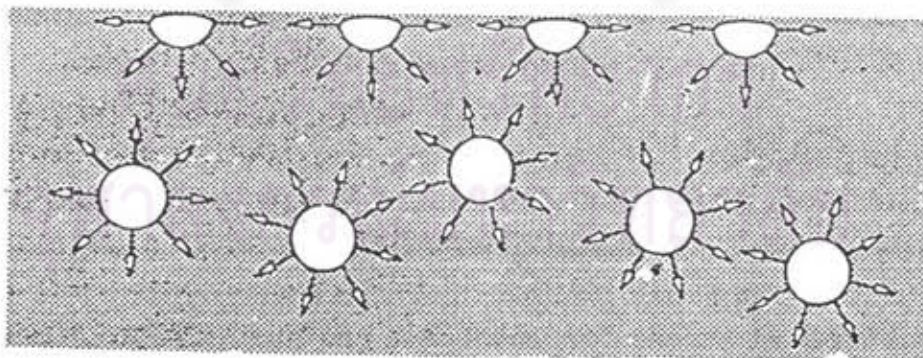

Figure 2.2 The forces of attraction between molecules in a liquid are even in all directions. At the surface of the liquid the forces are uneven. This uneven balance of forces causes tension and governs the formation of droplets

If oil is placed in water and is violently agitated, a large number of small droplets will form. As the interfacial tension between the water and the oil is quite large, the oil droplets will gather together to form larger droplets, and eventually a separate layer of oil will result. If some material is introduced into the system so that the interfacial tension between the oil and water is decreased, the rate at which the separating out or "breaking" of the emulsion takes place can be decreased greatly. The forces of interfacial tension can be decreased to such and extent that the emulsion is, for all practical purposes, permanent.

Procedure

1. Esterification [14]

Acids are frequently converted into their esters via the acid chlorides, as shown in scheme 2.9
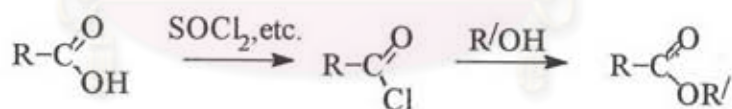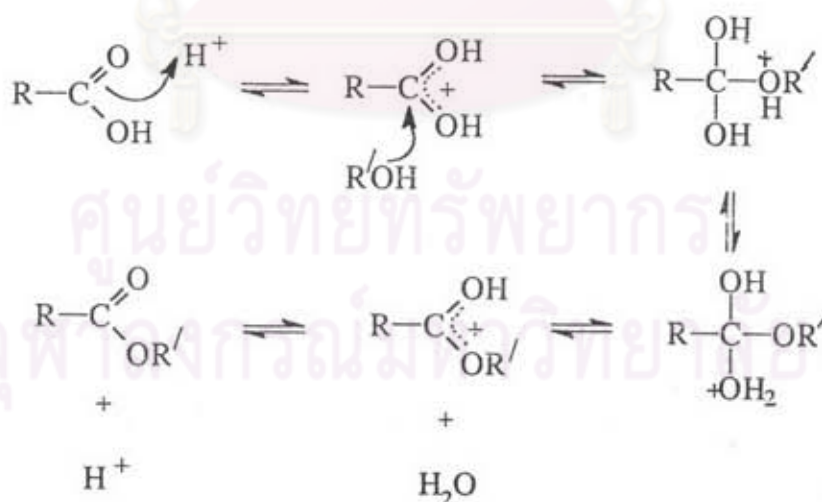

Scheme 2.9

A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of a little mineral acid, usually concentrated sulfuric acid or dry hydrogen chloride, as shown in scheme 2.10. This reaction is reversible, and generally reaches equilibrium when there are appreciable quantities of both reactants and products present.

$$R-C\overset{\displaystyle O}{\underset{\displaystyle OH}{}} \quad + \quad R'OH \quad \overset{H^+}{\rightleftharpoons} \quad R-C\overset{\displaystyle O}{\underset{\displaystyle OR'}{}} \quad + \quad H_2O$$
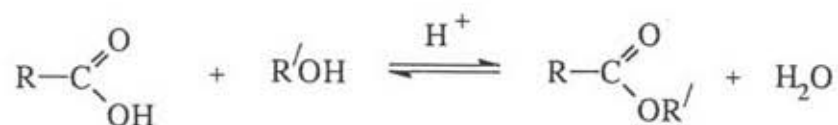
Scheme 2.10

The reversible reaction is a disadvantage in the preparation of an ester directly from an acid. The preference for the acid chloride route is due to the fact that both steps, preparation of acid chloride from acid, and preparation of ester from acid chloride are essentially irreversible and go to completion.

Direct esterification, however, has the advantage of being a single-step synthesis. It can often be made useful by application of the knowledge of equilibria. If either the acid or the alcohol is cheap and readily available, it can be used in large excess to shift the equilibrium toward the products and thus to increase the yield of ester. The mechanism of the acid-catalyzed esterification is shown in scheme 2.11.

Scheme 2.11

2. Epoxidation [1,15-18]

Epoxidation is the formation of cyclic three membered ethers (oxiranes). Oxiranes are extremely common reagents in synthetic chemistry because the ring system can be both created and destroyed easily, and in highly selective manner. The three most important routes to oxiranes in the laboratory are (i) the epoxidation of olefinic, (ii) intramolecular cyclization of alcohols bearing a leaving group on the adjacent carbon, (iii) nucleophilic alkylation of carbonyl compound. For method (i), peroxycarboxylic acids are the most commonly used laboratory reagents. The process is an electrophilic addition reaction and as such it is facilitated by electron-releasing groups on the double bond and by electron-withdrawing groups on the peroxyacid as illustrated in scheme 2.12
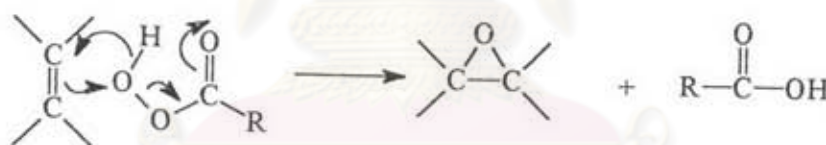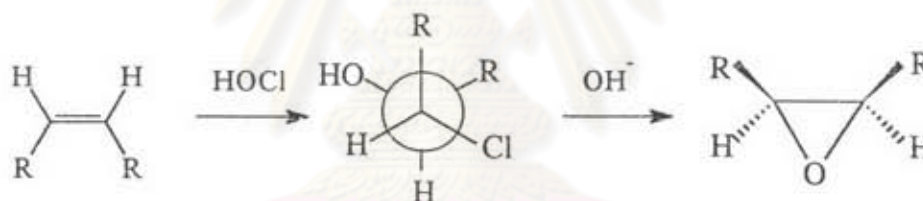

Scheme 2.12

A number of peroxy-acids have been used in the past, including perbenzoic, performic and peracetic acids, but these have been largely superseded, for the formation of epoxides at any rate, by m-chloroperbenzoic acid ; it is commercially available and is an excellant reagent for the epoxidation of alkenes. It is more stable than the other peroxy-acids and has even been used at an elevated temperature to effect the epoxidation of unreactive alkenes. The other peroxy-acids are rather unstable and generally have to be prepared freshly before use. Performic and peracetic acids, for

example, are olefin prepared in situ, and not isolated, by action of hydrogen peroxide on the carboxylic acid. With acetic acid the equilibrium is attained only slowly and sulfuric acid is usually added as a catalyst to hasten formation of the peroxy-acid.

Olefins can also be epoxidized with organic hydroperoxides in the presence of metal catalyst. An important development of the method is the epoxidation of allylic alcohol.

Intramolecular S_N2 reaction [method (ii)] provide an alternative method of synthesis of oxiranes. Olefins are again used as the starting materials. HOBr and HOCl are commonly used as the reagent, giving a halohydrin which is converted into the oxirane by base as illustrated in scheme 2.13.

Scheme 2.13

In method (iii) oxiranes can be obtained from carbonyl compounds by reactions with compounds of the general type R^1R^2CX, in which X is a good leaving group. The Darzens reaction is the classical reaction of this type, but it is generally limited to compounds in which R^1 or R^2 is a carbanion stabilizing group (CO_2R, CN, etc.). The use of sulfur ylide provides a more versatile alternative because a much wider range of substituents can be introduced. For example, spiro-oxiranes are available from the reaction of the ylide with carbonyl compound, as shown in scheme 2.14.
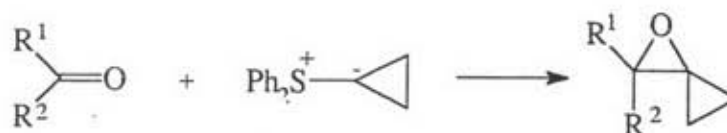
Scheme 2.14

Epoxides are extremely valuable commercially because of the many reactions they undergo. Most noteworthy of these are the addition of active hydrogen compounds such as ammonia, organic acids, alcohols, and water. Their ability to donate electrons to hydrogen atoms by hydrogen bonding is important in such diverse applications as ulcer therapy and the stabiliation of poly(vinyl chloride) resins. The fact that epoxides polymerize under thermal ionic and free-radical catalysis has encourageed considerable reseach on epoxy homopolymers and copolymers for industrial applications. The epoxide of long-chain α-olefins are potentially useful as detergent precursors. These few examples show the commercial usefulness of epoxides, particularly as chemical intermediates.
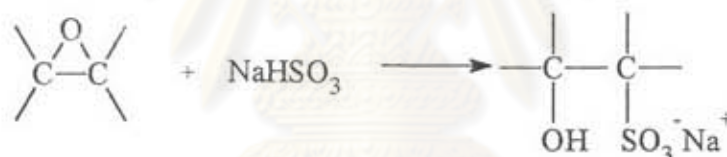
3. Sulfonation [1]

Sulfonation is chemical method for introducing the SO_3 group into an organic molecule, to give a product with $-SO_3-$ linkages in the form of a sulfonic acid ($-SO_3H$), a sulfonate salt ($-SO_3^-$). There are several methods to prepare them which have shown in table 2.4

Table 2.4 Reagent for sulfonation

Reagent	Chemical formula	Physical form	Principle uses
sulfur trioxide	SO_3	liquid gas	- widely used for organic compounds
oleum, 20 %, 30 % and 65 %	$H_2SO_4 . SO_3$	liquid	for alkylaryls for detergent dyes
chlorosulfuric acid	$ClSO_3H$	liquid	for alcohol, dyes
sulfuryl chloride	SO_2Cl_2	liquid	sulfonation of acetylene group, lab. mainly
sulfuric acid (96-100%)	H_2SO_4	liquid	used to sulfonate aromatics
sulfur dioxide plus chlorine gases	SO_2+Cl_2	gas mixture	chlorosulfonation of paraffinic hydrocarbons
sodium sulfite	Na_2SO_3	solid	sulfonation of alkyl chloride,epoxy compound
sodium bisulfite	$NaHSO_3$	solid	sulfonation of lignin
hydroperoxide+ bisulfite	$ROOH +NaHSO_3$	gas and solid	sulfonation of paraffinic petroleum fraction

In this study, sulfonation reaction was carried out by reacting with salts of sulfurous acid and epoxides. This reaction was first observed in 1868 by

Erlenmeyer and Darmstaedter, who found that sodium isethionate was formed when ethylene oxide and a solution of sodium bisulfite were heated in the sealed tube at 100° C. The method of preparation of isethionic acid and its salts from ethylene oxide has been described together with some sodium O-acylisethionates.[19] The reaction of indene oxide with sodium bisulfite at 80-90°C yeilded chiefly cis- and trans- indene glycol but the oxide and sodium sulfite give hydroxy sulfonate.[20] The reaction of cyclohexene oxide with sodium thiosulfate yeilded 2-hydroxycyclohexyl sulfonate.[21] The reaction of optically active terpene epoxide with sodium sulfite has been disclosed in U. S. Pat. No. 4,137,257 to give optically active terpene hydroxysulfonate.[22] The suggested mechanism for the addition of sulfite ion to the oxirane ring may be illustated in scheme 2.15

Scheme 2.15

The product development chemists are most interested in the physical and the sulfonate moiety, such as solubility, lubrication, well sulfonated emulsifier concentrates at the interface water phases, contributing to a stable emulsion, so too, in a broader sense, sulfonation process provide the mean to interface with, modify, or bridge aqueous and organic systems. The principle is utilized in the development of water-dispersible or water-soluble dyes, flavoring agent, and medicinals by introducing the water-solubilizing sulfonate group.

Overview

At the present time, sulfonated oils are commonly used as fatliquors in the leather industry to produce the softy and good strength characteristic leather. Fish oil is usually used as raw material because it produces the sulfonated oil which have good properties for lubrication the fibers of the leather. However, fish oil is expensive and tend to impart a residual odor to the leather. Therefore, these problems may be solved by using the other raw materials, having lower price and good odor, to reduce the cost of production.

Nowadays, the large amount of soybean oil is produced to use as food. The production must be separated free fatty acids from triglyceride. These free fatty acids have no market value and tend to make the pollution problem. The compositions of them have a great part of mono- and polyunsaturated fatty acids which have the reactive sites for sulfonation. So, the purpose of this study is to produce an alternate sulfonated oil as a fatliquor to use in the leather industry by using the free fatty acids of soybean oil as raw material.