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TRAINING MANUAL NO. 120

LEATHER CHEMISTRY FOR FOREMEN

Second Year Course

A.I.D.
Reference Center
Room 1656 NS

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PRACTICAL BASIC CHEMISTRY FOR FOREMEN

2nd Year

Prepared by

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FOREWORD

This manual is one of a series of three manuals on "Practical Basic Chemistry for Foremen" prepared by Albert E. Chouinard, Ph.D., Head of the Department of Leather Engineering, Lowell Textile Institute, Lowell, Massachusetts, as the basis of a series of lectures which were given under the sponsorship of the A. C. Lawrence Leather Company of Peabody, Massachusetts, to its Supervisory Staff.

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SKIN STRUCTURE

Second Year - Lecture #1

The first treatment hide or skin receives in the tannery is a bath of plain water, or an aqueous solution of a chemical. This process is called soaking. The procedure is of ancient origin. Aesop described the soaking of hides in a flowing stream back in 600 B.C.

This process has been greatly studied and is considered to be a very important factor in the making of good leather. Deviations in time and temperature of the soak reflect themselves in the finished product.

In common tannery parlance soaking is presumed to accomplish four things:

1. Restoration of the skin to the same pliable state as when flayed.
2. Removal of the blood, dirt, manure, etc.
3. Removal of salt in the case of salted skin.
4. The hydration of the skin.

There have been many and varied beliefs as to just what effect soaking has on the removal of protein materials. The effects or results are somewhat confused because not only is there the possibility of removal of protein material from the hide itself, a factor which is influenced by pH, salts present, time, temperature and even hide-water ratio; but also bacterial action can take place, this in turn causing depletion of the resulting leather.

Before we can clearly understand the effect of soaking or of any of the earlier treatments in the tannery, we should pause and consider the nature of the skin or hide.

Raw skin is not a homogenous substance covered with hair or wool, but rather it consists of several distinct layers or areas, as follows:

	Epidermis
True Skin or Dermis	Hyaline Layer or surface grain membrane
	Connective tissue Fiber bundle layer
	Corium (fibrous layer)
	Hypodermis (or flesh) adipose tissue

Leather is produced from the true skin, so that the epidermis and adipose tissue must be removed. The true skin consists of two layers often referred to as the corium minor and the corium major. In general terms the corium minor is referred to as the grain layer. This grain layer is that portion of the skin which is outermost. This layer occupies about one-sixth (1/6th) of the total thickness of the hide. Actually the grain layer of the skin or hide is changed very little in thickness during the animals entire life span. However, the corium major, that area just below the grain layer is the portion which increases in relative thickness as the animal ages. Thus in a young animal this ratio can be about 1 to 4, increasing to 1 to 6 in maturity. However, again this varies from one species of animal to another.

In life the grain layer is of paramount importance as this layer contains the hairs and hair roots or papillae, nerves, fat glands, sweat glands and muscles. In addition, this area is permeated by an intricate system of blood vessels.

Actually the following types of tissues exist in the skin or hide:

1. Epithelial
2. Connective
3. Muscular
4. Nervous
5. Glandular
6. Fatty
7. Blood.

Moreover, while the skin is itself considered to be an organ, it contains lesser organs:

1. Voluntary muscles
2. Involuntary muscles
3. Fat glands
4. Sweat glands
5. Nerves
6. Blood vessels.

The physiological functions of the skin are of very great importance. One of the main functions of the skin is to keep constant the temperature of the body it covers. This it does by permitting loss of heat by means of the sweat glands, or by retaining heat by means of the fat glands which can automatically cover the surface of the skin with oil and thus reduce surface evaporation.

The skin as received by the tanner is divided into three distinct and superimposed layers:

1. Flesh
2. Derma, or Corium
3. Epidermis

1. The flesh, a tissue, is strictly not a part of the skin proper. The skin is attached to the underlying body by means of areolar connective tissue. When the skin is removed or flayed from the carcass, part of this areolar tissue remains attached to the skin, together with varying quantities of adipose tissue, yellow connective tissue, blood vessels, nerves and

voluntary muscle. All of these tissues combined compose "the flesh" as it is expressed in tanning terminology. Removal of this flesh is necessary for the diffusion of tanning materials or other chemicals into the skin from its flesh side.

2. The derma, corium, or true skin constitutes the leather making material or skin, since both flesh and epidermis will have been removed prior to the tanning of the skin. The derma may be divided into an upper portion and a lower portion.

The upper contains glands, muscles, and hair follicles, and has been aptly designated the "thermostat layer" by Wilson, since it contains the organs concerned with the regulation of body temperature.

The lower portion of the skin is usually termed the "reticular" layer, since the interlacing collagen fibers of which it is composed present a net-like appearance. The proportion which the thermostat layer bears to the total derma thickness varies greatly with the age of the animal.

The main protein constituent of both dermal layers is collagen, which is arranged in interlacing bundles of fibers or fibrils. It has been suggested that the fiber bundles were enclosed in very thin sheaths of a substance called "fiber sarcolemma". These sheafs were demonstrated by Turley. Kaye and Lloyd have shown photomicrographically that when collagen fibers of fresh skin are swollen in acidic or alkaline solutions they show constrictions which seems to be due to encircling threads of reticulin. The derma also contains a smaller amount of yellow connective tissue fibers composed of elastin. These fibers are located mainly at the lower and the upper surfaces of the skin. Their function is not clearly understood.

The connective tissue fibers of the thermostat layer are finer than those of the reticular layer, and they become increasingly finer as the epidermis is approached and eventually become exceedingly fine and tend to lie parallel with the grain surface.

The point of the derma immediately in contact with the epidermis has been designated the "grain membrane" by Seymour-Jones. This grain membrane constitutes the grain surface of the finished leather. It has long been thought that the grain membrane is seperated from the stratum germinatum (the lowest layer of the epidermis) by an extremely thin film, called the "hyaline layer".

Turley has been able to quite definately demonstrate a distinct band of about 5 microns thickness covering the fibers of the derma surface and lining the hair follicles as well.

3. Epidermis - Like the derma, the epidermis is made up of superimposed layers. Whereas the principal constituent of the derma is collagen, that of the epidermis is keratin. The two proteins are of very different composition and respond to chemical treatment in different degrees with unhairing chemicals.

When skin is limed, the epidermis is decomposed, thus enabling the mechanical removal of the hair, whereas the underlying collagen is not adversely affected.

The portion of the epidermis immediately in contact with the derma (or the hyaline layer) is termed "stratum germinatum"; it is also called the (Malpihigian) "malpighian layer". It is composed of elongated epithilial cells. These cells increase in height and then subdivide one above the other. As subdivision continues, the older cells are pushed upwards away from nourishment and, consequently, lose their power of reproduction, until, finally they become dehydrated and lifeless and are gradually worn away at the outer surface of the epidermis. The successive layers of epidermal cells have been termed: stratum germinatum, stratum granulosum, stratum lucidum, and the outermost stratum corneum.

Thus, we may summarize the various layers of the skin and their relative positions:

<u>Epidermis</u>
- Stratum Corneum
- Stratum Lucidum
- Stratum Granulosum
- Stratum Germinatum

<u>Derma</u>
- Hyaline layer
- Grain membrane
- Thermostat layer
- Reticular layer
- Flesh

Kuntzel has questioned the correctness of any rigid classification of epidermal layers pointing out that what transpires is a continuous cell migration, which finally ends with the dead cell falling from the epidermal outer surface. He contends that this migratory process does not occur in layers since an individual cell may differ greatly from its neighboring cells in its migratory rate. He believes that a layer-like cell arrangement in the epidermis is to be found only in the stratum germinatum.

PROTEIN CHEMISTRY & SOAKING

Second Year - Lecture #2

Let us now turn to a consideration of the chemical nature of skin or hide. In main the skin is composed of proteins. Proteins in turn are made up of amino acids. At the present time it is considered that there are 22 amino acids which make up all the known protein materials. No one protein contains all of these, but rather various proteins contain definate amounts of various combinations of these 22 amino acids. In addition, the size of the protein molecule, that is the number of times in which the particular amino acids are joined together to form this molecule is peculiar to each molecule. Thus egg albumin has a molecular weight of about 40,000, while hemocyanin has a molecular weight of 5,000,000.

There are several ways of classifying the proteins which are based on their relative or distinctive solubilities, their isoelectric points and even their molecular weights. However, they are generally classified now as fibrous and globular proteins.

This is a particularly simple classification for the tanner. The first type, Fibrous, includes various proteins that serve as structural materials for animals very much as cellulose serves for plants. These include:

1. Collagen, the protein of connective tissue from which gelatin is derived.
2. Keratin, the protein of epithelial tissue, of hair, horn, feathers, and nails.
3. Elastin, the protein of the elastic connective tissue.

All fibrous proteins are characterized by pronounced insolubility in neutral solvents.

The second type, the globular or soluble proteins, are often grouped into six types:

1. Albumins, soluble in pure water.
2. Globulins, insoluble in pure water, but soluble in dilute solutions of salts of strong acids and bases (viz. sodium chloride).
3. Glutelins, soluble in very dilute acids or alkalies.
4. Pro-lamines, soluble in 80% alcohol solution, but insoluble in water or absolute ethyl alcohol.
5. Histones, strongly basic and soluble in dilute acid.
6. Protamines, strongly basic and soluble in water.

Proteins are extremely sensitive and easily undergo changes in various properties. The process is known as denaturation and is always accompanied by a decrease in solubility. Denaturation is effected by the action of acids or alkalies, heat, by certain solvents and chemicals, by ultra violet light, and even by shaking. The reaction is usually, but not always irreversible.

Curing brings about so many changes in the components of the green stock that the soaking process can only be explained and understood by taking all of these changes into account.

All existing curing methods depend for their efficiency upon the fact that the proteolytic bacteria are deprived of the water so necessary for their normal development. The most noticeable overall change occurring in stock during curing is shrinkage of the structure due to such dehydration. Apart from this important dehydration there are, however, several less noticeable but nevertheless important alterations which should briefly be summarized since they affect the subsequent processes to such an extent.

Collagen and elastin fibers shrink in all curing processes, the most marked being with sun drying. In the later case the fibers may become rather brittle.

Reticulin fibers will also become dehydrated and brittle and somewhat affected by sodium chloride.

The erector pili muscle shrinks and fats and oils of the sebaceous glands, dispersed through the corium and especially plentiful in the adipose tissue, are broken down, especially in sun-drying.

The sweat glands and veins collapse, but the arteries remain fairly well unaffected due to their strong walls of collagen and elastin.

It is, therefore, quite easy to understand how denaturation of some of the proteins takes place. Denaturation is by no means restricted to the globular proteins, but they show it most markedly. Decreased solubility is often the primary change in denaturation.

The soluble proteins form about 10% of the total protein matter in hide. In the corium major the largest portion is spread thinly and more or less uniformly around the fibers and fiber bundles in the interfibrillary lymph spaces. The blood contains relatively large amounts as soluble serum proteins. Finally, the fibroblasts contain mostly soluble protein material and are closely associated with the globular proteins.

The corium minor constitutes only 1/6th to 1/4th of the total hide thickness but it contains roughly 70% of the total soluble protein material in the hide. Here again large amounts are present in the interfibrillar spaces, in the blood and in the fibroblasts. The larger portion is, however, present as a dense layer in and immediately below the germinating layer of the epidermis. This layer is the seat of cell formation for the epidermis and here the soluble proteins undergo a change to produce the fibrous keratin.

Thus, how are the soluble proteins now affected by curing? In the simplest case, sun or shade-drying, the proteins become insoluble and denatured and in extreme cases of drying and heating will be completely coagulated. This final change is not easily, if at all, reversible and is part of the reason for the difficulty experienced in soaking back such stock.

Dry salting will combine the effects of wet salting with some of the effects of sun drying but the salt seems to prevent excessive denaturation by the heat.

The principles of soaking were thoroughly investigated by McLaughlin and his associates at Cincinnati. In this work it was pointed out that soaking is largely a reversel of the curing process. The dehydrated stock is allowed to rehydrate and the curing salt (if present) is removed.

Rehydration of the hide structure is closely related to the condition of the interfibrillar globular proteins. McLaughlin and Theis showed in 1923 that the degree of rehydration is inversely proportional to the degree of dehydration occurring during curing. Kaye-Jordon Lloyd indicated that excessive denaturation of the globular proteins cements the fibers together in such a way that they cannot swell properly in the soak. It would seem that under certain conditions of curing, let us say high temperature and high relative humidity, there are changes in the collagen fibers which prevent their thorough rehydration and swelling, but it is probable that the difficulty in hides and skins is mostly due to irreversible changes in the globular interfibrillar proteins.

Kaye and Jordon Lloyd appear to have been the first to study soaking specifically from the point of view of the desirability of removing the cementing substances. A patent was granted to them covering the use of such compounds as sodium citrate, sodium pyrophosphate and sodium ferrocyanide as additives to the soak liquor. It was found by others that improved soaking could be had by the use of dilute sodium chloride solutions. It was concluded that this was due to the better removal of interfibrillary proteins by such dilute brines. In a similar manner other salts such as sodium nitrate and potassium perchlorate were found to be effective.

More recently it was found that a 5% to 10% sodium chloride soak resulted in the production of better leathers. Moreover, it was found that polyvalent salts such as sodium polysulfide have a strong dispersing action on globular proteins.

A histological study of brining of heavy cattle hides originating in the Swift and Company Research Laboratories and published in 1944 gave definite evidence that salt penetration appears to take place exclusively through the flesh side of the hide and in none of the cases observed is there any evidence of salt entering through the epidermal area.

This is interesting as it indicates that the epithelial layer of the skin or hide is particularly impervious, particularly to the salt. Similarly in soaking there is sound evidence that the water will penetrate almost exclusively from the flesh side. Thus, if any of the globular proteins are removed from the hide at this time, particularly if they are denatured, they will travel outward in more or less one direction. In addition, as the grain layer contains the largest amount of these the corium or flesh side of the hide will be stripped free of globular proteins, soluble under these conditions, more completely.

A soak of about 2 days seems to be the maximum as regards the possibility of loss in strength or leather yield.

One of the earliest methods employed in soaking dried hides was the stale soak. This consisted of a repeatedly used soak liquor which was never changed. Actually these stale soaks must have been highly charged with protein matter and putrefaction bacteria which undoubtedly caused loss of collagen from each batch of hides.

One of the chief difficulties encountered in soaking dried hides is that of ensuring intimate contact of the soak liquor with the dried material. Surface tension effects are the root cause of the trouble which is mitigated by the use of so-called wetting agents. These latter reduce the surface tension of the soak liquor and, thereby, bring about its more intimate contact with the dried hides or skins. Naturally wetting agents can be used in soaking other than dried hides with beneficial results.

LIMING

Second Year - Lecture #3

The commonest method in use today for effecting the seperation of the epidermal system or layer from the true skin is also one of ancient origin and is known as liming, from the fact that saturated lime water is used.

In general, hides and skins after having been properly soaked, are immersed in an unhairing solution, the principal constituents of which are hydrated lime, $Ca(OH)2$ and water. In most cases, a sharpener is added to expedite the depilatory action.

McLaughlin has pointed out that there are at least four major objectives in the liming operation:

1. To act chemically upon the epidermal system, so that the skin may be properly unhaired.

2. To saponify the skin lipids (fats).

3. To swell and hydrate the skin proteins satisfactorily.

4. To condition the skin chemically and physically for subsequent operations.

A great many different modifications of the unhairing process are used by the tanners. These might be listed as:

1. The straight lime liquor, in which only $Ca(OH)2$ and water are used.

2. The lime and sodium sulfide or sulfhydrate liquor, in which a given percentage of sulfide or sulfhydrate are used in conjunction with lime.

3. The lime and arsenic sulfide liquor, in which arsenic trisulfide is added to the lime liquor.

4. The lime and amine liquor in which dimethylamine is added to the lime suspension.

5. The lime and cyanide process in which a given amount of sodium cyanide is dissolved in straight lime liquor.

6. The enzyme and sweating process, in which enzymes play an important role.

There is very little doubt that in the early days of tanning the use of lime was considered only in its relation to the removal of the epidermis and the hair. That is no doubt why straight lime liquors were used

universally. It is only relatively recently that any other significance has been associated with the liming process.

In heavy leather tanning long liming has been the rule even to the present. However, because of the necessity to cut down processing time most other types of leather are being given a much shorter liming period. This has been largely accomplished by the use of chemical additives, as listed above, and usually referred to as "sharpening agents".

Today it is quite common agreement that in the liming operation we have two important actions proceeding simultaneously, viz. a loosening of the epidermal structures, to be removed by mechanical means subsequently, this includes all the hair, the epidermis proper and some say even sebaceous glands. Secondly, a so-called "conditioning" of the hide or skin is claimed. It is believed that a profound effect is taking place on the connective tissue fibers. These fibers are said to become loosened and set free so that the resultant leather shall be strong, "mellow" and "round".

Many consider this last reaction of conditioning to be more important than the removal of the hair. It is unusual that this conditioning effect has been recognized only relatively recently. Moreover it is interesting to note that all of the changes in the liming operation of the last 50 years have been made by the use of sharpening agents which hasten the unhairing operation in spite of the fact that the conditioning is considered to be so important. It hardly seems reasonable to believe that an acceleration in the unhairing gives a corresponding and equal acceleration in the conditioning process.

It has no doubt been recognized that some adjustment is necessary, for in some cases where a "lime paint" is used (a mixture of slaked lime and sodium sulphide) a subsequent immersion in a lime liquor is used as the next step in the process. In this method the skins are painted on the flesh side with this mixture and left for several hours flesh to flesh. It is believed that ingredients of the paint react to form calcium sulfide or sulfhydrate which penetrates the skin from the flesh side until it reaches the epidermal tissues, which it destroys. Subsequently, the skins are immersed in lime liquor in order to obtain the other liming effects or "conditioning".

The usual method of liming is with milk of lime in pits, paddles or drums. The lime liquor may be freshly prepared when it is known as a "fresh" or "new" lime, or it may be a used lime liquor. A once-used liquor is called a medium or mellow lime, a twice used liquor is described as an old lime. It is well known that the hair is loosened more readily in an old lime than in a fresh lime, but that the maximum swelling and plumping of the skin is produced by the fresh lime.

The hair on skins immersed in an old lime liquor shows signs of loosening after 4 or 5 days, but it requires 10 or 12 days in a new liquor. By adding a small quantity of sodium sulfide or arsenic sulfide to any lime liquor, the hair loosening is accelerated and the hair can actually be loosened in one hour if a sulfide solution of high concentration (10 per cent) is employed. Such a solution not only loosens the hair but also completely destroys it.

LIME

This is a fairly good point at which to digress a little in order to study some of the chemical and physical properties of calcium hydroxide. Calcium hydroxide, such as we use in the tannery, is obtained from calcium oxide (CaO).

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15{,}540 \text{ calories}$$

Calcium hydroxide is known as slaked or hydrated lime. Some tanneries still manufacture their own slaked lime from calcium oxide (or quicklime) as indicated by the equation above. However, considerable heat is given off when water is added to quicklime and the reaction can be difficult and dangerous to control. Calcium hydroxide is cheap so that few people bother to use this particular operation today. To go back an additional step, we find that calcium oxide is commercially prepared by heating limestone in a kiln, (limestone is $CaCO_3$). The kiln is a tower, usually of masonry, which looks like a tall chimney (60 ft. high by about 7 ft. dia.). A sort of dutch oven type firebox is at the bottom and the kiln is filled with limestone. Heat is applied along with a current of air to carry off the CO_2 formed.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

We have found that most chemicals, particularly inorganic chemicals, are more soluble in hot water than cold water. However, calcium hydroxide is an exception as 0.185 grams is soluble in 100 grams of water at 0°C. as against 0.077 grams at 100°C.

SULFIDES OF SODIUM

Sodium sulfide can be prepared by passing hydrogen sulfide into the soluble base sodium hydroxide NaOH.

$$H_2S + 2NaOH \longrightarrow 2HOH + Na_2S$$

It can also be made by the reduction of the corresponding sulfate.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

This reaction just considered is the most common. The sodium sulfate is heated with carbon at a temperature of about 900°C. to yield the sulfide. The carbon monoxide is a by-product of the reaction. Sodium sulfide is not very soluble in water, but in the presence of the calcium ion, which is the case when it is added to lime, a substitution takes place.

$$Ca(OH)_2 + Na_2S \longrightarrow CaS + 2NaOH$$

Calcium sulfide is formed and it is said to be the agent which performs the unhairing.

SODIUM POLYSULFIDE

Sodium polysulfide is sodium sulfide to which has been added sulfur. The composition of this compound may vary from Na_2S_2 to Na_2S_5. There has been some use of sodium polysulfide in liming, but it is not as efficient as sodium sulfide. Sodium polysulfide finds its greatest use today as a soaking aid.

SODIUM HYDROSULFIDE

Sodium hydrosulfide is largely replacing sodium sulfide as an accelerator in the unhairing process. Actually it is available at a price comparable to that of sodium sulfide. In its liquid form (66% HOH) it is easier to keep it free from contact with the air as it reacts readily with the oxygen to form products which have little or no unhairing action. The solid product (70% hydrosulfide by wt.) must be dissolved and will occasionally cake in the container.

When sodium sulfide is dissolved in water it hydrolyzes to form 1 molecule of sodium hydrosulfide and 1 molecule of sodium hydroxide

$$Na_2S + H_2O \longrightarrow NaSH + NaOH$$

We know that the sodium hydrosulfide in turn in the presence of the $Ca(OH)_2$ combines to form calcium hydrosulfide.

$$2\ NaSH + Ca(OH)_2 \longrightarrow Ca(SH)_2 + 2NaOH$$

Thus when we add sodium sulfide to the lime solution all of the sodium ion present is converted to sodium hydroxide (NaOH) and the agent which performs the actual unhairing is the calcium hydrosulfide.

Let us consider this from another angle now; pure saturated lime water has a pH of about 12.5. This is due to the fact that $Ca(OH)_2$ is so slightly soluble that there is not a very great concentration of hydroxyl ions present in the solution. However, in the case of sodium hydroxide this salt is very soluble and a large concentration of hydroxide ions is present. This is particularly indicated by the fact that a sodium hydroxide solution will give a pH of 14 which is the extreme range of the pH scale.

It has been known for a long time that sodium hydroxide will unhair a skin or hide satisfactorily, but that its action is very severe. It is believed that the damage to collagen is very probable and no doubt the greater plumping action due to the higher alkalinity, as evidenced by the higher pH, will in turn yield a poor leather. The excessive swelling caused by sodium hydroxide is particularly evident in the reticular fibers and the other constituents of the skin such as the blood vessel system, the elastin, etc. This is said to result in grainy leather and drawn flanks.

Thus it would seem that even a relatively small amount of sodium hydroxide present with the lime will tend to cause excessive swelling and correspondingly poorer leather. Also, it would seem that while sodium sulfide gives a satisfactory unhairing action, the sodium hydroxide formed is not desirable, as a matter of fact it is not necessary.

Calcium hydrosulfide has the same activity on keratin as sodium hydrosulfide, but when added to lime liquors, it decreases the solubility of the lime and produces pH values well below the 12.5 of pure, saturated limewater. In making fine, smooth leather, it seems to be necessary to prevent undue swelling and plumping of the raw stock. Thus when calcium hydrosulfide is added to lime liquors, less swelling takes place than when lime alone is

used (there is no sodium hydroxide possible under this condition) and it is believed that a finer and smoother leather results.

We might carry this argument one step further, if we can assume all of the above facts to be true, and say that the quality of the leather is inversely proportional to the degree of swelling, or of the hydroxyl concentration. This statement is, of course, not well substantiated, but it certainly gives rise to some possibilities. It certainly is definite that a good control of swelling is warranted and that consideration must be given to the quantity and kind of chemicals added to lime solutions.

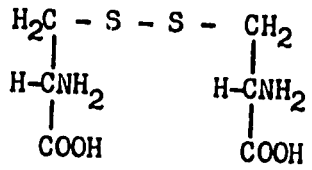
UNHAIRING

Second Year - Lecture #4

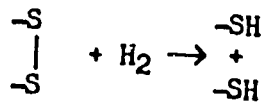
We know that the hair is held in position by epidermal tissue which completely surrounds the hair shaft. The epidermal tissue must be disintegrated if the hair is to be loosened. This disintegration is brought about in the sweating process by the action of certain putrefactive bacteria which thrive under humid conditions between 60o and 70°F. Bacteria cannot thrive in a lime liquor; any bacteria carried into the lime liquors by the skins are slowly but completely destroyed by the alkalinity.

The cell walls of the epidermis are composed of keratins and the hair consists also of keratins. When a skin is placed in a fresh lime liquor, the hydroxyl ions commence slowly to hydrolyze the keratinous tissues. Keratins are proteins which include in their polypeptide chain of amino acids, one sulfur-containing acid, cystine, which is attacked by alkali and brought into solution. This is evidenced by the presence of calcium sulfide in the solution, this in turn aids the unhairing action as soluble sulfides possess strong reducing power. This example is used to explain, at least to some extent, the unhairing action of lime alone. Thus it would also seem that the addition of sulfides would aid and speed up the action.

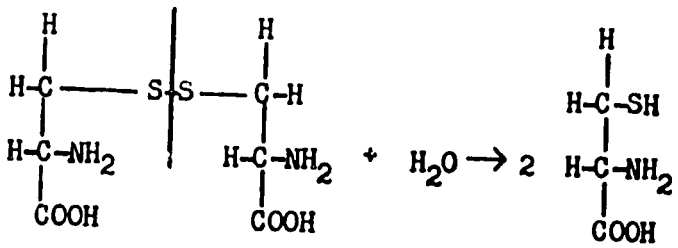
Cystine contains a disulfide linkage -S-S-



This cystine disulfide linkage is said to be broken by reducing agents as follows:



The effect of this cleavage in the cystine molecule is to produce the simpler amino acid, cystine, as follows:



cystine cystine

The decomposition of the cystine residue in the keratin molecule apparently destroys the keratin itself, and the decomposition products are dissolved by the lime liquors. Used lime liquors already contain some calcium sulfide derived from the dissolution of the epidermis. This calcium sulfide is a reducing agent which can quickly decompose the keratinous tissue in the next lot of skins immersed in the used liquor. Thus the hair is loosened more quickly in a used lime liquor than in a fresh lime liquor because it already contains some calcium sulfide, wheras the decomposition of the keratinous tissue by the hydrolytic action of the fresh lime is slow and until some calcium sulfide is formed it continues to be slow. Then the hair loosening action speeds up.

It is believed by some investigators that the hair loosening action of an alkaline liquor depends on its alkalinity, that is, on the hydroxyl ion concentration, also on the ability of the solution to produce reducing agents from the hair and on the power of the solution to preserve these reducing agents.

If the strength of the reducing agent in the lime liquor is too high the hair is completely disintegrated. Any chemical which is added to the lime liquor for the purpose of increasing any of the effects of the lime is known as a "sharpening" agent. One percent sulfide will hasten the depilatory action but will not destroy the hair. Two and one-half to three and one-half percent ($2\frac{1}{2}$ to $3\frac{1}{2}$%) will often pulp the hair and when as much as ten percent (10%) is used the hair is completely destroyed.

It is generally believed that liming is responsible for the removal of a large portion of the remaining soluble proteins. It is claimed that the removal of these soluble proteins opens up the interfibrillar spaces. It is further believed that the lime can then enter more easily and will break down the reticulin sheaths which bind the fibers together.

Some saponification and removal of surface fats takes place, but the lipids in the corium are affected only to a minimum if at all.

A new school of thought relative to the theory of unhairing has been expressed recently. The more recent theory criticizes the established theory for putting too much emphasis on the breakdown of keratin as the principal cause of hair loosening. This argument is based on the premise that there are many depilation processes or agents which do not involve any keratolytic action.

In the simplest case it is well known that when green hides are allowed to putrefy, the hair and epidermis can be removed quite easily. Hairslip on brined or wet salted stock is a common phenomenon. In both these cases the loosening is due to the enzymes secreted by proteolytic bacteria and the industry of wool pulling by the sweating process depends upon this very phenomenon. Furthermore, some enzyme preparations for hair loosening are commercially available.

Immersion of the fresh hide or skin for about 10 minutes in water at 60°C. will loosen the hair and epidermis. Dehairing of hogs and pigs by scalding is, of course, common practice and resin preparations are now marketed which are used along the same lines. It is interesting to note that too high temperatures or excessive immersion will defeat the object, since the hair and epidermis will then stick.

In 1906 Stiasny reported that ammonia in the lime liquor will increase the rate of unhairing and will cause unhairing also when used alone. The "sharpening" effect of amines in lime liquors has, of course, been known for some time and is used commercially.

Unhairing has been obtained with acetic acid and leather was actually produced from stock treated in this manner. It was suggested that hydrolytic action of the acid on a protein similar to mucoid was responsible for the loosening.

Solutions of 5 and 10 percent sodium chloride have been found to give satisfactory loosening of the epidermis and hair in fresh hides within a few days with or without changes of the solution. Even concentrated solutions of urea have shown an ability to unhair fresh hide.

Recent work on fresh hide showed also that saturated solutions of sodium fluosilicate (0.6 percent) gave loosening of the hair and epidermis. Supplementary work using cattlehides, calfskins, goatskins and sheepskins which had been wet-salted, dry salted and sun dried proved that unhairing can take place with saturated sodium fluosilicate solutions at room temperature in 6 to 14 days depending upon the type of stock and the curing method. The entire epidermis came off in sheets, bringing away the hairs and follicle walls.

In view of the various observations it has become clear in recent years that the loosening of the epidermis and hair is not only a function of the breakdown of keratin by reducing alkaline solutions, but that the soluble proteins of the corium minor play an important part too. The present theory of unhairing by lime liquors does not give the complete picture, and the removal of the globular proteins in the native or denatured state may be of much more importance than has been realized.

Gustavson compares the unhairing obtained by urea with that by sodium chloride and states that such unhairing is "probably due to the dispersing and modifying action of these agents on soft keratin and other a- proteins of the mucous layer, which in many respects show similarity to the globular proteins".

We may, therefore, think of the epidermis and hair as being embedded in and cemented to the corium minor by a dense layer of soluble proteins. Loosening of these structures must then occur if the soluble proteins are removed or affected in such a way that they no longer cement the epidermis and hair to the underlying tissues.

It is suggested that in the case of enzymatic unhairing (putrefaction of green or cured stock, sweating, etc.) the enzymes break down the globular and other soluble proteins such as young keratin to such an extent that they no longer have the ability to cement the epidermal structures to the tissues underneath. It might perhaps be mentioned that the soluble proteins are more subject to breakdowns by bacteria.

Unhairing by hot water is also due to a change in the soluble proteins as a result of thermal agitation. If the treatment is prolonged or the temperature too high, then coagulation will result and the epidermis and hair will adhere to the corium minor even more rigidly. This also appears to be

the explanation of the difficulty encountered in unhairing flint dried stock.

At the present time unhairing by sodium chloride has only been possible on fresh stock where no denaturation of the globular proteins has taken place. In salted or dried stock the denaturation of the globular proteins is only partially reversible in dilute salt solutions and the globular proteins are not broken down or dispersed in the same manner.

Sodium fluosilicate has such a strongly dispersive action on even denatured globular proteins that fully cured hides and skins may be unhaired with relative ease. In this case salted stock must be well soaked and washed first to remove sodium chloride which would otherwise remove or salt out the sodium fluosilicate from a saturated solution.

On this basis any agent which can disperse native or denatured globular proteins should act as an unhairing agent. This also seems to be the reason for the action of urea and the amines.

During the initial stages of liming a portion of the globular and other soluble proteins will be removed from the corium through the flesh side. Meanwhile the keratin is being broken down and dissolved, as indicated above at the beginning, thereby making the epidermis so porous and loose that the soluble proteins adjoining it can be removed with ease. Before such removal is complete, however, the stock is unhaired in normal practice. It is thus believed that a large amount of globular proteins and soluble breakdown products of proteins is carried forward into the subsequent processes.

CONDITONING EFFECTS IN LIMING

Second Year - Lecture #5

It is generally accepted that one of the most important, if not the most important, functions of the liming process is the conditioning of the skin, especially in view of the particular type of leather desired. This conditioning of the skin is generally referred to in scope; however there is definite experimental evidence that this conditioning varies for different types of hides and leathers. Moreover, the conditions of concentration, time, pH, etc. which govern this phenomena are not very well understood.

Theis says in his book: "Liming of skins and hides must then be considered a process necessary not only for the loosening and removal of hair but also for conditioning the skin or hide for the subsequent processes of bating, pickling and tanning."

Turley in considering the effects of liming points to the profound effect taking place on the connective tissue fibers. "These are becoming loosened and set free so that the resultant leather shall be strong, mellow and round. Failure to effect this results in hard, flat, tinny, papery leather."

In his study of a single fiber taken from the corium of a fresh steer hide he indicated that this fiber was made up of approximately fifteen fibers. Further, he indicated that each of these fifteen fibers was in turn built up from about thirty-five tiny fibers called fibrils. These he called the structural units of leather architecture. He claimed that: "If these fibrils are obtained free and discreet, and tanned as individuals, the resulting leather is strong and 'round'. Cases of 'flat', 'empty' leather resulting from an insufficient 'opening up' of these fibrils has been found."

Again there are indications that it has been necessary to decrease the time of liming to a matter of hours rather than days in some cases where the skin is being chrome tanned, this allowance being a compensation for the "loose" tanning obtained with chrome.

Turley again states: "In a good liming process, depilation and the 'conditioning' of the skins proceed at the same rate and, if this is not so, then it is possible to accelerate or retard either of these actions to give a satisfactory process."

In view of the foregoing statements it is quite easy to see that there is considerable variation regarding the proper processing conditions and effects. In addition, it is impossible in the light of present day knowledge to greatly modify or condemn these statements, for in each case a "good" leather is held up for proof. It would naturally lead one to believe that this business of conditioning a skin or hide is a matter of degree extended over a broad range, at the same time being susceptible to many variables, any of which will change the end results greatly.

One of the most important factors in this "conditioning" phase, one which is seldom, if ever, referred to is the kinetics, or speed with which any of these treatments take place. The undesirable effect of rapid drying of vegetable type leathers, especially heavy leathers is well understood. Also, much has been said about the damage caused to leather by exposure to excessive heat. In the first case there is a migration of the tanning material to the surfaces to cause a "poor" "cracky" grain loaded to excess with tanning material. In the second case the excess heat will cause shrinking of the surface exposed and even permanent damage or degradation. The damage is successively less as we go towards the center of the stock, except where exposure is so long that there is complete breakdown of the leather. Another well-known case is that which takes place when a hide is placed in a vegetable liquor which is so strong or concentrated that the tanning material precipitates near the surface and completely blocks any further penetration. This is commonly known as "case hardening".

All of these considerations are well known and taken into consideration by all good tanners. However, the same tanner will throw a soaked hide into a lime solution which has a pH of about 12.5, or more, in cases where other alkaline materials are present, without the slightest consideration or fear of the surface effects, or of the differential effects which take place due to the time which must be allowed for complete penetration and equilibrium.

There is little doubt that in this particular case consideration should be given to the pH of the liquor as well as the amount of time necessary to arrive at proper swelling. If the external surfaces are swollen too rapidly there can well result loose or "pipey" leather. For if the central portion of the skin is too far behind in swelling, it is possible that the external surface, particularly the grain surface, will be internally ruptured permanently.

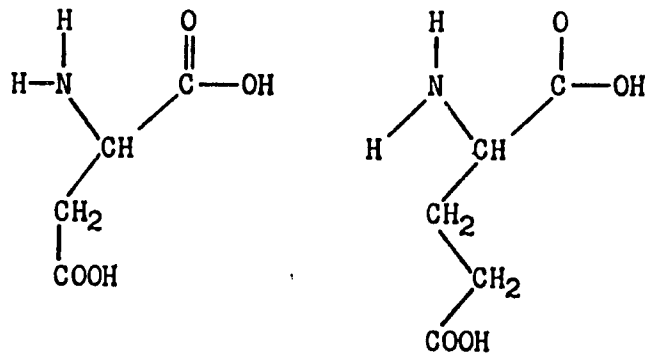
It is possible that some tanners have compensated for this in the practise of painting skins with a lime sulfide paste, particularly on the flesh side, before immersion in a lime solution. It is quite simple to understand this particular mechanism, as the paste treatment swells the hide or skin quite slowly due to the fact that little water is present and thus the swelling proceeds much more slowly. By the time that the skin is placed in the lime solution the skin has been swollen in a much slower and uniform manner. Thus, whatever further conditioning may be desired in the lime solution, such as removal of the globular proteins, will take place without harmful rupture or strain of the interwoven fibers.

A second obvious and desirable method, particularly for those who do not pretreat with a lime paste, would be immersion in baths of controlled ascendency of pH value. This it would be possible say to treat in a solution which would raise the pH of the skin say to 9.0, and once equilibrium or complete penetration has been reached, to follow in a bath to raise the skin pH to 11.0 etc., arriving eventually at a pH considered to be desirable for the conditioning treatment. One can immediately begin to postulate several variations of this, and it might well be that such a treatment, or series of treatments would accomplish many desirable effects. This is somewhat akin to the problems of the metallurgist who must anneal his iron in order to remove strains, and preheat in order to prevent cracking.

In view of these facts let us regard the theories relative to swelling and plumping.

Plumping is a molecular or chemical absorption of water by the collagen molecule. Swelling is the absorption of water between the fibers and fibrils. Water of swelling can be pressed out of swollen skins, but even pressures of 38,000 lbs. per square inch are insufficient to remove all the water of plumping. A swollen pelt is soft and flaccid, but a plumped pelt is firm and rubbery, almost like gristle. Comparative tests with solutions of equal normality show that ammonia solutions produce no plumping effect, fresh lime liquors give moderate plumping, whereas strong plumping is obtained in liquors sharpened with sodium sulfide or sodium carbonate. It is not the normality of the alkaline liquor which influences the plumping but the pH value. Ammonia solutions are only feebly ionized and their hydroxyl ion never attains that required to induce the plumping effect on a hide or skin.

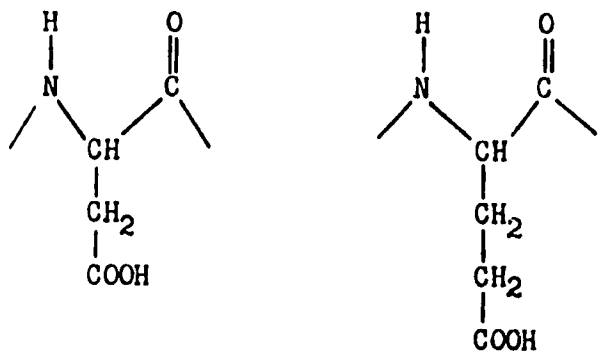
The polypeptide backbone chains, which constitute the collagen molecule, contain a large number of side chains from the amino acid components. Many of the side chains terminate in active centers. Aspartic and glumatic acids, for example, possess two carboxyl groups in the molecule, viz:



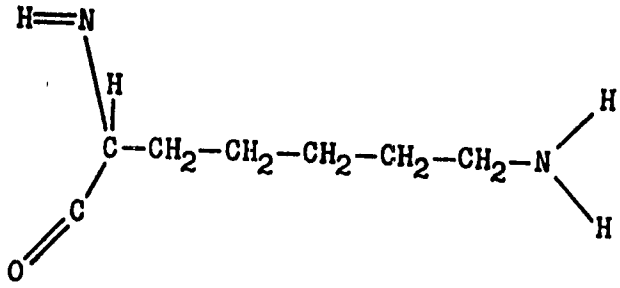
Aspartic acid Glutamic acid

One of the carboxyl (COOH) groups forms the link in the polypeptide chain, leaving the other COOH group in the side chain.

viz:



These terminal groups are reactive. Besides free carboxyl groups in the side chains, there are also free amino groups (NH_2) as in Lysine.



The side chains of two other amino acid constituents of collagen terminate in hydroxyl groups. All these terminal or end groups, viz. COOH, NH_2, OH are chemically reactive and free to react with the various chemicals exposed to the collagen molecule. Some of these residues or side chains project a considerable distance from the backbone of the main chain formed by the polypeptide link and tend to keep adjacent chains apart. It is further believed that active groups from one chain form short links of the cross link type with active groups of an adjacent group. Some of these linkages are what are known as salt linkages or bridges.

viz: $-NH_3^+ \; -OOC-CH_2-CH$

However, it is believed that the majority of the cross linkages between the backbones are probably of the co-ordinate type.

$CO = HN$

The polar or active groups of the side chain are hydrated. That is, they attract water molecules around them, somewhat as a magnet does iron filings.

The first effect of the immersion of skins in milk of lime is the combination of the hydrogen ions split off from free carboxyl groups in the skin collagen, with the hydroxyl ions in the lime liquor. This leaves calcium ions and collagen ions. The calcium ions are free to diffuse through the membranes, but the collagen ions can not. The skin tissue functions as a membrane and prevents the free diffusion of the colloidal collagen ions. This stoppage of diffusion of an entire group of ions sets up osmotic pressure. Such osmotic pressures always result from the unequal distribution of diffusable ions and water passes through the membrane until the pressure is equalized.

Water molecules migrate into the protein until an equilibrium has been established. This water causes a swelling of the skin which is called "osmotic swelling". Sodium hydroxide causes twice as much osmotic swelling as calcium hydroxide solutions of the same strength.

In addition to this osmotic swelling, a considerable amount of hydration occurs due to the polar groups (OH, NH_2, NH groups, etc.) in the collagen molecule. Besides this imbibition of water, there is a more important opening of the skin structure, viz. splitting of the fibers into their constituent fibers. Microscopical examination indicates the presence of such constituent fibrils. It is believed that the fiber bundles in limed hide for sole leather should be well split up into fibers and fibrils without these being separated from each other. They claim that the fiber structure should have a compact weave of steep angle, i.e. vertical weave.

Pelts for light leathers, it is claimed, should show fine splitting of the fibers into fibrils. It is felt that fine splitting is only accomplished after the encircling reticular tissue has been ruptured. It is stated that the reticular tissue round the fibers must be weakened either by the slow action of enzymes, or sharpened limes or quickly by treatment with a lime liquor of about pH 12.5. It is stated that acid plupming will burst the reticular tissue.

Water taken up as a result of increased swelling pressure causes an increase in the diameter of the fibers with a corresponding decrease in length; the angle of weave tends to become higher, and the hide increases in thickness and becomes firmer. This type of swelling is often referred to as "plumping". When water is taken up as a result of decrease in cohesion between the fibers, the fibers again increase in diameter but do not alter in length, laterial splitting up of the fibers becomes more apparent, and the skin tends to feel softer.

Two explanations of this preparatory effect of the liming are offered. One is that the liming weakens the forces of cohesion between fibers, thus opening up the fibrous structure and facilitating the penetration and attack of the bating enzymes, which then complete the decomposition of the collagen on the surface of the fibers; or completely remove all of the globular proteins present in the interfibrillar spaces. The other cause may be the partial hydrolysis of the interfibrillar mucins and reticulins by the liming process into simpler products which can be completely hydrolyzed by the bating materials.

ENZYMES, BACTERIA and BATING

Second Year - Lecture #6

When a skin leaves the lime unhairing solution and has been mechanically treated to remove hair, epidermis, flesh fat and surface muscles, it is in a highly swollen state, and has a pH value of about 12.5. The skin is now ready for bating, which, until about fifty years ago, was one of the most curious and secretive of all the operations of the tannery. This operation was so completely held in secrecy, and so jealously guarded that it has not been possible to trace its origin. It consisted in digesting the lime and unhairing skins in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched, and sufficiently porous to permit the passage of air under pressure. When hen or pigeon manure was used, the process was called bating, but when dog dung was used, it was called puering.

The work of two men, Joseph Turney Wood of Nottingham, England, and Otto Rohm of Darnstadt, Germany, freed the leather industry from this obnoxious and often expensive process.

It was determined that the enzymes present actually perform the bating operation, and Dr. Otto Rohm determined that it was possible to extract these same enzymes from the pancreatic glands of certain animals, particularly cattle and pigs. The pancreas is dried, ground fine and mixed with about 60% of Ammonium Chloride or "boric acid" and 35% of wood flour. This material gives the necessary deliming to the proper pH, and the enzymes present give the other desirable effects.

There are many types of bating materials on the market today, and while extravagant and unsubstantiated claims are made for some products, there is no doubt the strength and the character of a bating material are of importance. The proper selection of a bating material cannot be made merely on the basis of its so-called enzymatic strength; the nature of the beamhouse processes employed at a given tannery, the kind of raw material used, and the finished leather characteristics desired must all be considered in choosing the proper bate. The greater the knowledge of the tanner and leather chemist as to the function of bating, the more intelligently can they operate the processes.

Wood and his contemporaries proved that the active and necessary bate component is its proteolytic enzymes but, even today, our knowledge concerning the action of these materials is still quite limited. Before discussing this operation to any great extent, it is really necessary to define some of the terms used, as there is often a great deal of confusion regarding the definition of enzymes and bacteria. They are not the same or interchangeable. Enzymes are mechanical components - so-called organic catalysts, and although lifeless, are produced by all living forms of life, and often can be separated from them. Being catalysts, they can effect chemical changes when present in extremely small amounts. For example, invertase, and enzymes from the yeast can convert 1,000,000 times its weight of cane sugar to a mixture of glucose and fruit sugar, without in any way losing its activity. They are nature's

tools with which she does her chemistry, building up and breaking down her foodstuffs, her superstructures, and effecting her "repairs". Enzymes are equally effective in small quantities as in large, if sufficient time is allowed for the completion of the reaction. The use of higher concentration of the enzyme speeds up the velocity of the reaction, but does not affect the final product.

There is usually an optimum pH value for each enzyme, and the following are some examples:

Pepsin	- 2.0
Saccharas	- 6.0
Rennase	- 7.0
Lipase	- 7.0
Trypsin	- 8.5

The majority optimum pH valuation is between pH 6.0 and 8.0, that is, either just slightly acid or alkaline. Some enzymes are practically inert outside a very narrow range of pH values, thus trypsin is almost inactive in acid or neutral conditions, but very active in slightly alkaline solutions.

When the effective agent in puering was first sought, it was thought to be the bacteria which were detected, and the puer cultures of this bacilli were put on the market as a substitute for the dung. When it was discovered that the enzyme produced but this bacilli, and not the living organisms which brought about the bating effect, then enzymes in puer were precipitated and investigated, and were found to be the following:

Diastase	- Convert starch into sugar.
Rennase	- Curdles milk.
Lipase	- Hydrolyses fats.
Pepsin	- Hydrolyses proteins in acid medium.
Trypsin	- Hydrolyses proteins in alkaline medium.

It is most unlikely that either diastase or rennase play any roll in bating, but lipase may possibly function on the lime soaps and fats in limed skin. Pepsin could function if the skin was acid, but since it is always alkaline, there only remains trypsin as the effective bating agent. Trypsin, the chief bating enzyme, is a proteolytic enzyme, that is, it acts on protein material, hydolyzing, and so rendering it soluble. Proteolytic liquor actually means protein liquified.

The effect of trypsin is best seen in its action on solutions casein and gelatin. Solutions of casein can be precipitated by adding acid, but after the action of trypsin on such solutions, the amount of precipitation is reduced either partially or entirely. The trypsin has hydrolyzed or broken up the casein molecules into soluble products. Similarly, a 5% gelatin solution will no longer set after it has been reacted on by trypsin, which shows that the gelatin molecules have been disintegrated by the trypsin. Trypsin exerts only a slow hydraulic effect on collagen, though some is dissolved by its prolonged action. We know that liming causes collagen to become swollen, and we also know that this swelling can be largely removed by merely deliming with a suitable acid. However, it is believed by many that the swelling is not completely removed by the acid, that is, it is believed that a more completely fallen condition results from the application of both the deliming agent and

trypsin. The theorists say that liming probably initiates a peptisation process on the collagen fibers, that is, a weakening of some of the cross linkages between the fibrils, and moreover, that the effect of the trypsin is to continue this weakening or rupture, that is, it further opens up the collagen fibers begun by the liming operation, thus leading to enhanced absorption of the tanning material, and a quicker penetration.

We have considered enzymes as to types, activities, and specific actions in the hide. Now, let us consider for a short time, bacteria. Bacteria are the most forms of life— thought to be plant life -- and live on all types of foodstuffs, including proteins, fats and carbohydrates. They do this by means of the enzymes they produce. In simple language, bacteria may "eat" a hole in the skin with which they happen to be in contact. This is a local action. However, enzyme products, on account of their dispersion in the water, can exert only a general and diffused digestion, thus their action is not specifically localized. Therefore, by using a definite quantity of a standardized enzyme product, the action is uniform when at all reasonably applied, whereas with fermentation processes (that is, bacterial action) the results are dependent to a very great degree on the skill and experience of the person handling the operation, and at best, it is very difficult to standardize the operation.

Much experimental work has been done on the effect and control of bacteria in hides. The following is a very interesting experiment taken from one of the early works in this particular field:

A piece of clean corium was divided into three pieces. These pieces were weighed, and one was placed in sterile, distilled water, another piece in dextrose solution, while the third piece had a few drops of blood smeared on it and was then placed in distilled water. After soaking 48 or 72 hours, the three pieces of corium were transferred to a saturated lime solution (containing excess lime) and at the end of 24 hours, were weighed. The results were quite striking. (see table) The addition of a few drops of blood to the corium produced a large growth of proteolytic bacteria on it, causing it to become depleted and decomposing, and produced a loss of the ability to swell in the lime solution. The addition of dextrose, with the corium, caused the growth of non-proteolytic bacteria, and resulted in a much swollen corium, a large white weight gain, and no decomposition. Many experiemnts of this type have been run in an attempt to gain information regarding bacteria and their action on the hides. It is definitely known now that bacteria is undesirable and that, particularly, their action must be controlled. Thus, any reaction that depends upon their use is naturally a risky and usually a difficultly controlled reaction. We know that these bacteria can multiply very rapidly. We also know that they can concentrate their action on a localized area, so that it is possible a hole can be eaten entirely through the hide, while the remainder of the hide is not affected; and lastly, we know that their activity is a function of temperature and pH conditions. Fortunately, as we have already discussed, the proteolytic or collagen liquified bacteria are quite inactive in the green salted state and, also, in the lime state. However, if one depends upon the use of stale soaps, warm soaps, or even long soaps, the possibility of their action is greatly enhanced during this period. It is for this reason, that bactericides are often suggested for use in the soaking process.

TABLE

About 20 grams of Corium. 250 cc of Water and 250 cc of Lime Solution used in each instance.

Hours in water at 20°C.	Food added to water or hide	Hours in lime solution at 20°C.	Percent white wt. gain	Percent loss	Appearance of hide	Kinds of bacteria present in water surrounding hide
72	None	24	2.72	--	Fair	Few proteolytic and non-proteolytic
72	3% Dextrose	24	20.55	--	Excellent, plump and healthy	No proteolytic, manynon-proteolytic
72	Blood	24	-	71.59	Extreme decomposition	Large number of proteolytic

NOTE: Part of the swelling noted with dextrose solution is doubtless due to fermentation products, directly or indirectly.

The use of enzyme preparations, along with deliming agents such as Ammonium Chloride or Ammonium Sulphate, have removed the danger of any great bacterial action in the bating process under normal conditions, that is, at least we are adding material which contains bacteria, and depends upon bacterial action for its success. However, there are always bacteria present in the skin, even though they have kept dormant during the previous operations. These could cause damage if the bating operation was extended or not fully controlled. Bacterial growth is actively dependent on nutritive conditions, physical condition, acid or alkaline reaction of the environment, and respiratory conditions.

1. Regarding nutritive conditions, they must have a food supply upon which to live and grow.

2. Physical conditions. The effect of temperature on the growth and activity of bacteria, or on the hide, is important. It has been shown that bacterial growth and, hence, bacterial action is slow at low temperatures and increases with rise in temperature. Thus, a piece of corium soaked in sterile water at 24°C., and then in sterile calcium hydroxide at 24°C. for 24 hours, showed a slight percent weight gain of 1.68, and a fair amount of bacteria. A similar piece of hide soaked in sterile water at 37°C. for 48 hours, then in sterile calcium hydroxide 24 hours, was too decomposed to weigh, and there was a very large number of bacteria present.

3. The reaction of the Enviornment. It is well-known that the action of enzymes is greatly influenced by their enviornment and, this in turn, should affect the action of both proteolytic and non-proteolytic bacteria. This is clearly shown by the former results. A piece of hide placed in water alkaline to litmus with calcium hydroxide showed decomposition, and many proteolytic bacteria present after 72 hours at 25°C. A similar piece of hide placed in water acid to litmus with acetic acid, showed no decomposition after 72 hours and few proteolytic but many non-proteolytic bacteria were found to be present. Thus, it is readily seen that the alkaline reaction favors decomposition, whereas the acid reaction retards or inhibits it. In this particular case, the reaction is not as alkaline as would be experienced in liming, where we know the conditions are so alkaline as to again inhibit bacterial action. We also know from experience that we can preserve the skins very nicely in the acid condition, that is, in the pearl, without any great trouble and over long periods of time.

The above experiments explain this observed condition.

4. The respiratory conditions. Bacteriologists have quite completely established that certain bacteria will grow in the presence of oxygen, but not in its absence; and conversely, that other bacteria grow best in the absence of oxygen. It has been found by experiments that the proteolytic bacteria which attack the hide require oxygen for their growth and activity. If they are exposed to a large excess of carbon dioxide, they are rendered inert.

We might summarize the factors which favor bacterial temperature of the hide as follows:

Proteolytic bacteria - The presence of protein substances such as blood, a slightly alkaline reaction of the environment, a warm temperature, and the presence of oxygen. Conversely, the reverse of these conditions will naturally prevent bacterial decomposition.

BATING

Second Year - Lecture #7

The operation of bating is one which has been surrounded by mystery and confusion for many years. Probably more conflicting theories have been offered to explain the mechanism of bating than for any other operation in the tannery. Many of these theories have been based upon incomplete or specialized experimentation, or upon analysis of the effects observed in the finished leather. We have already seen in our study of the operations leading to bating that variations in temperature, time and concentration each have an effect upon the finished product. Moreover other factors which must be controlled or reckoned on such as bacteria, their enzymes, the type of hide and its condition, in turn offer additional difficulties. Thus it is quite easy to understand the difficulty which has been experienced in determining the definite effects of the bating operation in the presence of these other variables. The wonder of the matter is that we have been able to get as far as we have in the little time that concentrated study has been applied.

It would be useless to attempt to explain or outline any one particular bating treatment, for little of value would be derived as we know that this treatment must be carried out in such a manner as to allow for the conditions of the previous treatments as well as for the subsequent ones. It would seem to be more reasonable to attempt to learn what is accomplished by bating in a general way. Thus, if we can arrive at any general conclusions we may then use these in understanding and varying our particular processes.

Wilson's Theory

Our author (Wilson) lists the following actions taking place in the bating operation as being sufficiently important to merit consideration.

1. Removal of degradation products of the epidermal system; hair, epidermis and glands.
2. Hydrolysis of elastin fibers.
3. Hydrolysis of collagen fibers.
4. Falling
5. Regulation of pH value.
6. Deliming.
7. Bacterial action.

1. It is his belief that the degradation products of the hair, epidermis, etc. formed by the action of the lime and the sharpening agents, such as sulfides, used; are further degraded and removed by the action of the enzymes. He considers that to be the most important function of the bating operation.

2. Wilson performed experiments which led him to believe that the elastin fibers in the grain layer are removed. However, he indicated that the degree of removal was a function of the time. Moreover, for what he considered to be

complete removal a very long bating was required. In conclusion he admitted that he made excellent leather without the removal of elastin.

3. In his studies of the hydrolysis of collagen fibers by trypsin, the active enzyme in bating material, he concluded that considerable time is necessary for complete destruction. He postulated that the action is slow but that it is appreciable in ordinary bating.

4. Falling is the opposite of plumping and experimentation has shown that protein material such as a skin will swell to a maximum point on the acid side at about a pH of 2.5 and on the alkaline side at about a pH of 12.5. Intermediate between these points there are minimum points of swelling often referred to as points of maximum falling. On the acid side the value is pH 5.0 and on the alkaline side the value is about 7.5. This latter value of 7.5 is of interest as it is at this point that maximum enzyme activity takes place in bating. Wilson indicates that maximum falling is a function of temperature, however we must assume that all other factors are constant.

5. Wilson believes that the uniform pH obtained in the bating process is necessary for subsequent operation of tanning. That is, if it is not uniform it will be tanned variably. Thus, if all of the skins in a pack are not uniformly at the same pH the tanning will be different in skins within this pack.

6. It is Wilson's belief that true deliming does not take place in the bating operation without the addition of acid. He prefers an acid treatment before bating.

7. Bacterial action was found to be a factor by Wilson in the following cases; continued use of the same bate liquor and increase in temperature to a range which will encourage growth. His use of bates made from mixtures of old bate liquors with new liquors is interesting. This merely brings forward the old controversy regarding the use of enzyme preparations alone as against bacterial action on the hide.

Theis's Theory

In many ways Theis considered the possible effects of proteolytic enzymes in the bating treatment as did Wilson. In his theory he adds two factors not directly considered by Wilson.

1. Effect upon the reticular tissue of the skin.

2. Effect upon the coagulable proteins (albumins, globulins, etc.) which may remain in the limed skins.

In addition it was his belief that the presence of enzymes is essentially without influence upon the falling of the whole skin during bating.

It might be proper to add that in his book Theis indicates that bate enzymes have little or no effect upon skin collagen, elastin or reticular tissue. In his conclusion he states that, "The only necessary enzymatic action which appears to have been reasonably well established to date is

the dispersing effect of proteolytic enzymes upon the interfibrillary protein present in the skin as it reaches the bate paddle." he goes on to state that the extent of enzymatic action required is entirely dependent upon the nature of the soaking and liming which has preceded the bate. Thus following his theory, if a large proportion of interfibrillary protein has been removed in the soak by the addition of sodium chloride, or of sodium polysulfide, the bating treatment must be reduced, or "inferior leather will result." Conversely, "If the bulk of interfibrillary matters has been left in the skin, a more drastic bating is required."

There are several of Theis's statements which require amplification. For it seems that if, as he states, the enzymes in bating have no effect upon elastin, collagen or reticular tissue, and that they merely attack and remove the coagulable proteins; there should be no great effect upon the finished leather if the treatment were run a little too long or too strongly. It certainly seems that there should be no necessity for allowing for the slight variation in quantities of these proteins removed in the soaking or liming processes.

English Theory

The theories as generally held by the British researchers is well expressed by Woodroffe in his book. To start off he states that bating brings about the following results in the skin:

1. Removes most of the lime.

2. Produces a silky grain.

3. Removes all swelling and plumping (bated pelts are slippery, non-elastic or flaccid).

4. The scud or dirt, short hairs, grease and lime soaps, dark coloured pigment traces of epidermis are all loosened and easily removed by scudding.

5. Remains of hypodermic tissue (flesh) are loosened so that they can easily be removed by scraping.

6. Air can be forced through skins.

7. Increases the degree of stretch possessed by the finished leather.

These effects are predicated largely upon the belief that the weakening effect upon the cross linkages between adjacent collagen fibers and fibrils begun in the liming operation is continued by the tryptic enzymes in the bate material. It is stated that this enhances absorption of the tanning material and leads to quicker penetration.

It is stated that preliminary swelling of the collagen with neutral salt solutions or the presence of these salts in the bate liquor renders the collagen more susceptible to hydrolysis by trypsin. Thus it is believed by Woodroffe that the effect of trypsin on collagen depends on the previous history of the pelt and particularly on the degree of swelling to

which it has been subjected. He states that swelling is the initiation of a peptizing action whereby the pelt is rendered more highly susceptible to the action of trypsin.

Woodroffe further states that the severence of the cross linkages between fibrils produced new points of chemical activity and that the tanning material can combine with these polar groups set free.

He feels that the slippery feeling noticed on the skin surface may be partly due to the conversion of the outer surfaces of the fibers into gelatin. He states that this may be brought about first in the liming and lastly by the enzyme trypsin in the bating.

Removal of the hair roots and scud is predicated on the mechanical removal of these materials as a result of the loss of swelling. This is further enhanced he states by the weakening of the network of elastin fibers which surround the hair follicles and impede the exit of the hair.

Regarding porosity Woodroffe states that this is related to the closeness of the packing of the fibrils and fibers. He states that any action which cleanses the fibers, reduces their thickness or removes any interfibrillar matter will tend to increase porosity. Thus he feels that the chief cause of increased porosity is due to the separation of the fibers and fibrils. In his book he adds that the reticular tissue is primarily responsible for binding together the collagen fibers into bundles and causes the constrictions in the bundles when they are swollen with acids or alkalies. "This tissue is weakened by prolonged treatment with lime liquors but it is digested by trypsin under alkaline conditions. Such weakening and digestion of the reticular tissues releases the fiber bundles and fibrils from this encircling and constricting tissue and so produces fine splitting of the collagen fibers and fibrils because, 'fine splitting can only take place if the reticular tissue is ruptured to the proper degree'."

He feels that it is probable that the stretch and "run" in glove leathers is due to the removal or considerable weakening of the reticular tissue, which constricts the fiber bundles and gives resilience. In his consideration of the effect of bating on the elastin fibers he feels that while their complete removal is not a function of bating, wrinkles and growth marks are more easily eradicated from the skin if the elastin is weakened or removed.

Turley's Theory

In one of his talks Turley states, "I believe that bating or puering is essentially a 'balanced action' consisting of two distinct phases, one a scouring or cleaning action removing the remnants of the epidermal system - the so-called 'scud' - left over from the liming process, the other the bringing of the fibers of the connective tissue to the right physical condition for the subsequent tanning. The first action is brought about by enzymes, the second by materials which remove lime or other alkali from the collagen fibers."

In practice he states that there are all degrees of these two actions, ranging from mild to relatively enzyme action, and partial or complete liming. In the production of one and the same kind of leather, some tanners

today practice either partial or complete deliming, and each has its own significance in the manner in which it "balances in" with the preceding and subsequent leather making processes.

Kritzinger's Theory

Kritzinger performed considerable research, particularly along the lines of protein chemistry, to determine the effect of the various beamhouse treatments on the hide. He felt it to be reasonably safe to attribute the fallen condition of bated stock mostly to the removal of line and the dressed swelling (hydration) by means of acids during deliming or acid salt used in conjunction with bating. He says that no amount of ordinary deliming will produce stock through which air and water can be squeezed or which will produce soft leather. He points out in his work that flesh splits are only negligibly affected, if at all, by bating, but that grain splits are affected most markedly.

The presence of lipolytic enzymes is given to explain some removal of fats. This plus the warmth of the operation will wash out some of the lipids. To these factors he attributes at least part of the effect of "slippery" feel of bated stock.

The following functions are stated by Kritzinger to be the essentials of normal bating;

1. Deliming and decreasing of the alkaline swelling whereby the differences between the various structures are smoothed out.

2. Opening up of the structure so that water and air may pass through freely by removal of the interfibrillar proteins which remain especially in the corium minor despite the previous processes.

3. Breakdown of the erector pili muscle and adjustment of this muscle to a higher temperature whereby a smoother grain is assured.

This last function is interesting and has not been considered before. It is based on the assumption that the erector pili muscle is still quite able of contraction even after bating, in some cases. If a skin from a light but warm bate is dumped in cold water there is sure to be a contraction of these muscles to give rise to gooseflesh. If the stock is tanned in this state, then the grain is bound to be rough and coarse. Similarly stock from the cold lime liquors and deliming bath will show coarse grain due to the gooseflesh.

Work performed by Anderson showed that bating affects the muscles and breaks down the protein as well as eliminating gooseflesh by the warm treatment. Thus concludes Kritzinger, the smoothness of the grain in bated stock is, therefore, largely a function of the breakdown of these muscles. But at the same time it is also due to the bate smoothing out the different degrees of swelling in the various fibrous structures. The porosity is probably largely due to removal of the interfibrillar proteins.

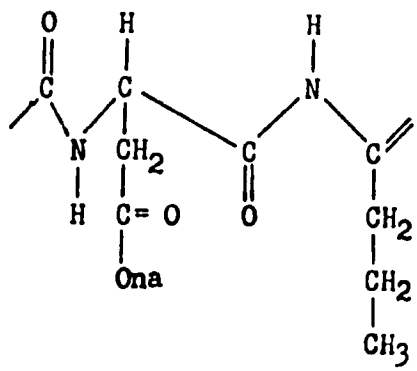
PICKLING

Second Year - Lecture #8

The term "pickling" may be defined as the process of treating bated hides and skins with mixed solutions of acid and salt. The process is of importance for two different reasons, namely, the conditioning of hides and skins for subsequent tannage or the preservation action necessary for their long storage.

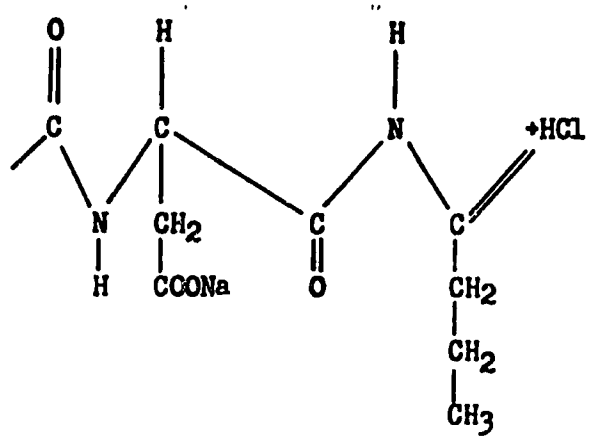
'Turley' stated that pickling is a prelude to tanning and may in some ways be considered as an initial tannage in that the skins are preserved in this condition and their character out of the bate is fixed or set. - "Pickling may influence the qualities of the finished leather to a marked degree and any marked deviation from the normal procedure cannot afterwards be satisfactorily compensated for."

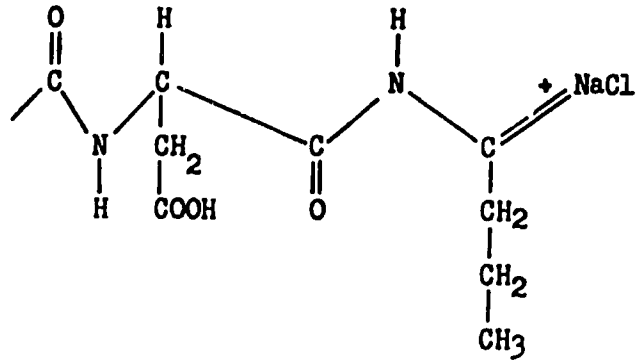
During contact with the alkaline unhairing bath, the skin proteins have become swollen and alkali-fixation has occurred corresponding to that normally obtained at pH 12.5 to 13.0. The sodium and calcium ions are bound to the proteins thusly: -



In addition to the Na or Ca ions thus fixed, unbound alkali is diffused throughout the skin tissue. This, however, is usually removed in the subsequent bating and washing operations, and can be largely discounted. During the bating process, the pH value of the skin tissue is decreased from 12.5 to a value of about 7.5 to 9.0 depending on the manner by which the operation was carried out. In consequence of the bating operation, a portion of the bound alkali is removed and only that alkali remains which corresponds to that normally present at the particular pH value of the bating.

During the early period of pickling, the acid acts first upon the protein-alkali compound, thusly:





Most pickle solutions used have an equilibrium pH value ranging from 1.5 to 2.5. If acid alone were used, the hide would swell beyond that which is desired. If salt is present, however, the amount or degree of swelling can be controlled. It is in this particular pH range that maximum acid swelling takes place and, therefore, sufficient salt (NaCl) must be added so that only the desired degree of swelling occurs.

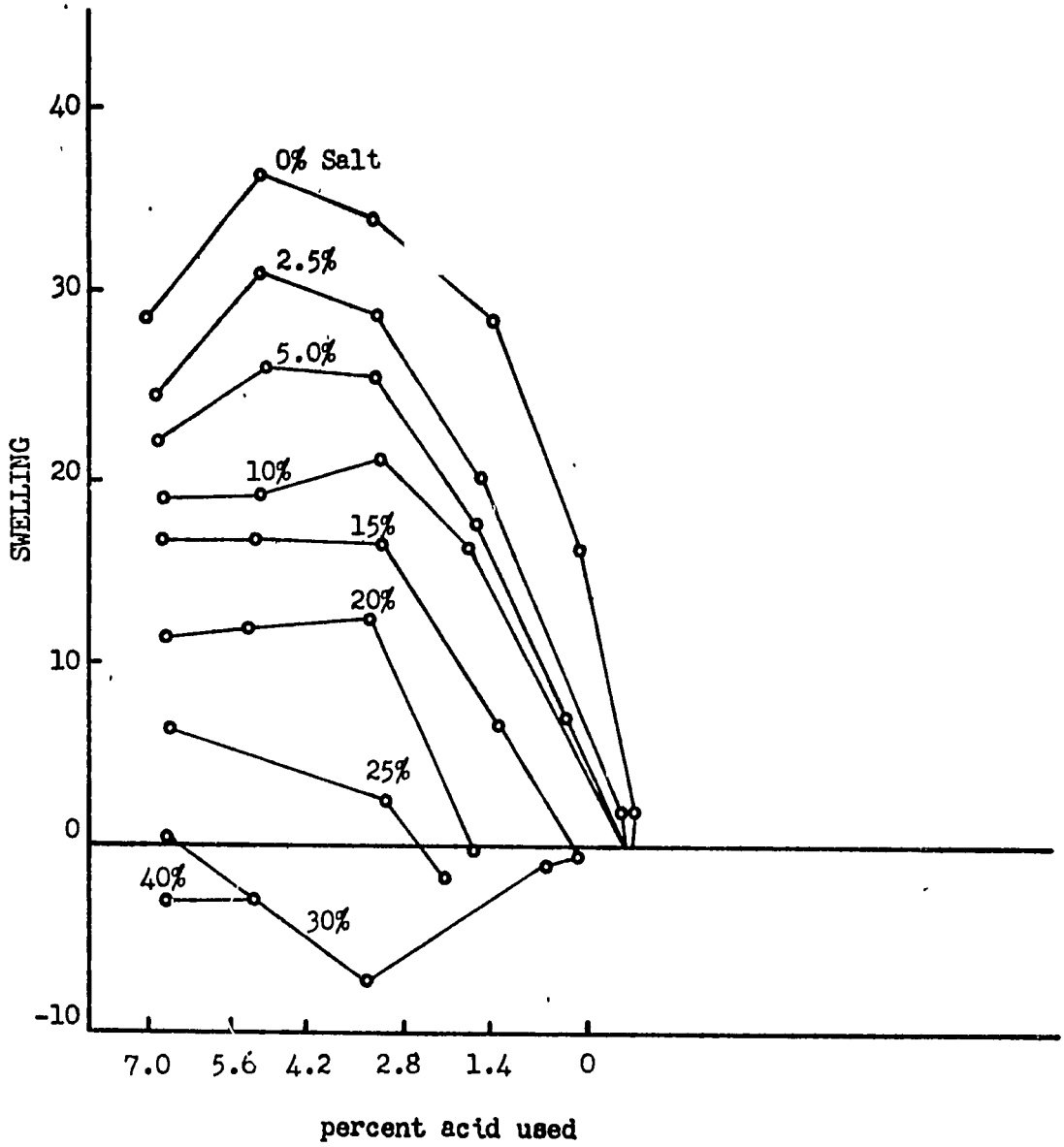
In addition to the bound acid, the skin contains or holds within itself a certain amount of acid-salt solution and for this reason both the bound and free acid in the skin must be taken into account in the subsequent tannage.

The following factors were established, by Dr. Theis in his work, to be necessarily considered:

a. Acid concentration.
b. Kind of acid.
c. Neutral salt concentration.
d. Volume of pickle solution in relation to skin.
e. Hydrolysis and peptization factors.
f. Temperature effects.
g. Deliming effects.
h. Preserving effects.
i. Effect on skin grain.
j. Effect on subsequent tannage.

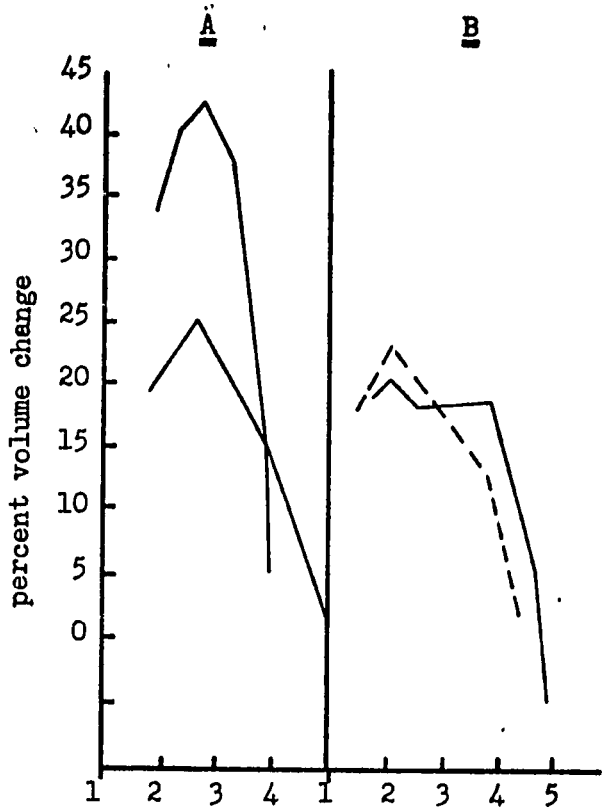
The acid-salt relation on swelling or weight gain is quite important and the following graph depicts this quite well. It is of interest to note that for any given acid concentration there is a definite depression in swelling caused by the added salt. This depression of swelling is much more

pronounced in the region where acid solutions containing no salt give a maximum swelling value.



With the use of between 20 and 27.5 percent salt there is no rise to a maximum swelling value at the higher concentrations of acid. For the lower concentrations of acid, the swelling curves decrease sharply with decreasing amounts of acid. For the 30 and 40% salt curves, it will be noted that over the whole range of acid concentration there was no swelling, but in fact a negative swelling effect.

The maximum swelling of skin in a sulfuric acid solution (no salt) is considerably less than that with hydrochloric acid.



Final pH of Pickle

Section A

Shows swelling versus pH for hydrochloric acid (HCl) and sulfuric acid (H_2SO_4).

Section B

Shows swelling versus pH for hydrochloric-sodium chloride (HCl-NaCl) and sulfuric acid-sodium chloride (H_2SO_4-NaCl).
150 milli mols NaCl per liter

It is interesting to note that even though the hide showed different swelling capacities in the different acids, the depression value of swelling by salt was practically the same.

Hydrolysis and Peptization of Skin

'Theis' in his work on pickling came to the conclusion that the H_2SO_4-NaCl system should give a more solid and firmer piece of leather than the HCl-NaCl system. This assumption was based on work whereby he determined the amount of nitrogen evolved in the pickling operation in terms of varying NaCl concentration with both H_2SO_4 and HCl. He also measured the effect of temperature on these same variables. Thus, as he found less nitrogen evolved, in each case, for the H_2SO_4-NaCl pickle he concluded that less protein is hydrolyzed and thus that this pickle should give a more solid and firmer piece of leather.

Effect of Volume Ratio

Most pickling is performed on a volume ratio of ten parts of pickle liquor to one of bated skin (10-1). Work has been performed which shows that these ratios can be varied quite widely, above certain low minimum values, if the pH of the pickle solution is kept constant and the amount of salt varied correspondingly. That is, the pH of the pickle is important, in relation to the equilibrium effected in the hide by the amount of acid bound up by the hide. Thus it does not matter how much acid water solution there is surrounding the hide once it has reached equilibrium. However, the salt concentration must be varied widely as the solution volume is changed in order to keep the salt ion concentration constant.

The Nature of Swelling

When we place a skin in a pickle solution it will swell to various degrees (and may even fall) depending upon the amount of acid and salt present. The crux of the matter is to select that degree of swelling which seems to give the best leather for our particular tanning operation and then control this so that we can attain equilibrium within the hide just before pickling is stopped at the particular ratio to give the desired swelling.

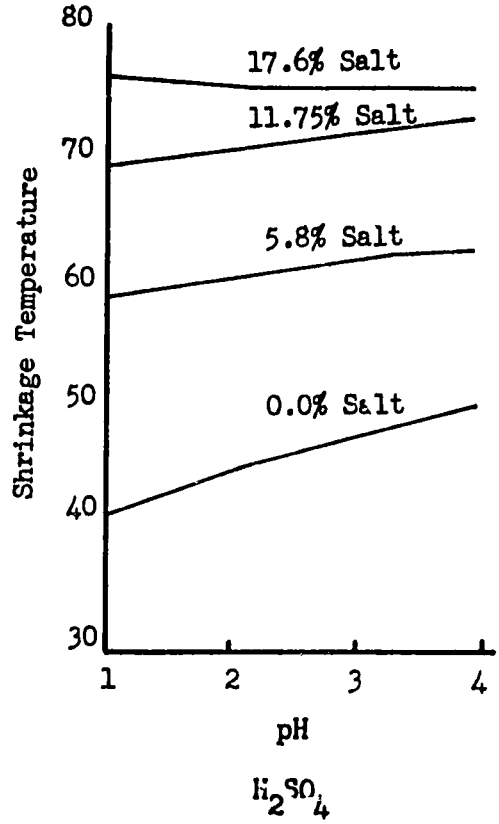
It has been shown that in a hide or skin the equilibrium is almost completely attained after two (2) hours. From this point on it would be most important to be able to adjust the acid salt ratio to just that which has been determined by swelling experiments to be the desired point. Another two (2) hour period would pretty well give equilibrium throughout the adjusted hide. No doubt under normal conditions this might easily be maintained for many hours is so desired.

Swelling has been defined as due to the flow of liquid from the less concentrated solution to the more concentrated solution either within or outside the skin as the case may be.

One other point to note in this equilibrium is that the bound acid in the skin is usually balanced by the amount of tanning material which will displace it. However, the free acid exerts effects as it enters the tan liquor and changes its pH or composition. This is particularly evident where there is a variation of salt-acid ratio from pack to pack which is in turn tanned by a liquor of uniform concentration.

Thermal Stability

The following graph shows the effect of increased salt concentration on shrinkage temperature.



These data show for the skin pickled in such solutions:

a.) that as the pH value of pickling increases, the resistance to temperature increases,

b.) that this increase in temperature resistance continues as the salt concentration of the pickle is raised, and

c.) that if sufficient salt is present in the acid pickle, regardless of pH value, the resistance to temperature becomes almost constant.

Pickling for Preservation

Pickled skins are usually divided into two categories: one, skins which have had only a light pickle, and the other, skins which have been strongly pickled. In the first case the skins may have been pickled for only a few hours in a dilute pickle and are expected to be tanned within a few days at most. This type of pickling is in preparation for subsequent chrome tannage. If such skins are held in the "pickled state" mold growth often ensures and may cause considerable damage.

In the second case, skins with a "high" pickle may be held for several months before processing.

Molds are not exacting in their requirements for growth in that they grow well upon most moist organic material and over a wide range of pH values. Molds found belong to about three major families. Certain colors or pigmentation are associated with mold growth - black, green and red seem to predominate. The pigment produced may exist in the part of the mold above the surface of the skin, in the seed-like parts. This is easily, mechanically removed. If, however, the root-like parts produce the pigmentation, it is much more difficult to remove. And last, if the color is not confined to some part of the mold, but diffuses into the skin itself, the pigment acts like a dye and is likely to remain throughout the subsequent processing. Molds under favorable conditions may secrete a great variety of enzymes, viz: Lipase, amylase, raffinase, zymase, invertase and protease. Some of these are proteolytic (dissolve proteins) and may actually digest the skin itself.

It has been found that mold growth is generally inhibited by the presence of more than 12 percent salt; but some molds have a greater salt tolerance than others.

A pickle with 12 percent salt and 1.5 percent sulfuric acid was found to be very satisfactory. The addition of 1 percent sodium acetate made the pickle much more efficient in preventing mold growth. Also, addition of 0.025 percent para-nitrophenol aided materially in this respect.

Depickling

Pickled sheep and lamb skins generally contain 2.4 to 3.0 percent of salt and about 1 percent of sulfuric acid. If such skins are immersed in water, the ratio of salt to acid which diffuses into the water cannot exceed 2.4 to 3.0, which is far below the limit of 8 to 1 necessary to prevent the swelling of the skins in a pickle. Consequently, the effect of immersing pickled skins into water is to produce swelling. The addition of 5 percent of salt to the water increases the ratio of salt to acid to 7.4 to 8.0 which is sufficient to prevent swelling.

A method used to prevent this swelling is to remove or neutralize the acid, a process known as depickling. Pickled skins can be depickled by drumming them with cold water containing 5 percent of sodium thiosulfate, or borax equivalent to their acid content. The use of hypo results in the formation of sulfur which is absorbed by the pelts and produces a slight sulfur tannage.

$$Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + S + SO_2$$

This sulfur tannage is slight and does not affect subsequent tannage beyond bleaching the color of the grain.

Skins which have been pickled and depickled are different from those which have not been subjected to these two processes. Many natural tanning materials contain weak acids or salts of weak acids which are present in sufficient quantity to remove the acid in the skin carried over from the pickling operation. Chestnut, myrobalans, hemlock and sumach are such materials.

QUANTITATIVE ANALYSIS

Second Year - Lecture #9

Chemistry became an exact science when quantitative methods of analysis were introduced. The progress of modern chemistry is dependent upon exact quantitative measurements. The composition of matter and its transformations are determined by precise analysis.

Scope of Quantitative Analysis

Quantitative analysis has for its object the determination of the quantities of constituents present in a given amount of compound or mixture. For convenience it is usual to divide the subject of quantitative analysis into two branches: the one dealing with the analysis of the various compounds of the metallic and non-metallic elements, - this is known as inorganic analysis; the other dealing with the analysis of the compounds of carbon with hydrogen wherein the hydrogen can be replaced entirely or in part with oxygen, nitrogen, chlorine, or sulfur, - this is known as organic analysis.

Methods of Quantitative Analysis

In general, to effect an analysis the procedure of the analyst is to prepare a representative sample, then effect its solution by appropriate means (that is assuming that he is working on a solid material such as salt, wattle, etc.) From this point on the further work of the analyst really divides itself into two quite distinct steps, the first having to do with the isolation of the desired constituent from such of the others as might interfere with its subsequent determination; the second having to do with the actual determination of the desired constituent after the previous removal of the interfering constituents.

Thus in analytical work we often attempt to analyze a solution for a certain constituent while it is in the presence of other components of a solution. We must always work in such a manner that the presence of the undesirable components does not in any way affect the accurate determination of the desired constituent. We then determine a method which will separate this constituent only and completely from the solution or we treat it with another chemical solution of known quantity which reacts with the desired constituent equally and in a measurable manner.

There are four general methods of analysis employed:

1. Gravimetric method.
2. Volumetric method.
3. Colorimetric method.
4. Gas analytical methods.

Actually the names of each of these methods is a clue to the manner in which they are performed. Methods #1 and #2 are the most common employed in our industry and thus we will concern ourselves mainly with them in our discussions. In gravimetric analysis the desired constituent is obtained as a precipitate by the use of a chemical precipitating agent, the precipitate so obtained being purified and weighed.

Volumetric methods of analysis are the so-called titration methods, in which the amount of the desired constituent is determined by allowing it to react with a measured volume of reagent. Thus if we wished to determine the exact amount of acid present in a pickle we would titrate a measured volume of the solution with an alkali of known strength, determining the exact amount of alkali necessary to neutralize (or equal) the acid present. Then by simple calculation the exact amount of acid present would be known.

Ionic Nature of Reactions

Most of the reactions upon which quantitative methods are based take place in aqueous solutions and are, for the most part, ionic in nature. The solutions of reagents, and samples, consist most generally of solids, liquids, or gases dissolved in water. The most important property shown by aqueous solutions of inorganic materials is that the dissolved matter ionizes (dissociates) more or less into electrically charged atoms called ions. The extent or degree of ionization varies much with the nature of solute and solvent as well as with the concentration and temperature.

The Law of Combining Weights

The chemical composition of a pure compound is always the same. That is, a given chemical compound always contains the same elements united together in the same proportions by weight.

Thus water, H_2O, is always the same in composition anywhere and any time. It is always made up of two atoms of hydrogen combined with one atom of oxygen. Thus, if we analyze a unit weight of water, say 1 gram, we will find it to contain 0.1119 gram, or 11.19 percent by weight, of hydrogen and 0.8881 gram, or 88.81 percent by weight, of oxygen.

We already know from our work in the first year that all of the elements have a relative weight called the atomic weight. This weight has no definite value, but is merely a relationship between various elements showing how much greater or less in size and mass one element is than another.

Again we know that elements, and compounds made up of elements, combine in definite whole units according to their valence. By adopting the system of atomic weights we are enabled to calculate the composition of pure compounds and the proportions by which elements and compounds enter into reaction. It necessarily follows that the combining (atomic weights) are directly proportional to the actual weights. This is in brief, the Law of Combining Weights, which can be stated thus:

> Reactions take place between weights of chemical substances which are proportional to the atomic or molecular weights of the reacting elements or compounds.

Thus, if we know the actual weight (in grams, pounds, grains, or any other units) of one of the components, we can by a simple direct proportion between the actual weights and the combining weights calculate the actual weight of the other components of the reaction. This relationship is the basis of quantitative reactions.

Errors and Precision

Because quantitative analysis is concerned with small quantities the laboratory apparatus and techniques used must be very accurate in order to arrive at precise and useful results. The errors of an analytical method are of several different kinds, some of which can be reduced to a negligible amount and other cannot. Errors arising from careless technique much as faulty sampling, mistakes in weighing, incomplete precipitation, washing and ignition, losses of material or inclusion of dust and foreign matter during manipulation, failure to match end points during titrations, disregard of temperatures, and mistakes in recording and computing data - all of these can be practically eliminated by paying the closest attention to the details of manipulation, by the use of clean apparatus and by developing a certain amount of skill and dexterity in technique.

Theory of Gravimetric Precipitation Methods

Gravimetric methods of analysis are those in which the desired constituent is separated and weighed in the form of a pure compound or pure metal. In all cases the determination rests upon a direct weighing of the final product. That is, we actually completely remove the thing that we wish to measure from the solution in which it is dissolved. We do this by treating it with a particular chemical agent which will cause it to precipitate as a solid. Then we can filter the solid material from the solution, dry it and weigh it. Thus, if we wish to accurately determine the amount of salt in a particular pickle, we take a carefully measured volume and treat it with silver nitrate $AgNO_3$. Silver chloride is formed and as silver chloride is very insoluble in water, it precipitates and the silver chloride is filtered, dried and weighed. Actually we measure the amount of sodium chloride (NaCl) which was present in terms of the silver chloride which was formed and precipitated.

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl\downarrow$$

The usefulness of this reaction and all reactions of gravimetric analysis hinges on at least four important requirements.

Completeness of Reaction

It is quite evident that in order to measure the NaCl present in terms of the AgCl formed, all of the NaCl present must be converted to $NANO_3$ and AgCl. Now last year we learned that in all chemical reactions of this type a point of equilibrium is reached. That is, the NaCl and the $AgNO_3$ will combine to yield $NaNO_3$ and AgCl up to a certain percent, at which point no more is formed.

Say for instance:

$$NaCl + AgNO_3 \xrightarrow{95\%} NaNO_3 + AgCl\downarrow$$

This means that 95% of the NaCl and $AgNO_3$ is combined to form $NaNO_3$ and AgCl and that 5% of the AgCl + $AgNO_3$ is still present due to the fact that a point of equilibrium has been reached. Theoretically this means that if some of the AgCl and $NaNO_3$ formed were to recombine to form $AgNO_3$ and NaCl that a corresponding amount of NaCl and $AgNO_3$ would then be free to combine in order to maintain the equilibrium or balance.

However, we also know that when one of the products formed can be removed as a gas or a precipitate the equilibrium is displaced in this particular direction and often becomes virtually complete. This is the condition which is desired in all good gravimetric work.

Insolubility of the Precipitate

It is quite easy to see from the above that the precipitates formed must be very insoluble for two reasons:

1. In order to cause the equilibrium to shift to the right for complete formation of the product desired.

2. In order to have all of the product formed in a form which may be separated from the other materials and which when weighed represents virtually all of that material which was present.

Physical Characteristics of the Precipitate

Odd as it may seem, we have to practice care and often additional treatment in order to have the precipitate in a form which is readil handled. The ideal characteristic of a precipitate is a coarsely crystalline state, in which condition filtration and washing are most easily accomplished. If the precipitate is too fine or is gelatinous it is quite easy to see that considerable trouble might be experienced in removing it from the original liquor.

Definiteness of Chemical Composition

The precipitate must be freed from adsorbed impurities by washing and filtration and then dried or ignited to a form whose chemical composition is known, before it can be weighed.

Technique of Gravimetric Analysis

There are several important steps which are followed in all gravimetric analyses:

I. Sampling

This must be carefully taken in order to be representative of the entire batch. In the case of liquids the mass should be well stirred or several samples taken from different levels and combined and the final sample taken from this mixture. This last procedure is also followed for solids.

II. Weighing the Sample

The sample of the precipitate formed as the case may be, must be weighed n an instrument sufficiently sensitive and accurate to give a reading three places beyond the decimal point.

III. Dissolving the Sample

In the case of a solid sample - say quebracho - the sample must be dissolved in order to properly treat it. However, in the case of the pickle which we have already discussed, the salt would already be dissolved and this step would not be necessary. In its place a carefully drawn sample would be measured in terms of volume, that is, a sample would be taken with a pipette which measured a definite volume, say 50 milliliters, very accurately.

IV. Precipitation

The chief concern in precipitation is to so arrange details, whenever possible, as to favor the production of large grained crys-

tals. This can be done by several techniques, such as, slow addition of the precipitating agent or precipitation in warm solutions.

V. Washing and Filtering

Impurities present must be removed either by washing the precipitate with suitable solvents or if the impurities are solid particles redissolving, filtering and reprecipitating.

VI. Drying and Igniting

If the precipitate is collected on filter paper it must be ignited at a temperature sufficiently high to burn all of the filter paper. If the precipitate is likely to be damaged at this temperature then it is collected in a porcelain crucible called a "Gooch" crucible. It is then put in an oven and heated just enough to remove the moisture.

VII. Cooling and Weighing

The crucible now being dry is placed in a desiccator to cool in an atmosphere free of water. This is done in order to obtain an accurate weight for if the crucible is warm it will cause air currents or convection and the balance will not come to a uniform resting point for accurate weighing.

The Calculations of Gravimetric Analysis

As stated previously, the calculations of gravimetric analysis are based upon the law of Combining Weights.

Thus, in the case of the amount of salt in a pickle:

$$AgNO_3 \ \& \ NaCl \longrightarrow NaNO_3 + AgCl$$

$$169.89 \ \& \ 58.45 \quad 85.00 + 143.34$$

The equation for the reaction is set up and the molecular weights for the reactants is placed under each reactant. If the equation is balanced and correct then these weights represent the relative amounts of each chemical present. Thus, we see that (1) one part of NaCl with a relative weight or value of 58.45 will yield (1) one part of AgCl with a relative weight or value of 143.34.

We can now set this up as a proportion:

$$\frac{NaCl}{AgCl} = \frac{58.45}{143.34} = \frac{x \text{ grams } NaCl}{y \text{ grams } AgCl}$$

Thus, if the original 50 milliliters of pickle yielded 7.00 grams of AgCl we would determine the amount of NaCl present in the original 50 c.c. sample as follows:

$$\frac{NaCl}{AgCl} = \frac{58.45}{143.34} = \frac{x}{7.00}$$

solving for x:

$$x = \frac{58.45 \times 7.00}{143.34} = 2.856 \text{ grams NaCl}$$

Thus, 50 milliliters of pickle contained 2.856 grams of NaCl, which in terms of percent would be calculated as follows, by determining the amount in 100 milliliters of twice that in 50:

$$2 \times 2.856 = 5.712$$

Therefore, the solution would be 5.7% NaCl.

QUANTITATIVE ANALYSIS

Second Year - Lecture #10

Volumetric Analysis

In the volumetric methods of analysis the weight of reagent necessary to complete a chemical reaction is ascertained by determining the volume of solution of known concentration required to react with the material being analyzed and from this weight the amount of desired constituent in the sample can be calculated.

The strength of the reagent must be accurately known and its total volume carefully measured. Some visible means must be provided for determining when the reaction is completed. The process of determining the exact volume required is called titration.

Theory of Volumetric Analysis

Reactions which are used as the basis of volumetric methods of analysis must go practically to completion. There are three main types of volumetric analysis used.

1. Volumetric precipitation methods
   This depends upon the practically complete precipitation of a compound containing the element. The precipitate is not filtered and weighed but an indicator is used which gives a color change at the very moment that the last amount of precipitate is formed, thus accurately indicating the endpoint.

2. Neutralization methods
   Neutralization is fundamentally reactious between acids and bases, and depends upon the interaction of hydrogen ions with hydroxyl ions. The neutralization of an acid by a base and of a base by an acid can be so arranged experimentally that a titration can be carried out, whereby the total acidic or basic strength of the solution may be determined.

3. Oxidation-reduction methods
   Method utilizing reactions wherein the particular element being analyzed is involved as in ion which undergoes an increase or decrease in charge. The transfer of electrons is involved between two ions in all of these reactions.

In order to have any reaction be acceptable for use in quantitative analysis it must meet two requirements:

1. The reaction must be essentially complete.

2. The reaction must be irreversible.

Standard Solutions

In all of the three main classes of volumetric analysis, the unknown constituent is brought into contact with another reagent with which it reacts according to some definite equation and to yield a product by one of the three methods already discussed.

It, therefore, follows that the accuracy with which we determine the unknown constituent is a function of the accuracy used in making up the reagent solution. The strength of the reagent must be known accurately and not be subject to variation. If then a measured volume of the reagent is added, whose exact strength is known, sufficient to complete the reaction with the desired constituent and a means is provided of telling when the reaction is completed, we have a method of determining the weight of constituent which has reacted with the known amount of reagent.

Here the law of combining weights is involved (refer to previous lesson) since reactions always take place between weights, here expressed in grams, which are proportional to the atomic or molecular weights of the reacting substances. In volumetric analysis the weights of unknown and reagents, which react according to the Law of Combining Weights, are dissolved in water and their ions usually react.

Thus the solution which contains the reagent must be accurately made up to be used as a norm, or standard, and is thus called a Standard Solution. The preparing of this solution is known as standardization.

Indicators

An indicator is a substance which must give a sudden color change in the region of the equilibrium point. That is, it must change its color at a pH value which is as near as possible to the equilibrium point reached in the reaction.

An indicator must possess the property of not reacting with the titrating solution until the principal reaction is complete and then on the addition of a small drop, to manifest a quick color change, forms a precipitate or in some other way indicate that the main reaction has been satisfied.

The point of addition of reagent solution to unknown solution wherein the color change of the indicator takes place, is usually referred to as the end point. It is understood that this point should closely coincide with the true equilibrium point of the reaction which we are measuring.

Accurate Measuring Vessels

Since the accuracy of volumetric methods is so largely dependent upon the correct measuring of volumes of solution, accurately calibrated burettes, pipettes and flasks must be used.

Although the unit of volume is the liter, measurements in an actual titration are made in milli liters or thousandths of a liter (a liter being equal to about a quart).

Fundamental Requirements

Thus we may summarize the most essential requirements of volumetric analysis as follows:

1.) A reaction which is essentially irreversible and runs to practical completion.

2.) A standardized, stable solution whose strength is accurately known and which reacts quantitatively with the substance being determined.

3.) An indicator which marks the completion of the reaction.

4.) Accurate measuring apparatus.

Volumetric Precipitation Methods

As we have already seen, this method involves the interaction of two compounds wherein a precipitate is formed. However, in this case the precipitate is not measured or weighed, but merely the point at which the last bit of precipitate was formed.

A good example of this method is that which is used by the leather chemist in order to determine chlorides. If we have a material such as iron chloride, aluminum chloride, calcium chloride or even sodium chloride, we may determine the amount of any of these metals present alone in a solution by measuring its interaction with silver nitrate to form silver chloride which is precipitated. The end point of the reaction is determined by adding a few drops of a 5% solution of potassium chromate, which gives a brick red precipitate of silver chromate.

For chlorides the main reaction is:

$$Cl^- + Ag^+ = AgCl\downarrow$$

and when this reaction is completed, a drop of silver nitrate in excess will react with the chromate ion.

$$CrO_4^= + 2Ag^+ = Ag_2CrO_4\downarrow$$

producing the purplish red precipitate of silver chromate.

The Theory of Neutralization Reactions

Methods by which the acidity or alkalinity of solutions is determined are based on neutralization reactions and depend fundamentally upon the interaction of hydrogen ions with hydroxyl ions. By this means it is possible to determine the acidity or alkalinity of a solution.

In this type of analysis we are concerned with the equilibrium point when all of an acid is neutralized, or reacted, with a base or vice versa. That is, in order to determine how acid a solution is, or how much acid it contains, we must treat it with its opposite a base so that when all of the acid has been combined with the base we may have a measure of how much acid was present. The base, or hydroxide, which we use has been prepared by us

and thus we know its concentration in terms of volume. In other words, we know how much of the hydroxide is contained in each liter, or even each milli-liter of the solution.

This is much like the case of the storekeeper who weighs produce on a scale. He wishes to determine the quantity of that which he is to sell and he does it by balancing it against a weight of known value. When the two balance, that is, reach a state of equilibrium, he can then read the total of the weights which he has added on one side to arrive at the weight of the produce. This crude example typifies the general theory of volumetric analysis. For we usually try to balance off an unknown quantity with a known quantity and having determined the point at which they are in equilibrium we assume them to be equal.

Two very important considerations become immediately evident:

1. We must determine at just what range of acidity or alkalinity the equilibrium takes place. This range is somewhat different for various combinations of acids and bases.

2. We must select an indicator which will change color just when this equilibrium point has been reached.

Reactions between Strong Acids and Strong Bases

There are certain acids and bases which are considered to be strong, that is, active and highly ionized. For example, the mineral acids HCl, H_2SO_4, etc. and the alkali hydroxides like KOH, NaOH, etc.

Suppose that one gram-mole of HCl is allowed to react with 1 gram-mole of NaOH, viz:

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

One gram-mole each of NaCl and H_2O is formed. If we could ignore the presence of the water, this reaction would indicate that the acid and base had combined completely to form NaCl + H_2O. Thus, if we wanted to measure the point at which this reaction was complete, we could measure the pH when only NaCl and water (H_2O) formed are present.

Water Equilibriums

Water in its behavior as a weak electrolyte ionizes to a very small extent into hydrogen ions and hydroxyl ions, thus:

$$HOH \rightleftharpoons H^+ + OH^-$$

According to the Law of Chemical Equilibrium the expression becomes:

$$\frac{C_{H^+} \times C_{OH^-}}{CHOH} \longrightarrow K \cdot (\text{ion of HOH})$$

Rewriting this to:

$$C_{H^+} \times C_{OH^-} = K\ (\text{ion}) \times C_{HOH}$$

A liter of water at 25°C. weighs 997 grams; 997 divided by 18 (the molecular wt. of water) equals 55.4. Therefore, a liter of water consists of 55.4 gram-mols; we may say that the concentration of water in a liter of water is 55.4 molar.

Or probably to get a relative idea of the meaning of these negative numbers, suppose that we had 100 grams of water, the equilibrium would be written thus:

$$\frac{C_{H^+} \times C_{OH^-}}{C_{HOH}} = \frac{0.0000001 \times 0.000001}{100} = K\ (ion) = 1 \times 10^{-16}$$

Thus, we see that in 100 grams of water we have 0.0000001 grams of H^+ and 0.0000001 grams of OH^- present. This shows that very very little of the water is ionized. However, even this small amount must be reckoned with in order to understand what takes place when other ions are added to it.

Instead of using the term 0.0000001 we move the decimal point over to the left seven (7) places and express it in terms of multiples of 10 and it is thus: 1×10^{-7}.

Then we can say that the concentrations of H ions and OH ions in a liter of water is:

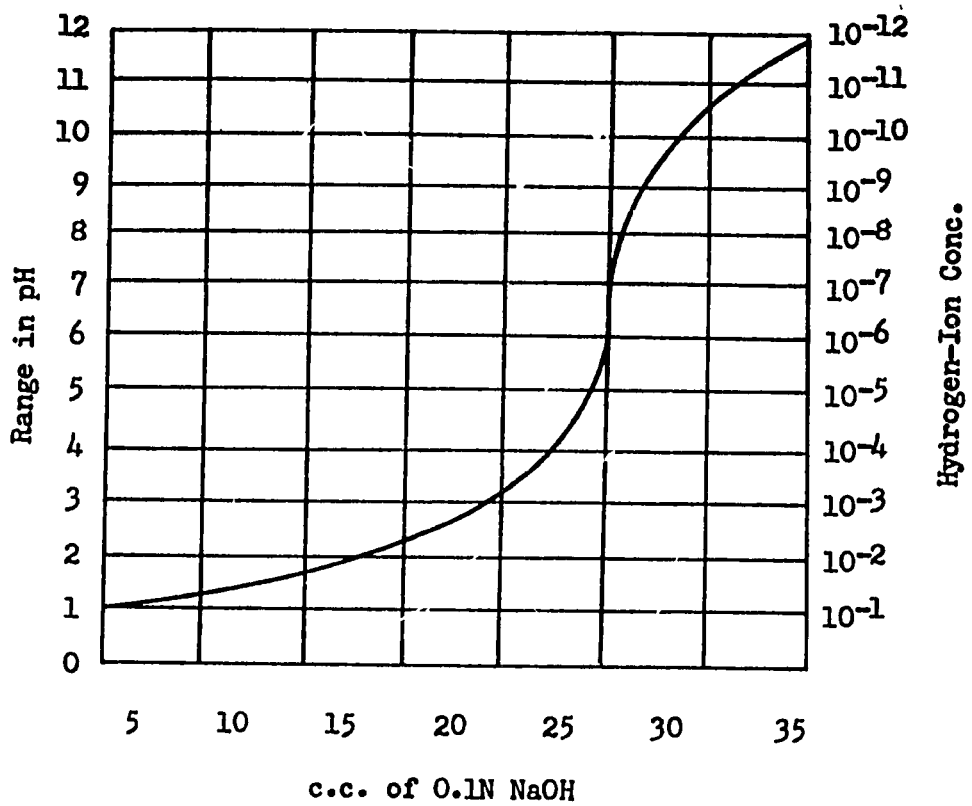
$$C_{H^+} \times C_{OH^-} = K_w = 1.0 \times 10^{-14}$$

The concentrations of H^+ and OH^- in a liter of water are equal in number, each equaling 1×10^{-7}.

Thus, when we add an acid we have more than 1×10^{-7} H^+ ions present and when we add a base we have less than 1×10^{-7} H^+ ions present. Thus, if we can have a means of measuring whether we have more or less than 1×10^{-7} H^+ ions present we can determine the equilibrium points of our titration reactions.

In the case of the HCl + NaOH reaction mentioned above, when the reaction is completed we have only NaCl and H_2O left. If the NaCl which is ionized almost completely to $Na^+ + Cl^-$ is not affected by the H^+ and OH^- present from the water, to change their relative amounts the end point should be at neutrality, that is, when the concentration of H ions and OH ions each equals 1×10^{-7} or a pH of 7.0.

Thus, if we select an indicator which will change color at about a pH of 7.0, we can determine when the equilibrium takes place. For at that point a small amount of base or acid added will cause a considerable change in the H^+ ion concentration or, in other words, the pH. This can be readily seen by looking at the titration curve of HCl and NaOH.



This is the titration of a strong acid by a strong base. Suppose we take 25.00 c.c. of a 0.1 normal HCl solution, and gradually add from a burrette measured volumes of a 0.1 normal NaOH solution and note the changes taking place in the hydrogen ion concentration or in the pH, we will get the curve shown above. It is easy to see that when we reach 25 c.c. of NaOH added (which is the equivalent amount) there is a sudden change in H ion concentration so that a slight excess will give a great change in H ion conc. or in the equivalent term pH. Thus, if we have an indicator which changes color, in this change we have a visual measure of the end point and thus a means of measuring the concentration of an unknown acid with concentrations of a known base or vice-versa.

HYDROLYSIS EQUILIBRIA

Second Year - Lecture #11

Reactions Between Weak Acids and Strong Bases

When a weak acid such as acetic acid is titrated with a strong base like sodium hydroxide, we have another example of a neutralization reaction:

$$H\ C_2H_3O_2 + NaOH \rightleftharpoons NaC_2H_3O_2 + H_2O$$

However, this time we do not have a high degree of ionization in each case. The acetic acid is not highly ionized, but if the water was not present we would still theoretically have a condition analogous to the reaction of hydrochloric acid with sodium hydroxide. The sodium acetate formed can in turn combine with the water in such a manner that the reaction could reverse itself so that acetic acid and sodium hydroxide would be formed. Thus, the reverse of neutralization is known as hydrolysis.

Hydrolysis

This concept of hydrolysis is quite important and is one which has significance not only in quantitative analysis, but in many of our daily plant operations. For this reason we should dwell at this point until we can feel that we have explored the idea to our satisfaction.

As good an example as any to show this point is NH_4Cl, ammonium chloride. We know that most bate materials contain in addition to the pancreatic enzyme a salt such as ammonium chloride or ammonium sulfate, and it does not matter to a great degree which is used as they both are used for the same purpose. When the limed stock is added to the bate it has a pH value of anywhere from 12.0 to 13.9 depending upon the treatment used. After a reasonable amount of time to allow equilibrium to take place, we find that the bated stock has a rather uniform pH in the range of 7.5 to 9.0. In other words, we have decreased the pH of the solution just as if we had added an acid to the solution instead of a salt. This is not caused by the pancreatic enzyme, but rather it is necessary for the enzyme to reach its point of greatest activity at this new pH.

Thus, when we add NH_4Cl to a water solution, it combines with the water in a manner which is the reverse of the neutralization reaction just considered. viz:

$$NH_4Cl + HOH \rightleftharpoons NH_4OH + HCl$$

Thus, it is now quite easy to see how hydrolysis is the reverse of neutralization. Actually when we add the NH_4Cl to the water NH_4^+ and Cl^- ions are formed.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

We know that while water is very poorly ionized - about 1×10^{-7} gram ions of each of H^+ and OH^- present - that these can combine with the $NH_4^+ + Cl^-$ now present. viz:

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$HOH \rightleftharpoons OH^- + H^+$$

$$\downarrow\uparrow \qquad \downarrow\uparrow$$

$$NH_4OH \qquad HCl$$

Each of these two new reactions, the formation of NH_4OH and the formation of HCl are governed by equilibrium constants. In other words, if HCl is highly ionized normally; then in this case little will be formed, merely the ions will be in solution. This is the case for HCl, but in the case of the equilibrium for NH_4OH the displacement is the reverse and the associated form of NH_4OH is present to large degree and considerable OH^- ions are taken out of solution to cause its formation. Thus, there is a predominance of H^+ in the solution which is what we also have when we add acid to a solution and the solution of the salt, therefore, gives an acid reaction in this case. The reverse is true if we were to add a salt to the water which associated with the water for form a weakly ionized acid. We then would have a basic solution.

Now we can readily see the effects that many salts used in the tannery have on the pH of our solutions - the acidic effect of NHCl and the alkaline effect of sodium carbonate.

Therefore, many of these salts which we use in the tannery are used merely to get a finer control of pH than could be obtained with a base or an acid, and all that we control is the H^+ (hydrogen ion conc.) or the OH^- (hydroxyl ion conc.). We don't intend that the salt as such affect the leather in any way.

Now returning to our first reaction, that between acetic acid and sodium hydroxide and writing it in the ionic form, we can readily see that poorly ionized acetic acid is formed and H^+ is removed from the solution.

$$Na\ C_2H_3O_2 \rightleftharpoons Na^+ + C_2H_3O_2^-$$

$$HOH \rightleftharpoons OH^- + H^+$$

$$\downarrow\uparrow \qquad \downarrow\uparrow$$

$$NaOH \qquad HC_2H_3O_2$$

Thus the equilibrium for this type of reaction is reached at a pH beyond 7.0. Likewise an indicator must be used which is sensitive to a change of the range in pH of 7.0 to 9.0.

<u>Reactions Between Strong Acids and Weak Bases</u>

This is merely a reversal of the previous conditions. A good example is the titration of HCl with NH_4OH, viz:

$$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$$

and by hydrolysis:

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$HOH \rightleftharpoons OH^- + H^+$$

$$\downarrow\uparrow \qquad \downarrow\uparrow$$

$$NH_4OH \qquad HCl$$

Thus, we see that the NH_4^+ ions and the OH^- ions associate to form NH_4OH, but that the H^+ ions and Cl^- ions do not. Therefore, OH^- ions are removed from solution and the solution is acidic to about pH 5.0 for a 1/10th normal solution.

This explains why one indicator is suitable for one titration and another is suitable for a second different titration. Various indicators change color at certain definite pH ranges. This phenomenon is peculiar to the particular indicator in each case. Thus indicators can be chosen which by their colors will indicate definite pH ranges from 1-14.

Summing up the three cases that we have studied is possible as follows:

Combination	Nature of Hydrolysis	Region of Equilibrium Point	Indicator
Strong Acid + Strong Base	None (neutral)	pH 4-9	M.O. or P.P.
Weak Acid + Strong Base	Somewhat (basic)	pH 7-9	P.P.
Strong Acid + Weak Base	Somewhat (acidic)	pH 4-6	M.O.

M.O. signifies methyl orange
P.P. signifies phenolphthalein

The Calculations of Volumetric Analysis

In every volumetric procedure two sets of computations are usually required:

1. Calculating the exact strength of the titrating reagent from the standardization data, and

2. Calculating the amount of constituent in the material from the titration data obtained in the analysis of the sample.

Volumetric methods are merely indirect weighing methods. The weight of reacting constituent is determined from the volume and strength of the solution used in titration.

Units for Designating Strength

The strength or concentration of the titrating solution must be determined by a separate titration against a known amount of pure substance. Its value may then be expressed as follows:

1. Titre system
   By the term titre is meant the grams of solute or reagent actually contained in a milli-liter of solution, or the weight of any substance which will react with or be equivalent to 1 milli-liter of the solution.

2. **Normality System**

By the normality of a solution is meant its concentration compared to an exactly normal solution. That is, if a solution is designated as 0.1 Normal it means that this solution contains 1/10th as much of the material as one which contains the normal or equivalent weight.

Thus, for HCl, if the solution contained exactly 36.465 grams of HCl per liter we would have one equivalent weight of HCl per liter calculated from its atomic weights and a 0.1 Normal solution would contain exactly 3.6465 grams per liter.

An apparent advantage in using the normal system is that equal volumes of all solutions of identical normality will completely react with each other. Thus, 20 milli-liters of 1 normal HCl will exactly neutralize 20 milli-liters of 1 normal NaOH solution.

If we have on hand a certain potassium thiocyanate solution which contains 0.004858 grams of KCNS per milli-liter and since the gram-milliequivalent weight KCNS is $\frac{97.17}{1000} = 0.09717$ (we divide by 1000 to convert to the amount in 1 m.l.), the ratio is $\frac{0.004858}{0.09717} = 0.05$; thus the solution is 0.05 normal.

Calculation of Percentage by the Titre Method in Volumetric Precipitation

For example, we are attempting to determine the percent of pure silver in a rough sample weighing 0.200 grams. 35 m.l. of a potassium thiocyanate solution are necessary to fully precipitate the silver in solution and give the color change in the indicator.

The potassium thiocyanate solution was made up so that 30 m.l. precipitated 0.2548 grams of pure $AgNO_3$. Thus, 30 m.l. is equivalent to:

$$\frac{Ag}{AgNO_3} \frac{(107.88) \times 0.2548}{(169.89)} = 0.1618 \text{ grams of silver}$$

and 1 m.l. of the KCNS solution is equal to $\frac{0.1618}{30}$ or 0.005393 g. of silver. This is the titre.

Using this value in the problem where 35 m.l. of the solution were necessary to precipitate the unknown silver:

$$35.00 \times 0.005393 = 0.1888 \text{ grams of silver}$$

This divided by the original weight of the sample will give the percent:

$$\frac{0.1888}{0.2000} \times 100 = 94.40 \text{ percent}$$

The general equation is:

$$\frac{\text{volume x titre in terms of desired constituent}}{\text{weight of sample}} \times 100 = \%$$

Calculations of Neutralization Methods

The total acidity of an acid solution is determined by titration with a standard base. Conversely, the alkaline strength of a basic substance is determined by titration with a standard acid. Acids or bases are usually standardized (that is, their strength is determined) by determining the volume necessary to completely react with a known weight of a pure substance.

Thus, to standardize an HCl solution we would use pure Na_2CO_3 according to this relationship:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCL + CO_2 + H_2O$$

Thus, if 30 c.c. of an HCl solution is needed to neutralize or react with 0.1620 grams of Na_2CO_3 we have:

$$\frac{0.1620 \text{ grams}}{30.00 \text{ m.l.}} = 0.005400 \text{ grams of } Na_2CO_3 \text{ per m.l.}$$

This means that one milliliter of the HCl is capable of neutralizing 0.005400 grams of Na_2CO_3; this is the Na_2CO_3 titre or value.

If we set up a proportion based on the molecular weights we can arrive at the HCl value. viz:

$$\frac{Na_2CO_3}{2HCl} = \frac{0.005400}{x}$$

or

$$\frac{105.994}{72.930} = \frac{0.005400}{x} \quad x = 0.003715 \text{ grams of HCl in each m.l.}$$

This is the HCl titre or equivalent.

In order to calculate the normality we compare the amount of HCl present in 1 m.l. of the solution as given above with the amount present in 1 m.l. of a solution containing a gram milliequivalent. That is, a solution made up to have 1 equivalent weight per liter. In the case of HCl the equivalent weight would be the molecular weight.

$$\frac{36.465}{1000} = 0.036465 \text{ (gram milliequivalent)}$$

$$\text{Therefore: } \frac{0.003715}{0.036465} = 0.1019 \text{ N.}$$

The HCl solution is 0.1019 normal.

If we had the following problem - What is the percent of CaO in a limestone sample, if 0.5000 gram required 32.75 m.l. of 0.5 NH_2SO_4 for neutralization, we would proceed as follows:

Determine the number of grams of H_2SO_4 which are contained in 32.75 m.l. of 0.5N H_2SO_4.

Equiv. wt. equals 1/2 mol. wt. $= \frac{98.08}{2} = 49.04$

Therefore, 1 ml gram equivalent $= \frac{49.04}{1000} = .049$

$$\frac{.5N}{IN} = \frac{x}{.049} \qquad x = \frac{.5 \times .049}{1} = 0.0245$$

thus, 0.0245 grams of H_2SO_4 per m.l.

The total amount of H_2SO_4 used is:

$$32.75 \times 0.0245 = .8023 \text{ grams}$$

The reaction is as follows:

$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

56.07 98.08 x

$$\frac{56.07}{98.08} = \frac{x}{0.8023} \qquad x = \frac{56.07 \times .8023}{98.08} = .4586$$

Therefore, 0.8023 g. of H_2SO_4 is equal to 0.4586 g. of CaO,

and $\frac{0.4586}{0.5000} = 91.72\%$ CaO in the sample.

pH and OXIDATION-REDUCTION

Second Year - Lecture #12

There is a very important relationship which has been established in regard to aqueous solutions, namely,

> In pure water, or in any aqueous solution, whether it is that of an acid, a base, or a salt, there are always present both hydrogen ion and hydroxyl ion, and that whatever the concentration of the one, the concentration of the other is such that the product of the two concentrations is a constant for any given temperature, that is,

$$C_H \times C_{OH^-} = \text{Constant for any given temperature}$$

Or fixing the temperature at 25°C. we have specifically -

$$C_H \times C_{OH} = 1 \times 10^{-14}$$

Hydrogen Ion Determination

Particular interest has developed in measurement of the concentration of the hydrogen ion in solutions for several reasons. The hydrogen ion concentration is the most exact measure of the "acidity" of a solution. It is also of great importance in the control of certain reactions, in the determination of enzyme action, the rate of bacteria growth and so on.

We know that water consists of many millions of particles which in the liquid state are close to each other. Chemically speaking, we know that the compound water is made up of two atoms of hydrogen and one atom of oxygen joined together by what we term to be chemical bonds. These bonds are quite stable and also when the atoms are thus joined they are quite inert. However, it is one of the phenomena of chemistry that when compounds are placed into water that some of the molecules dissociate into charged particles which we term ions. Because these particles are charged we are able to measure the quantity present, as the more that are present the greater the charge.

Water which is a common solvent is largely unionized, however, a small fraction of the molecules are ionized, thus -

$$HOH \rightleftharpoons H^+ + OH^-$$

If, for instance, we have one (1) liter of water, there would be $\frac{1000}{18}$ gram mols of water present. That is, 18 is the molecular weight of water, which divided into the wt. of 1 liter of water (actually 997 g.) will give the number of molecular wts. in terms of grams that are contained in 1 liter of water. Of this relatively large weight of molecules in terms of grams, an amount corresponding to 0.0000001 gram mols of H^+ are formed and a similar amount of OH^-.

Now the chemist expresses large numbers and fractions in terms of exponents. The magnitude of a quantity is expressed in the exponential form by writing the digits as coefficients multiplied by ten raised to the proper power. Thus the number 1000, which is the product of 10 x 10 x 10, or 10 cubed, is written exponentially 1×10^3. The number 0.001, the product of 0.1 x 0.1 x 0.1, is written 1×10^{-3}. The number 7000 becomes 7×10^3, and 0.007 becomes 7×10^{-3}. The number 1,000,000 (one million) is expressed as 1×10^6.

Multiplication by use of Exponents

To multiply two or more quantities, the numbers are first expressed exponentially. The coefficients are then treated in the ordinary way and the exponents are added algebraically.

viz.

Multiply 45,000 by 0.051

Since 45,000 becomes 4.5×10^4 and 0.051 becomes 5.1×10^{-2} we have by multiplying the coefficients and adding the exponents -

$$45{,}000 \times 0.051 = (4.5 \times 5.1)\ 10^{4-2}$$
$$= 22.95 \times 10^2$$
$$= 2.295 \times 10^3$$
$$= 2.3 \times 10^3$$
$$\text{or} = 2300$$

Division by the use of Exponents

When dividing two quantities after expressing them in the exponential form, the coefficients are divided in the ordinary manner, and the exponents are subtracted algebraically.

viz.

Divide 3730 by 15.21

$$\frac{3730}{15.21} = \frac{3.73 \times 10^3}{1.521 \times 10^1}$$
$$= 2.45 \times 10^2$$
$$\text{or} = 245$$

Theory of Reactions

It has been mentioned at various times that inorganic compounds dissociate or ionize in varying degrees. In other words, one compound ionizes more than another. It is thus reasonable that each compound has an ionization or dissociation value which we refer to as a constant. Actually this value is constant only for a definite temperature and concentration. To the chemist this constant is a measure of the activity or strength of a compound.

For example 0.1 molar hydrochloric acid is 92% ionized, that is -

$$HCl \rightleftharpoons H^+ + Cl^-$$

At this concentration 92% of it goes to H^+ and Cl^- and 8% of it remains associated as the molecule HCl. In this solution we have 0.1 x 0.92 = .092 gram ions of H^+

$$\text{or } C_{H^+} = .092 = 9.2 \times 10^{-2}$$

Also, for Cl^- we have 0.1 x 0.92 = .092 gram ions Cl^-

$$\text{or } C_{Cl^-} = 9.2 \times 10^{-2}$$

Now we are usually most interested in the concentration of the hydrogen ion, which in this case is:

$$C_H = .092$$

and converting this to pH values by the use of logarithms

$$pH = 1.04$$

Thus, we see that 0.1 molar hydrochloric acid is highly ionized and the pH is correspondingly high.

In the case of acetic acid, using also a 0.1 molar solution, the degree of ionization is only 1.34%.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Only 1.34% of H^+ and of $C_2H_3O_2^-$ (acetate ion) are formed. The rest, 98.66%, is unionized acetic acid.

Therefore, the C_{H^+} = 0.1 x 0.0134 or 0.00134 gram ions, and converting this into terms of pH by the use of logarithms we obtain a pH = 2.87

While we consider this to be fairly acidic, it is less so than hydrochloric acid. It should now be quite apparent that it takes a good deal more acetic acid to accomplish the same job than of hydrochloric acid. It is almost of the order of 100 to 1. We, therefore, measure the strength of an acid or base in terms of the amount of H^+ or OH^- that is yielded. Therefore, it is quite easy to see why acetic acid is considered a weak acid and hydrochloric acid is considered a strong acid.

When we add an acid or a base to perform some reaction, we are not interested in the amount that is unionized for what will not enter into the reaction. We are only interested in the amount of H^+ that is formed for it is this ion which reacts.

Therefore, if we wished to change a pH of a solution over a wide range we would use HCl or H_2SO_4 as either of these would yield a large amount of H^+ necessary in this case, such as the case when we take stock from the bate to the pickle. However, if we wish to make a minor adjustment we would be better off to add just a small amount of acetic acid, which would vary the H^+ conc. only a small amount.

That is why in certain types of tanning work lactic acid is used to vary the H^+ conc. over a slight range.

Finally it follows that in practically every instance in beamhouse work and in tanning all we are doing is varying the H^+ conc. and we select acids and bases which are strong or weak to so control it. (When we say strong or weak we should now mean strongly or weakly ionized.) In our work we measure this hydrogen ion concentration in terms of pH, which is merely a whole number which represents the magnitude of the concentration.

Going back to the original statement we know that water is poorly ionized - $C_{H^+} = 1 \times 10^7$
and that when it ionizes it also forms 1×10^{-7} OH^-
The product of these two is $1 \times 10^{-7} \times 1 \times 10^{-7} = 1 \times 10^{-14}$.

Therefore, concentration of H^+ and OH^- in water is equal to:

$$1 \times 10^{-14} = Kw$$

And when we add the acetic acid to the water the concentration of the H^+ ions increases so that it is about 0.00134 or a pH of about 2.87, and if the concentration of H ions increases this amount, the concentration of the OH ions must drop a corresponding amount for the product of the two must always equal 10^{-14}:

$$C_{H^+} \times C_{OH^-} = 10^{-14}$$

Theory of Oxidation and Reduction

Oxidation is regarded as an increase in positive charges or as a decrease in negative charges associated with ions and atoms. Reduction is regarded, as the reverse, as a decrease in positive charges or an increase in negative charges. For example, when iron changes from the ferrous to the ferric state, there is an increase in the number of positive charges from +2 to +3, viz Fe^{++} to Fe^{+++}. When stannic tin, Sn^{++++}, is changed to stannous tin Sn^{++} there is a decrease in the number of positive charges associated with the atom of tin - this is a reduction.

Oxidation and Reduction in Terms of Valence and Electron Transfer

An increase in the number of positive charges is the result of the loss of electrons by an atom, a radical or anion. A gain of electrons results in a decrease of positive charges. The excess or deficiency of electrons associated with an atom is known as its valence. The ferrous ion, Fe^{++} for example, has an excess of 2 positive charges; it has resulted from a neutral atom of iron losing two electrons and its valence is said to be 2.

In the broadest sense, then, Oxidation means the loss of one or more electrons and reduction means the gain of one or more electrons.

In every reaction where there is a transfer of electrons from one kind of atom to another, the electrons lost by atoms of one element must be gained by atoms of another element. In other words, when one element is oxidized, another element is reduced.

Let us take an oxidation-reduction reaction as an example. We will first consider the oxidation and reduction changes and finally the manner in which the equation is balanced.

$$FeCl_2 + K_2Cr_2O_7 + HCl \longrightarrow FeCl_3 + CrCl_3 + KCl + H_2O$$

This is the equation written in unbalanced form and it shows that the ferrous chloride $FeCl_2$ is oxidized to the ferric (trivalent) condition, whereas the chromium in the potassium dichromate is reduced to the chromic (trivalent) condition, the oxygen of the dichromate uniting with the hydrogen of the acid to form water.

In ionic form, this unbalanced form becomes:

$$Fe^{++} + Cr_2O_7^{=} + H^{+} \longrightarrow Fe^{+++} + Cr^{+++} \quad H_2O$$

The chromium atom in the dichromate ion has a valence of 3; each chromium atom suffers a reduction of three positive charges. Since there are two atoms of chromium in each dichromate ion, each atom of which loses three positive charges, the total loss will be six - for each dichromate radical. The six charges lost by one $Cr_2O_7^{=}$ ion must be accounted for by the gain of charges on the iron. Since each ferrous ion shows an increase of one positive valence on becoming a ferric ion, the six charges from a dichromate ion are assumed by six ferrous ions. Finally, the seven atoms of oxygen from the dichromate ion require fourteen atoms of hydrogen from the acid to form seven molecules of water.

Thus - $6\ Fe^{++} + Cr_2O_7^{=} + 14H^{+} = 6\ Fe^{+++} + 2\ Cr^{+++} + 7\ H_2O$

or $6\ FeCl_2 + K_2Cr_2O_7 + 14\ HCl = 6\ FeCl_3 + 2\ CrCl_3 + 7H_2O + 2\ KCl$

DEGREASING

Second Year - Lecture #13

The skin of any animal contains certain amounts of fats, greases, oils and waxes. These chemicals are not uniformly dispersed throughout the skin or hide, but rather are concentrated at various dispersal points. In hides such as cow or steer hides these lipids find their greatest concentrations in the flesh or adipose tissue. A second region of concentration is just below the epidermal layer; this latter concentration is built around the hair follicles. These two concentrations just considered are horizontal dispersions. In cow and steer hides there is a third area of dispersion to be considered, an area of vertical dispersion, the kidney area.

In the average skin or hide sufficient of these lipids are removed in the beamhouse operations, that little or no trouble is experienced in the finished leather from grease stains. The flesh side is usually split or shaved sufficiently to remove the fatty tissues and the concentrations in the thermostat layer are readily removed in liming and subsequent operations as they are quite close to the surface. We know that the bate material in addition to trypsin contains an enzyme lipase which hydrolyses fats. This particular enzyme reaches its optimum activity at a pH of 7, which is not too far from the range of trypsin, or the range of the usual bating operation. Moreover even though the maximum activity of lipase is at pH 7, there must be an appreciable, but lesser activity in the bating range. It is the opinion of many researchers that the slippery feeling experienced on the surface of bated stock is due to these lipids which have been hydrolyzed.

The kidney areas in these skins or hides is often able to hold sufficient grease, in spite of the beamhouse operations, to cause considerable trouble in the finished leather. This is evidenced by a stained surface and a lack of uniformity in the manner in which these areas will accept dyes and finishes.

It is one of the odd situations of this industry that we must remove these lipids in order to make good leather and once having done so, we must then return them in order to get proper pliability and feel. However, this is not as incongruous as one might be led to believe, for the lipids in the skin are so located as to serve the best purpose of the living animal. These lipids must then be so located that they lubricate the hair and feed the various cells and tissues. These purposes are of no value whatever in the terms of leather. Leather requires these greases and fats in order to provide a mechanical sort of lubrication of the fibers to give a suppleness and also to overcome the harshness imposed on the fibers by the tanning material.

There are, however, certain skins which because of their biological necessities require considerably more than the usual amount of lipids during the period that the skin functions as an organ of the living animal. Goatskins, and particularly sheepskins, fall into this category.

Generally sheepskins, because of their wool, are soaked, limed, bated and pickled before they reach the tanner. In this condition there is yet considerable grease in the skin and measures must be taken for its removal before proper finishing can be performed. This is normally done in the pickled state.

Work performed on vegetable tanned leathers indicated fat stains would occur in leather which had a natural fat content exceeding about seven to ten percent on the dry basis, in the first rough dry. This is an interesting figure when compared to that obtained by the various degreasing figures used on sheepskins.

Histologically, the lipids of sheepskins can be demonstrated as cellular depositions in the corium and subcutaneous area. Concentrations of fat cells are generally located along a plane just below the wool fiber roots. In the sebaceous, or fat, glands the breakdown of the cells of high lipid content results in the deposition of the lipid in the gland. When exuded into the wool fiber follicle, or upon the epidermal surface, this lipid constitutes a protective film. Excepting the phospholipid concentration, the concentration of epidermal lipid constituents of the sheepskin exceed the concentration of the same constituents in the steer hide by from two to four times. This points out the necessity for degreasing sheepskins. A skin, not considered to be extremely greasy, was analyzed and found to contain lipid to the extent of 32 percent of its dry corium weight.

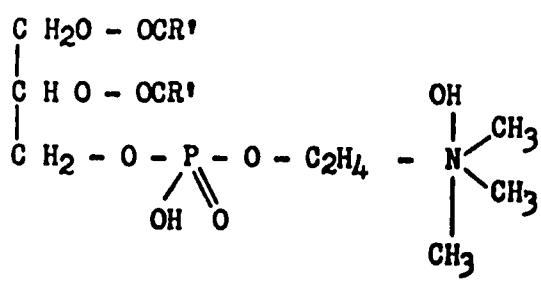
The following figures point out this latter relation quite well. A fresh sheepskin was analyzed as follows:

	Subcutaneous	Corium	Epidermal
Percent of lipid on dry weight	93%	31.8%	21.8%

From these figures we can readily see that the adhering flesh tissue is made up largely of fat cells. However, there is still a very large concentration in the true skin, or corium. Furthermore, we know that this is largely concentrated in a plane just below the hair follicles.

These various lipids which we have been discussing fall into a rather general classification known as fats, waxes and lipoids.

Phospholipids:- These are esters of glycerin in which two of the hydroxyl groups are replaced by a large molecular weight fatty acid; the third hydroxyl group is replaced by phosphoric acid, which in turn has one of its hydroxyl groups replaced by an ammonium type of nitrogen compound such as choline.



Cephalin is a lipoid similar to the above except that in the place of choline it contains aminoethyl alcohol. ($NH_2-CH_2-CH_2OH$)

Cholesterol: - $C_{27}H_{45}OH$ is an unsaturated secondary alcohol. It is found widely distributed in animal tissues.

Fat:- This as we already know is a triglyceride. That is the triple ester of glycerine with various long chain saturated or unsaturated acids.

viz:

$$\begin{array}{l} CH_2-OOR \\ | \\ CH-OOR \\ | \\ CH_2-OOR \end{array}$$

Usually more than one definite type of acid is combined in the same molecule. These constitute a large portion of the lipids of the corium.

Waxes: - These are also esters, but esters of high molecular weight alcohols with high molecular weight acids. Lanolin is such a compound, although it is referred to by many as a fat rather than a wax. It consists of the ester of cholesterol and variour fatty acids such as stearic or oleic.

In the earlier days of sheepskin tanning sheepskins were degreased by a method which involved pressing the grease out mechanically. This was never a very satisfactory method as the amount of grease removed was not uniform from skin to skin and from lot to lot. Much depended upon the operator and various mechanical variables. Moreover, the pressures necessary often caused damage to the fibers of the skins.

This method was followed by a solvent degreasing method which employed a solvent of the kerosene type. One of the more common of these solvents is one in which the lower boiling fractions have been removed in order to minimize the fire hazard. One modification of this process is known as the emulsification process, the removal of the grease is dependent upon the use of a brine chaser to displace the solvent-grease mixture from the skin. The other modification now coming into more prominence is the centrifugal process. In this process the solvent-grease mixture is removed by whirling the skins in a centrifuge of a type similar to those employed in commercial dry-cleaning establishments.

In the emulsification process there is a great possibility of considerable variation in the amount of grease removed. This is sometimes offset by a second degreasing. A further complication is that some tanneries use emulsification acids while others do not. In general, an emulsification aid has been found to be more advantageous for the greasier skins or in wintertime. As a rule these aids have been sulfated oils.

The centrifugal process is not used too extensively even today as considerable special equipment is necessary. However, its greater efficiency has been clearly established. Solvent recovery is made easier by this method and good solvent recovery methods yields a grease which can be used either as such in stuffing, or even modified to an oil.

Both of these processes involve the use of a solvent and considerable interest has been shown in selecting the most suitable solvent. In view of the fact that this grease is made up of fats, waxes and lipoids, their solubilities in any solvent will be differential at the best. In addition it has been found that the best solvents can not be used because of fire hazards, toxicity or greater cost. Chloroform will perform an excellent job in this respect, but it is too toxic for use in the plant. Trichloroethane is also excellent, but unsuitable for the same reason. Certain ketones, such as methyl isobutyl ketone are also very good, but offer the danger of flammability.

As I have already stated, sulfated oils are often used as an emulsification aid. These are anionic materials and upon reflection would not be considered to be the most satisfactory emulsifiers in view of the high acidity of the pickled skins, which can break them down if the degreasing operation is run for any great length of time. This same condition holds true in the fat liquoring of alum tanned leathers where the tendency of the fat liquors to break is quite common.

Experiments have been conducted using cationic emulsifiers with considerable success. One commonly used is known to the trade as "alum oil". Experiments have also shown that the amount of these cationic emulsifiers need not exceed 2% on the solvent weight. Also it was determined that the addition of 2% of the emulsification aid to the brine chaser increased the efficiency of the solvent-grease removal.

Histological samples of sheepskin taken before and after degreasing, show a considerable concentration of fat cells in the center of the corium. After degreasing, this concentration has disappeared and the remaining fat is dispersed evenly through the skin. There is no doubt that uniform distribution of the residual grease after degreasing is a most important consideration. A good degreasing technique is worthless if it permits excessive concentrations of grease in isolated areas.

The permissible amount of residual grease in the sheepskin to avoid spue in the finished leather is not agreed upon by various sources. However, laboratory results have shown that the centrifugal method is capable of removing a sufficient amount of the grease in all cases, especially where a second treatment is used for real greasy skins. Samples of sheepskins degreased by the emulsification-brine method, however, indicate that there is often insufficient removal.

In both of these methods the first step is very similar, that is, addition of the solvent which dissolves the lipids and particularly extracts them from the areas of high concentrations. In the brine method the emulsification aid is added in order to get a more complete removal. This possibly causes emulsion formation of some of these lipids with the water present in the hide. The brine bath drives out the kerosene phase which is not soluble in the water, taking the lipids along in the solvent and also displacing that which has been emulsified. Thus it is easy to see that an emulsification aid in the brine also will give a more efficient removal. That is, that which is already emulsified will not be broken down and perhaps even an additional amount will be further emulsified during this extraction. This type

of extraction is not clean cut, due to the water phase and the emulsion phase. At the base considerable of this emulsified material will remain in the skin due to the large particle size of the emulsion. After all, this is to some extent a material similar to a fat liquor. For this reason, a second treatment is necessary to get a removal sufficient to arrive at a percentage below the danger point.

The centrifugal method operates on the basis of true solution of the lipids in the solvent. In this case the particle size is molecular and complete removal is only a function of the amount of the solvent left in the skin after treatment. Thus it is possible to get a very good degree of removal in one treatment. A second treatment will give very good removal. Thus, if the ratio of removal in this method is 80% effective (that is, 20% of the solvent can't be centrifuged out) the first treatment would remove 80% of the total grease (80% of about 35-40%), leaving 20% behind after centrifugation, that is, about 7-8%. This is assuming sufficient solvent and agitation was used in order to get complete solution. The second treatment would again be about 80% effective, thus leaving behind about 2% of lipids. These figures would be off in practice because some of these lipids are not too soluble in the solvent. That is, there is a variation in solubility of the different constituents. However, this same trouble is experienced in the less efficient brine method.

CHROMIUM - THE WERNER CO-ORDINATION THEORY

Second Year - Lecture #14

Chromium (atomic no. 24, atomic weight 52.01) belongs to the family which also included molybdenum, tungsten and uranium. It is found chiefly in ferrous chromite ($Fe(CrO_2)_2$), which constitutes the mineral chromite. This is mined chiefly in California, Rhodesia, and New Caledonia. It is also found in nature in crocoisite ($Pb\ CrO_4$), which is a chromate of lead.

Derivatives of Chromic Acid

Potassium chromate (K_2CrO_4), sodium chromate (Na_2CrO_4) and the corresponding dichromates are made directly from chromite. Finely powdered chromite is mixed with potash and limestone, and roasted. (The lime is employed chiefly to keep the mass porous.)

$$4Fe(CrO_2)_2 + K_2CO_3 + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ K_2CrO_4 + 8\ CO_2$$

The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO, Cr_2O_3) to that of chromic anhydride in the potassium chromate.

Potassium chromate is pale-yellow in color, and is very soluble in water. Potassium dichromate is made commercially by adding sulfuric acid to the crude solution of the chromate obtained from chromite.

viz: $2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + H_2O + K_2SO_4$

The sodium salt $Na_2Cr_2O_7$ is made in a similar manner.

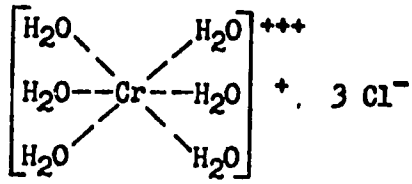
The Chemistry of Chromium Salts

One of the most important factors in the development of the chemistry of chromium compounds has been the Werner co-ordination theory, which was first suggested in 1891.

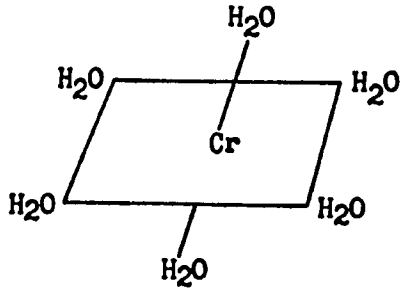
The term "valency" in the early days of its use was defined as the combining power of an element in terms of monovalent atoms - hydrogen being taken as a monovaelnt standard, or oxygen as a divalent. The chromium atom, for example, was stated to be trivalent in that it combined with three monovalent chlorine atoms in the compound $CrCl_3$ (chromium trichloride). Considerable difficulty arose in formulating the constitutional formula of so-called molecular or complex compounds formed with apparently saturated molecules. An example of this is $CrCl_3.6H_2O$. On the surface this compound would appear to be similar to $CuSO_4$ which forms a hydrate $CuSO_4.5H_2O$. However, whereas the 5 molecules of water in the copper sulfate may be removed in a desiccator, such is not the case with $CrCl_3.6H_2O$. The water molecules are not merely attracted to the $CrCl_3$ as water of crystallization, but rather are attached to the chrome itself by a form of valency bond.

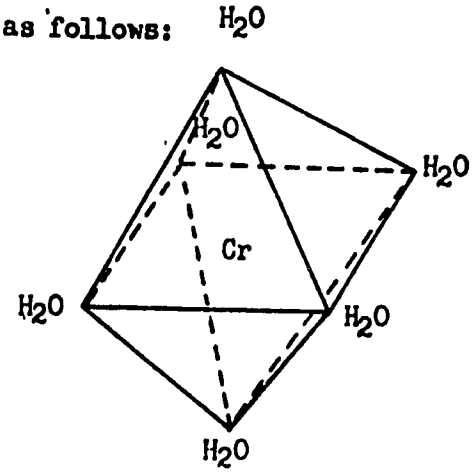
It appeared to Werner that some atoms, such as chromium, are capable of exerting two different types of valency. For example, in the case of hydrated chromium trichloride, there are three principal valencies for chromium, and these are occupied by the three chlorine atoms, whereas the water molecules are linked by auxiliary valencies.

In this method, the auxiliary valency groupings (six in number for chromium are shown associated with the chromium atom, and form with a complex ion, the whole being bracketed as shown below, the auxiliary linkages being denoted by dotted lines.



Werner designated this ion in a space diagram as follows:





This indicates that the water molecules are attached by a form of valence to the chromium as a complex and symmetrically arranged around the atom. The three chlorine atoms are attached to this complex ion by principal valence as in the case of NaCl. Thus in aqueous solution they may break away and ionize:

$$[Cr(H_2O)_6]\ Cl_3 \rightleftharpoons [Cr(H_2O)_6]^{+++} + 3Cl^-$$

It is possible to have one, two or three of these chlorine atoms enter into the complex as a co-ordinated atom. When this takes place the chlorine replaces one or more of the H_2O molecules as the case may be as the coordination number of six cannot be violated. Each chlorine co-ordinated into the complex is bound so that it does not ionize in aqueous solution and also the charge on the complex varies accordingly.

$CrCl_3$, $6H_2O$ gives a violet solution with cold water; however, boiling changes the color to green. The difference in the two solutions is due to the different ions furnished by hydrated chromic chloride under different conditions. From the green solution, which contains $Cr(H_2O)_4Cl_2^+$ and Cl^-,

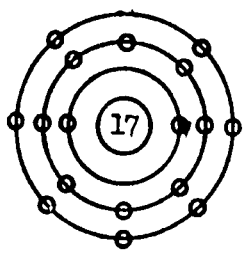
silver nitrate precipitates immediately only one-third of the chlorine as silver chloride. From the violet solution, which contains $Cr(H_2O)_6^{+++}$ and $3Cl^-$, all of the chlorine is at once precipitated.

These groups co-ordinated or associated with the central atom no longer give their characteristic ionic reactions and are, therefore, described as "masked".

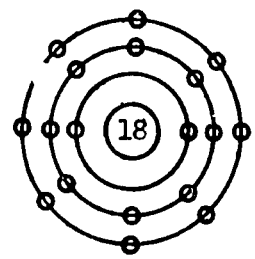
In the lectures on Inorganic Chemistry we studied the general structure of elements. We will review a little of this in order to better understand the co-ordination theories. Every atom has a nucleus, composed of protons and electrons. This nucleus is heavy and relatively motionless and it is surrounded by a number of electrons which revolve about it in layers or spheres. The number of electrons and protons in the nucleus and the number of electrons surrounding it is specific for each element and varies from element to element.

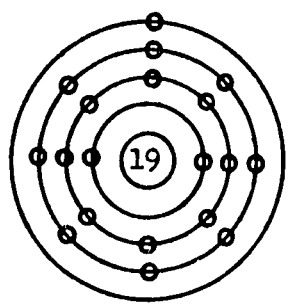
Some attempt is made in the diagrams which follow to give a picture of the arrangement of the orbital electrons for a number of elements, firstly arranged in the order of their orbits and, secondly, as models showing roughly certain features in the arrangement of the electrons.

Chlorine 2-8-7
Atomic number 17



Argon 2-8-8
Atomic number 18





Potassium 2-8-8-1
Atomic number 19

Actually these diagrams are in one plane and merely indicate the number of electrons in each sphere. The electrons are spaced around the nucleus in eliptical orbits or spheres in three dimensions.

We can see that chlorine is short one electron in its outer sphere. It can accept an electron from another atom such as Na or K to complete this sphere of 8 electrons. Argon has 8 electrons in its outer sphere and, therefore, does not need any more. This explains why Argon is inert and will not enter into chemical reaction with other atoms. Potassium has one electron in its outer or valence sphere which it will give in chemical reaction, thus becoming positively charged.

Chromium has four sheaths or orbits of electrons around its nucleus. In chromic salts the suggested arrangement of the unionized chromium atom is 2-8-11-3. The electrons in the outermost set of orbits (in this case 3) are considered to be the valency electrons and their number determines the valency of the element in question.

Chemical reactions can, therefore, be pictured as the tendency of the electrons to re-distribute themselves among the atoms involved so as to form more stable arrangements, such as occur in the inert gases like Argon. Chemical combinations or linkages may be divided into three types:

1. Polar or ionizable linkages between the oppositely charged ions of a salt, viz. NaCl

2. Non-polar, non-ionizable linkages, such as are especially found in organic compounds, viz. CH_3Cl

3. The co-ordinated linkages of Werner, which are capable of linking apparently saturated molecules, viz. $Cr(H_2O)_6\ Cl_3$

The first type may be depicted by sodium chloride:

$$Na + \cdot\underset{\cdot\ \cdot}{\overset{\cdot\ \cdot}{Cl}}\cdot \longrightarrow Na^{+} \quad :\underset{\cdot\ \cdot}{\overset{\cdot\ \cdot}{Cl}}:$$

sodium atom chlorine atom sodium ion chlorine ion

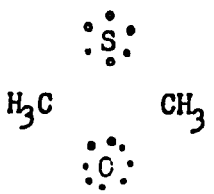
Sodium has donated its lone outer valence electron to chlorine becoming positively charged and chlorine has gained this electron becoming negatively charged. Also, chlorine has 8 electrons in the outer valence shell of its ion which is the inert gas type of structure. In this type of compound the atoms are held together by an electrical attraction. In this case there is an unbalance or uneven distribution of charge.

The second type of valency, the co-valent linkage, results when electrons are shared between two atoms so that each shared electron enters into the constitution and contributes toward the stability of both atoms. The resulting compounds are non-ionizable. This sharing of electrons can only occur in pairs and the pair of electrons shared between two atoms is the ordinary valency bond.

For example, nitrogen has 5 electrons in its outer orbit and can take up 3 electrons, the hydrogen atom can take up 1 electron. Thus, in the case of ammonia, NH_3, each hydrogen gives one electron and the nitrogen three electrons towards the sharing of three pairs. Thus, each of these atoms by sharing electrons attains a stable number of electrons in its outer sphere (2 in the case of H_2, first orbit; and 8 in the case of N_2).

This covalent link implies a definite directional bond, which is non-ionized.

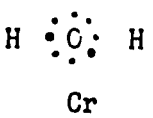
In the third type of valency linkage there is a combination of electro-valency and covalency, known as co-ordinate valency.



two covalent links and one coordinate link on the sulfur atom

dimethyl sulfone

In the Werner theory of valency, the chromium is depicted as co-ordinately linked with six water molecules to form a complex ion with three positive charges. The atom of chromium can form six co-ordinated valencies instead of the four found in lighter elements and so can build an outermost sheath of twelve electrons which, round certain large atoms, can form a stable state. It can further be shown that each of the six water molecules mentioned as associated with chromium, is liked to the central chromium atom by means of a co-ordinated valency, the oxygen atom of the water providing both shared electrons to form a co-ordinate link with the chromium atom.



The other five molecules are attached in a similar manner. This explains why the water molecules are not present as solvent and any groups replacing them in the chromium complex are not individually ionized. The chromium atom belongs to the group of atoms which have their outermost and next outermost electronic sheaths imperfectly filled - the number of electrons in the completed sheaths being 8 and 18 respectively. The valency group of electrons is not fixed in this type of atom as one or more electrons from the next incomplete group may be utilized for chemical combination. Thus, the chromous ion Cr^{+++} has been given an electronic structure represented by two, eight and twelve, with a group of twelve electrons in the third sheath, although a third electron is readily removed by chemical reaction to give the chromic ion with

a two, eight eleven arrangement. It has already been mentioned that this is an unstable configuration and the chromium ion with its positive charges forms an outer sheath of twelve electrons by coordinating with six water molecules.

The addition to the chromium ion of six molecules of water which are coordinately linked, allows the chromium ion to enter into the sharing of twelve electrons (sharing six pairs of electrons associated with the six oxygen atoms in the six water molecules), thus adding twelve electrons to the above arrangement and attaining the stable configuration two, eight, eleven, twelve.

CHROME COMPLEXES AND OLATION

Second Year - Lecture #15

As we have seen, the ordinary valence theory fails to account for the fact that certain atoms or molecules normally considered as being saturated, still possess sufficient combining power to hold other atoms or molecules firmly. In order to explain this fact, Alfred Werner introduced the conception of auxiliary or secondary valence. Ordinary valence was termed primary valence. This idea is called the theory of auxiliary valences or the coordination theory, and it has been very useful in the study of compounds of the higher order whose formation cannot be explained by the ordinary valence theory. A "compound of the higher order", is one formed by the union of two or more saturated molecules, that is, molecules whose constituent atoms are all completely satisfied in accordance with the valence theory. An example of this is when $CrCl_3$ combines with $6H_2O$ to form $Cr(H_2O)_6\ Cl_3$. Both the water molecules and the chromic chloride molecule are saturated molecules according to the ordinary valence theory. Yet it is possible for them to combine in a form whereby the water molecules are oriented around the chromium atom by means of donating electron pairs to form a complete shell. Furthermore, the chlorine atoms are still free to ionize and thus leave the influence of the molecule.

Thus, under the Werner valency concept a chromium salt can be divided into seven classes or types:

viz:-
1. $[Cr(H_2O)_6]\ Cl_3$, $[Cr\ a_6]\ X_3$
2. $[Cr(H_2O)_5Cl]\ Cl_2$, $[Cr\ a_5\ X]\ X_2$
3. $[Cr(H_2O)_4Cl_2]\ Cl$, $[Cr\ a_4\ X_2]\ X$
4. $[Cr(H_2O)_3Cl_3]$, $[Cr\ a_3\ X_3]$
5. $[Cr(H_2O)_2(SO_4)_2]K$, $[Cr\ a_2\ X_4]\ M$
6. $[Cr(H_2O)(OH)(C_2O_4)_2]\ K_2$, $[Cr\ a\ X_5]\ M_2$
7. $[Cr(OH)_2(C_2O_4)_2]K_3$, $[Cr\ X_6]\ M_3$

TYPE 1.

We have already considered Type 1. Another salt in this class is chromium sulfate $[(H_2O)_6Cr]_2(SO_4)_3$ and also $[(H_2O)_6.Cr]_2(SO_4)_3.SO_4K_2.12H_2O$ - chrome alum. In the latter case the potassium sulfate is hydrated - that is, it contains 12 molecules of water as water of crystallization. This water could be removed in a desiccator. However, the 6 molecules of water coordinated to the chromium atom are firmly attached. Water solutions of this type of salt are generally violet because of kation $[(H_2O)_6.Cr]^{+++}$. Salts of this type have no tanning action.

TYPE 2.

$[Cr(H_2O)_5\ Cl]\ Cl_2$ is an example of the general type $[CrA_5\ X]\ X_2$. It would ionize to $[Cr(H_2O)_5\ Cl]^{++}$. Salts of this type usually give a green solution. An important member of this group is $[(H_2O)_5.Cr.OH]^{++}$, which is usually used as the sulfate $[(H_2O)_5.Cr.OH]\ SO_4$. This is the 33 percent basic salt so largely used in chrome tanning.

This salt can be prepared from Type 1 as follows, using either chromium sulfate or chrome alum and caustic soda (NaOH):

$$[(H_2O)_6\ Cr]2\ (SO_4)_3 + 2NaOH \rightarrow 2\ [(H_2O)_5.Cr.OH]SO_4 + Na_2SO_4 + 2H_2O$$

33% basic chromium sulfate

Thus the hydroxyl group has replaced one of the water molecules coordinated with the chromium atom and the valence of the complex is changed from +3 to +2. This process can be reversed with the addition of acid.

TYPE 3.

$[Cr.a_4\ X_2]\ X$ These salts ionize into two ions only, $[Cr.a_4\ X_2]^+ + X^-$. There are two which are interesting from a tanning view point, $[(H_2O)_4.Cr(OH)_2]\ Cl$, dihydroxo-tetraquo-chromi-chloride. This is the 66.7 percent basic chromium chloride; and $[(H_2O)_4\ Cr(OH)_2]2\ SO_4$, hydroxo-tetraquo-chromic-sulfate, the 66.7 basic chromium sulfate.

TYPE 4.

$[Cr.a_3.X_3]$ Substances of this type are not ionized and many of them are insoluble in water. One of the more important is $[(H_2O)_3.Cr(SO_4)_3/2]$ which is present at least temporarily in many heated chromium sulfate liquors; also $[(H_2O)_3.Cr(OH).(C_2O_4)]$ which is the chief constituent of a tanning liquor prepared from an equimolecular mixture of chromium trichloride, sodium oxalate and sodium hydroxide. It has been suggested that chrome leather contains chromium complexes of this type.

TYPE 5.

$[Cr.a_2.X_4]\ M$ The complex is now an anion usually combined with an alkali metal. The chromium and any acid groups within the complex are masked and the addition of ammonia or other alkalies in small amounts brings about no precipitation of chromium until the complex is broken up. A good example is the following acid, disulfato-diaquo-chromic acid:

$$[(H_2O)_2.Cr.(SO_4)_2]\ H$$

This can be produced by heating normal chromium sulfate. It has been shown by Stiasny that commercial solid chromium sulfate and chromium sulfate tanning extracts contain anionic chromium complexes of this type wherein the chromium and SO_4 groups are masked.

A further substance of this type which is of importance in that it can be used for giving the grain a preliminary treatment protecting it against bate liquors, but which does not, of itself, give leather which will withstand the boiling test, is given by the formula:-

$$[(H_2O)_2.Cr.(C_2O_4)_2]\ K$$

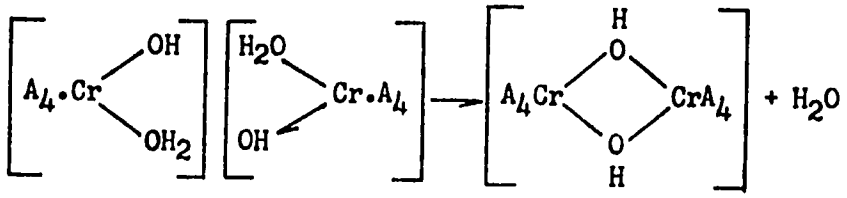
This salt is produced by the reducing action of oxalic acid upon potassium dichromate.

TYPES 6 & 7.

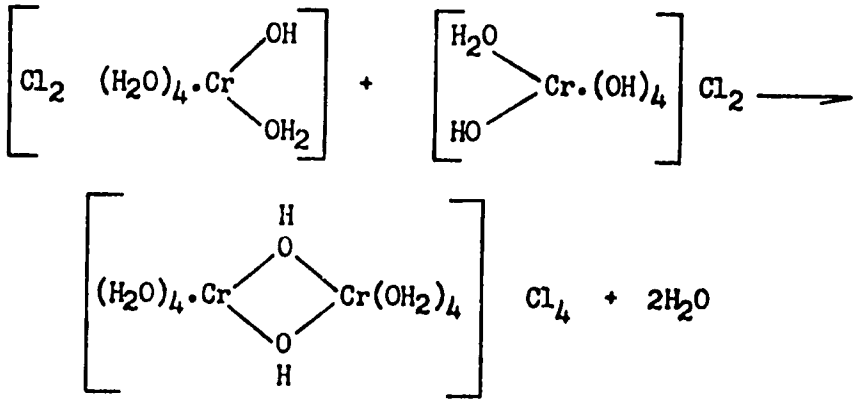
These two types are of no great consequence to the tanner.

OLATION

Olation takes place when two hydroxyl groups coordinately linked or adjacent chromium molecules are joined, one hydroxyl group being combined with hydrogen ion from a water molecule within the complex. It is also possible to form a diol linkage in this case with the removal of a molecule of water.



For example, basic chromium chloride solutions which have been heated or allowed to stand may, with certainty, be considered to contain such compounds; as follows:



In a similar manner, more complicated olated compounds can arise, particularly from more basic solutions; for example, six molecules of the 66.7 percent basic chloride, $[(H_2O)_4.Cr.(OH)_2]Cl$, can give rise by olation to a chromium salt containing six diol groupings. According to Stiasny, this strongly olated compound forms a semi-colloidal solution. With an increasing degree of olation the size of the molecules increases and the solution approaches nearer and nearer the colloidal condition. This is believed, by many people, to be essential from a tanning standpoint since particles of an intermediate size are necessary to give a chrome liquor which will tan. Too small particles have no tanning properties and too large particles are unable to penetrate the collagen fiber. Olation converts a chromium solution into the semi-colloidal or colloidal condition.

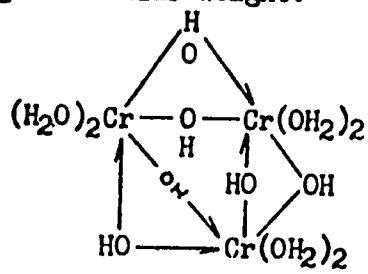
It has been shown that by olation a 33 percent basic chromium chloride solution, on heating or ageing, can give rise to a compound of a molecular weight of 282. In a similar manner it has been shown that basic chromium chloride solutions of still higher basicity, that is 83 percent, can give olated compounds of a molecular weight of 1350.

A basic chromium salt, which is completely olated, can still increase in molecular size by polymerization on further heating its solution. Olation and polymerization proceed in a way on parallel lines as they are affected by the same factors, that is:

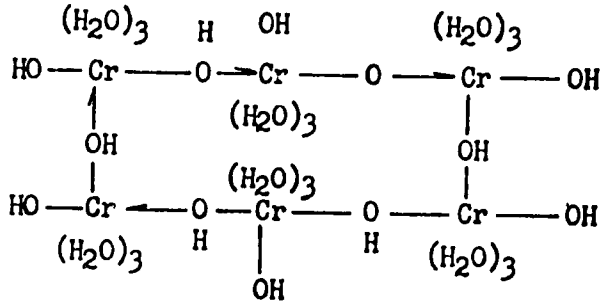
1. Increase in basicity.
2. Ageing.
3. Temperature.

The two processes are, however, different. Olation is a condensation process whereby water is eliminated from within the coordinated spheres of a pair of chromium molecules to yield an increase in molecular size. In the polymerization process simple, or small, olated compounds join together (there is no elimination of water.

The degree of olation is the proportion of ol groups to the total number of hydroxyl groups. We must keep in mind that each time olation takes place between two chromium molecules a pair of OH groups is inactivated. A complex can be 100% olated and of low molecular weight, whilst another might be 50% olated and of a high molecular weight.



This compound is 66.7% basic, 100% olated and has a molecular weight of 366, while:



This compound is 66.7 percent basic, 50% olated, and has a molecular weight of 846.

An important feature which accompanies the process of olation of all basic chromium salts is the increase in acidity of the solution. When a chromium salt is dissolved in water, hydrolysis occurs as follows:

$$[(H_2O)_6.Cr]X_3 \rightleftharpoons [(H_2O)_5.Cr.OH]X_2 + HX$$

This basic salt can olate, giving

$$[(H_2O)_4.Cr.(OH)_2]X_4$$

Further hydrolysis occurs with the setting free of more acid, thereby increasing the acidity of the solution. These changes occur slowly and can be hastened by heating. Basic chrome liquors become more acid on standing. For example, the 33% basic chrome liquor produced from a normal chromium salt by the addition of sodium hydroxide hydrolyses in water as follows:

$$\left[(H_2O)_5 \cdot Cr \cdot (OH)\right] X_2 \rightleftharpoons \left[(H_2O)_4 \cdot Cr \cdot (OH)_2\right] X + HX$$

Thus, if a chrome liquor is made basic, then on standing the acidity of the liquor slowly increases, partly due to hydrolysis and partly to olation.

It has been noted that hydroxo compounds (compounds with OH groups) interact immediately with acids such as HCl. On the other hand, olated basic salts (ol compounds) are relatively stable to acids (interaction is slow). If dilute hydrochloric acid is added to an ol compound, then interaction only occurs very slowly, but may be hastened by the use of a stronger solution of acid or by heating, the complex being split up. The action is the exact reverse of olation.

The resistance of this olated linkage is influenced in this respect by the other groups in the complex. The order of increasing resistance of the ol linkage as affected by other groups in the complex is as follows: Tartrate-oxalate-formate-acetate-sulfate-chloride-nitrate. This is also the order in which these groups are held within the complex.

CHROME LIQUORS

Second Year - Lecture #16

Chrome liquors are usually prepared from chrome alum, sodium or potassium dichromates or technical by-products from oxidation processes in which chromic acid has been used as an oxidizing agent.

If the liquors are to be made from chrome alum, this is made basic, usually with sodium carbonate, and in general an addition is made of neutral salts (mainly sodium chloride). Sometimes additions are made of so-called masking substances, such as sodium formate, oxalate or sulfite, with the intention of slowing up the tanning process, a procedure which is particularly desirable in the early stages if a smooth, lightly tanned grain is desired. Additions of other tanning materials, such as aluminum salts, formaldehyde, synthetic tannins, are sometimes made and these exert their influence upon the properties of the chrome leather.

The preparation from dichromate necessitates the use of reducing agents, such as glucose or sulfur dioxide, to mention but two out of the large number which is available. Each reducing agent produces its own characteristic chrome liquor, the properties of which show up in the leather produced from the liquor. Reduced dichromate liquors are more difficult to prepare than chrome alum liquors. The relative cost of the two types of liquor depends largely on the prices of the chemicals involved.

A point to be considered by the practical man, however, who is balancing the merits of home-made liquors against technical liquors, is that liquors made in the tannery are under more direct control as regards their composition and tanning properties than purchased liquors. Furthermore, alterations in the composition of the tanning liquors are much more easily carried out with tannery-made liquors than with prepared liquors.

One-Bath Liquors made from Chrome Alum

The alum generally used is potassium chrome alum with a molecular weight of about 1000. It contains 10.4% of chromium, whereas sodium or potassium dichromate contains 3-1/3 times as much. If dissolved in water in the cold, it ionizes into the following ions $[Cr(H_2O)_6]^{+++}$, + K^+, and $SO_4^{=}$. The chromium content of this solution can be determined from the specific gravity, a saturated solution of specific gravity 1.0885 at 15°C. containing 18.3% of chrome alum. The pH value of the cold saturated solution, freshly prepared, is 2.8. This solution when freshly made, is violet, the color being due to the complex ion $[Cr(OH_2)_6]^{+++}$; on standing it gradually becomes green and progressively more acid as hydrolysis and formation of olated compounds occurs. This hydrolysis gives rise to basic chromium sulfates and free sulfuric acid.

Chrome alum solutions prepared hot are green and contain strongly olated chromium compounds and free sulfuric acid. It is possible to prepare stronger solutions of chrome alum if the solution is prepared hot and then cooled than

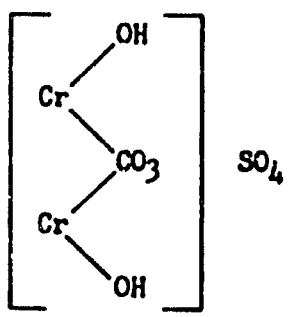
if the whole preparation proceeds at the ordinary temperature. Satisfactory tanning properties can be imparted to a chrome alum solution by the addition of sodium hydroxide, sodium carbonates or similar alkalies. The effect of the addition of an alkali is to produce basic chromium sulfates, the nature depending upon the amount added. The following practical points relating to the making of liquors of this type basic are of interest. Increasing additions of alkali:

1. Lower the acidity and the swelling properties of the liquor.
2. Lessen the precipitation figure of the liquor, chromium salt.
3. Increase the speed with which olation occurs and the extent of the occurrence, at the same time increasing the size of the chromium complex.
4. Increase the colloidal character of the liquor.
5. Reduce the proportion of the sulfato groups which are held in the complex.
6. Raise the astringency of the liquors.
7. Increase the amount of chromium taken up by the skin, other things being equal.

Thus, the preparation of only slightly basic for beginning tanning requires the addition of less alkali than is the case with the later liquors in the tanning, which are, as a rule, astringent more.

It is felt that leather made from chrome alum liquors dissolved hot is better than leather made from cold liquors. Ageing of the cold liquors removes some of the differences. If sodium carbonate is used to neutralize these liquors, it is believed that basic complexes are formed which contain carbonato groups (CO_3). The sodium carbonate in other words is not wholly used up in making the liquor basic (introducing OH groups into the chromium complex) but is partly used in the introduction of the CO_3 radical into the complex. Thus, it produces liquors of a lower basicity and a different composition from those resulting from the addition of an equivalent amount of caustic soda.

viz:



These "carbonato" liquors undergo the following changes on standing:

1. They lose CO_2.
2. The basicity value increases for both chromium salt and liquor.
3. Olation slowly raises the acidity of the liquor.

This is an example where a liquor on standing becomes more acid whilst its basicity increases.

One-Bath Liquors made from Dichromate

Dichromates are reduced in the presence generally of sulfuric acid, or sometimes hydrochloric acid, by means of a suitable reducing agent. Whilst in two-bath chrome tanning the reducing agent must be effective in dilute solution and rapid in action at room temperature (usually thiosulfate is used for this purpose), the choice of the reducing agent in the preparation of one bath liquors is much greater. Fundamentally, any material which reduces chromic acid in hot, fairly concentrated solutions may be used. For example, the following inorganic materials: sulfur dioxide, sodium sulfite, sodium bisulfite, sodium thiosulfate, sulfides, hydrogen peroxide, etc. and the following organic substances: glucose, cane sugar, molasses, glycerin, cellulose extracts, spent vegetable tanning materials, oxalic acid, etc.

Sulfuric acid is the acid most commonly used in preparing technical tanning liquors. Where acid has to be used in addition to reducing agent, the amount used is governed by the desired basicity of the chrome liquor. This basicity cannot be greater than a certain amount depending on the nature of the reduction, as a certain amount of acid is necessary in order that the reduction process may be brought to completion. When glucose is used as the reducing agent there is no consumption or production of acid provided conditions of concentration and temperature are maintained so that oxidation to CO_2 and water occurs.

In the preparation of one-bath liquors from dichromates, care must be taken that the reduction is complete. This can be easily tested as follows: a few drops of the liquor are placed in a test tube, diluted with about 5 cc of water, ammonia added and the solution boiled and filtered. If the filtrate is colorless then the reduction is complete; if it is yellow unreduced chromate is present.

It is one thing to reduce a liquor to a definite desired basicity and another to adjust a liquor of an incorrect basicity by adding acid or alkali. A liquor which has been corrected by the addition of sodium carbonate olates on standing, becomes acid and gradually increases its precipitation figure. If corrected with an acid (H_2SO_4), then the opposite occurs, on standing the liquor becomes less olated, less acid and suffers a reduction in its precipitation figure. Changes such as these receive little consideration in many tanneries, but according to Stiasny they explain many of the irregularities which are met in the tannery.

Glucose Liquors

The use of glucose in the preparation of one-bath chrome liquors was suggested as long ago as 1897 by Procter, who recommended the following quantities: 3 parts by weight of dichromate, 6 parts by weight of concentrated hydrochloric acid (or 3 parts of concentrated sulfuric acid). When reduction is complete, make up to 100 parts. The reduction is brought about by the continuous addition of sugar, which keeps the whole mixture at the boil. On the laboratory scale, about 15% of sugar (on the weight of dichromate) is nearly enough to give complete reduction, but on a works scale, larger amounts must be used as conditions are often less suitable for the oxidation of the sugar to CO_2 and water. The formation of intermediate products of the oxidation of the sugar has also to be considered. These can lower the basicity of the

liquor and can also exert a masking action in that they enter the chromium complex and shield it against the precipitating action of alkalies and at the same time reduce the astringency of the chrome liquor. In order to reduce the masking action to a minimum, the use of an excess of sugar must be avoided. A lowering of the temperature at which reduction takes place, for example, lowers the basicity of the final liquor.

The methods of preparation differ considerably and result in tanning liquors which have particular properties according to the method used. Variations occur in practice in the choice of acid (sulfuric or hydrochloric), the proportion of glucose to dichromate, and also in the order of addition of the various materials. In some cases, excess of glucose is carefully avoided by completing the final stages of reduction by the addition of another reducing agent, such as sodium bisulfite. In other cases, an excess of glucose is deliberately added. With reference to the order of addition, the glucose can be added slowly to the hot mixture of dichromate and acid or the acid slowly to a hot mixture of dichromate and sugar, or finally, the dichromate can be added to a mixture of sugar and acid of medium strength.

Thus, it is evident that in the production of glucose reduced liquors, the working conditions must be carefully controlled if a liquor of constant properties is desired.

According to Stiasny, in one bath chrome tanning, it is generally advisable to start the process with liquors which are only slightly astringent and then continue and complete the tannage with liquors of increasing astringency. Or, as he explains it in his golden rule of tanning: "Start with liquors containing small particles and continue with particles of increasing size."

Thus chrome tannage, in general, should commence with liquors of low basicity and continue with increasing basicity. This can be achieved practically by the periodic addition of solutions of sodium bicarbonate or borax during the course of the tanning, but the amount of alkali added will depend upon the amount of acid in the skins and also upon the nature of the tannage. Thus we can see that pickling not only brings the skins into a uniform condition of acidity but it also adjusts the basicity of the chrome liquors, checking olation, delaying precipitation and keeping the liquors mellow.

SUMMARY

1. The astringency of chrome liquors depends on the nature of the chromium salt formed. Chromium sulfate liquors are more astringent than chromium chloride liquors, and both of these are more astringent than liquors made by the reducing action of orgaric compounds.

2. Astringency is affected by basicity, the more basic liquors being the more astringent. Hence liquors with very low pH values are less astringent than liquors with higher pH values. Pickling before tanning hlps to mellow the tannage.

3. Raising the temperature of a chrome liquor increases its astringency, probably through increase of olation. Diluting a chrome liquor does not reduce its astringency. The more astringent the liquor the greater is the fixation of chromium by the collagen.

4. Salts have a physical effect reducing the plumping induced by acid liquors.

5. For good grain and full leather, the tannage should be mellow at the start and astringent at the finish. Hence, the tannage should start in organically reduced liquors of low pH, moderate salt content (to check plumping) and moderate temperature.

6. Chrome liquors made by reducing dichromates with glucose or other organic materials give a softer fuller leather than those made by reducing with sulfur dioxide or sulfites. This is probably due to the nature of the acid groups penetrating the chrome complex, and the extent to which they displace water groups.

TWO-BATH PROCESS AND NEUTRALIZATION

Second Year - Lecture #17

The two-bath chrome tannage, as it implies, consists of two baths, the chrome bath and the reduction bath. This system of chrome tanning was particularly adapted for glazed kid. The skins, usually pickled, are first treated for two to four hours in a solution of sodium dichromate (6%) and hydrochloric acid (3%). The intent is to produce about 3 to 4% chromic oxide in the final leather. The chromic acid is always prepared by the action of a mineral acid, generally hydrochloric acid.

The chief constituent of the chrome bath is chromic acid, formed according to the following equation:-

$$Na_2Cr_2O_7 + 2HCl = 2\,NaCl + \underset{\text{chromic acid}}{2\,CrO_3} + H_2O$$

It has been thought that both the sodium chloride and the residual dichromate exercise some effect on the process. The solution has a low pH but there is no swelling of the pelt. Excess neutral salt hinders the absorption of the chromic acid, a slight excess of dichromate appears to favor it. The skins assume a yellow color throughout their entire thickness, but they are not tanned, as shown by the fact that the whole of the chromic acid can be removed by washing the skins in water.

The skins out of the first bath are horsed up overnight and covered to protect them from the light. On exposure to light, skins in this yellow condition become discolored. It is believed that the skin tissues can be oxidized in the presence of light and partially destroyed. The process of "horsing up" is performed to insure more complete penetration of the solution into the fibrils; this also helps prevent bleeding in the second bath.

The reduction bath comprises a treatment in a bath of hypo and weak hydrochloric acid. The chromic acid on the fibers of the skin is reduced to a basic chromium salt, a tanning material and the skins are thus converted into leather. The reduction is not merely a conversion of the chromic acid into basic chromium chloride. A good leather will not result, for instance, if the hypo-acid bath is replaced by a solution of sulfur dioxide which we know to be a good reducing agent.

The reduction of the chromic acid by hypo and acid is complicated by several possibilities and the progress of the reaction is dependent upon the temperature and concentration of the reducing bath.

The objects to be aimed at in the second bath are two-fold:

1. The complete reduction of all the chromic acid in the skin.
2. The formation and fixation of a chromium compound of the correct basicity in the leather.

These objects can be obtained with certainty if the proportion of acid used during the process is carefully controlled, and if the amount of hypo used is sufficient to insure an adequate surplus being left unused at the end.

The following is a listing of six very important variables which can affect the quality of the leather obtained:

1. proportion of hypo to goods
2. proportion of goods to liquor
3. proportion of acid used and the method of adding
4. temperature
5. period of action
6. formulation of a standard method of hypoing.

One can immediately perceive that the above considerations are often encountered in other processes; however, it is not our intent to go into each of these in detail as it does not particularly serve our present purpose.

The Chemistry of the Two-Bath Chrome Tanning Process

The underlying idea which is the basis of the two-bath process is that by impregnating the skins with a solution of chromic acid and then reducing this to the basic chrome tanning compound, the latter is formed where it is required, namely, directly in contact with the collagen fibers. It must be noted that the conditions of the reduction of the dichromate to basic chromium salt in the two-bath process are different from those which occur in making a one-bath tan liquor, since the concentration of the reducing agent is less and the temperature is considerably lower.

In the process of the reduction colloidal sulfur is often formed as follows:

$$Na_2S_2O_3 + 2\ HCl \longrightarrow 2\ NaCl + SO_2 + \underline{\underline{S}} + H_2O$$

An even greater amount of sulfur is obtained if sulfuric acid is used in place of hydrochloric acid. In many cases this colloidal sulfur formation is desired as it is believed to act as a lubricant for the fibers in a manner analagous to graphite on a steel or bronze bearing. This has been particularly true in the case of hair-on leathers manufactured for use in industrial applications, particularly for looms in the textile industry.

It is interesting to note the color changes which take place in the skin in the hypo-acid reducing bath. When placed in the bath the skins were yellow. This changes to a pale bluish-green in the final state; however, it passes through a brownish-yellow stage to brown; then olive-green, green and finally the final bluish-green. If the reduction stops at the brownish stage it is an indication that not enough acid has been added. At this stage chromic dioxide would have been formed. viz:

$$CrO_3 + Na_2S_2O_3 \longrightarrow Na_2SO_4 + S + \underset{\text{chrome dioxide}}{CrO_2}$$

We know that in the one-bath chrome process glucose sugar reduced liquors yield only partially oxidized organic compounds in most cases instead of complete oxidation of the sugar to $CO_2 + H_2O$ which is the theoretical end point. Prominent among these partially oxidized products is the oxalate ion and the formate ion which can enter the chrome complex and yield a so-called "masking" effect. That is, they can hinder olation and possibly even polymerization. In a similar manner in the two-bath process it is known that in the hypo bath radicals of the formulas $S_2O_3^{=}$, $S_4O_6^{=}$, $S_5O_6^{=}$ and other polythionates are present along with $SO_4^{=}$. It is believed that some of these, if not any of them, can enter into the chrome complex and produce more stable compounds. One striking fact about two-bath chrome tanned leather is its comparatively low content of Cr_2O_3, a fact which may be associated with the type of radicals which are co-ordinated in its complex. One-bath chrome leather requires a minimum content of 4.5% of Cr_2O_3 to stand the boiling test compared with a minimum of approximately 3.0% for two-bath chrome leather. This is believed to be due to the formation of larger complexes by the entrance of the radicals mentioned above, as derived from the hypo.

The Washing and Neutralizing of Chrome Leather

The processes now to be considered apply both to leather tanned by the one-bath process and also the two-bath process of chrome tanning.

Washing is carried out with the object of removing most of the salts and some of the acid present in the leather. The salts are derived from residual calcium from the liming process and from the chemicals used in hypoing, and consist mostly of chlorides, sulfates, thiosulfates and tetrathionates of sodium and calcium. Washing will remove these salts quite completely, but it is necessary to go to further work in order to remove the excess acid. This process is known as neutralization.

The following chemicals have been used by various tanners to effect this particular change:

1. Caustic Soda	1% soln. = pH of 13.3
2. Sodium Carbonate	1% soln. = pH of 11.0
3. Sodium Bicarbonate	1% soln. = pH of 8.5
4. Borax	1% soln. = pH of 8.9
5. Basic Sodium Phosphate	1% soln. = pH of 8.7
6. Sodium Thiosulfate	1% soln. = pH of 7.0

We can immediately see that there is considerable variation in the acid removing power of these six neutralizing agents. Sodium bicarbonate and borax have been two particularly satisfactory agents for this purpose in most cases.

We know that chrome tanned leathers are particularly very acid as they leave the tanning liquors. This is particularly so when considerable olation has taken place or even hydrolysis. In both cases free hydrogen ions are released. Also, another factor to be considered is that this releasing of hydrogen ions continues for some time after removal from the tanning liquor, particularly in the "horsing up" stage. This free acid would adversely affect dyeing and fatliquoring at this point.

A high hydrogen ion content in the leather would lead to uneven dyeing since the shade developed with the acid dyestuffs depends on the pH value. Also direct dyestuffs give best results on practically neutral leather. Fatliquor emulsions are usually broken down by even low hydrogen ion concentrations and if this happens the oils and fats will be deposited as a greasy film on the surface of the leather affecting its finished appearance as well as leaving the center "starved" or lacking in lubrication for the fibers.

There are two other factors which take place in the neutralizing operation. Since hydrogen ions are removed, further hydrolysis and olation of the chromium complexes is encouraged. It is possible that by this means the eventual equilibrium of complex formation is hastened. Also, during the neutralizing, chemical changes are taking place which involve both the basic and the acidic ions of the alkaline neutralizing agent used. Thus, while the basic ions (bicarbonate or borate) play their usual role of neutralizing the acidic (hydrogen) ions, the neutralizing agent interacts to some extent with the chrome tanning compound on the fibers, leading to an exchange of acid groups such as the sulfate group within the chromium complex. This was particularly shown by an investigator who determined the total amount of sulfur present in several neutralized leathers in the blue, each one being neutralized by a different alkali. viz:

Neutralizing agent	g sulfur to 52 g chromium in neutralized blue
Sodium bicarbonate	4.7
Sodium borate	2.0
Sodium thiosulfate	38.3
Sodium tetrathionate	51.3
Sodium phosphate	3.4
Sodium silicate	4.0
Sodium oleate	10.9

These figures show in a striking way how the total sulfur content of a leather rises if the anion of the neutralizing agent contains sulfur.

This shows why the total sulfur content of a two-bath leather is always much greater than that found in a one-bath liquor (the thiosulfate and tetrathionates of the hypo bath have entered the complex). Possibly the penetration of the thiosulfate and tetrathionate radicals into the complex of the one-bath leather explains the fundamental difference between these two leathers.

CHROME TANNING THEORIES - EMULSIONS

Second Year - Lecture #18

We have seen that the chrome salts used for tanning skins are not simple compounds, moreover we have also seen that they may differ in their constitution and molecular size depending upon their mode of preparation. Therefore, it is difficult, if not virtually impossible, to discuss them or their uses without giving due consideration to the various conditions which control the many possible states in which they may exist. It is also significant that we know just which of these states is the most suitable for our purpose. The composition of even the simplest chrome tanning solution is very complicated.

According to Stiasny the chrome tanning complex must be semi-colloidal; moreover, tanning power increases with the molecular size of the chromium complex which is a function of the basicity of the liquor and the degree of olation. Chrome tanning liquors are thus to be regarded as semi-colloidal and after diffusion within the hide they may, on account of the basic properties of the collagen which would favor olation, approach more nearly to the colloidal state, which would prevent their rediffusion out of the hide substance and into the tanning liquor.

There are several theories as to the manner by which chromium or its salts combine or affect a skin to make leather. It is not our intent to consider these at any great length as this knowledge is not necessary for our purpose, as well as the fact that considerable work will yet have to be performed before a complete and satisfactory answer is available - one which will answer all of the questions and satisfy every one concerned.

1. At the present time it is assumed that combination between basic chromium salts and collagen by primary valencies (electrovalencies such as exist between sodium and chlorine in salt), may occur as a first stage in the tanning process to some extent.

2. The main chemical reaction in tanning is believed by some to be due to a coordination (by secondary valencies) of the chromium complex and the collagen. There is also believed to be the possibility of coordination between some group (probably the amino group), and the chromium atom of the complex, displacing a group previously present in the complex.

3. Chrome leather resists the action of boiling water. This has been attributed to be due to the inactivation of these groups in the collagen molecule which attract water molecules. These water molecules are displaced by the chromium molecules in the tanning process and this may in some way explain the difficulty experienced in wetting back chrome tanned leather. It has also been noted that chrome tanning makes leather resistant to the action of the enzyme trypsin. As trypsin normally attacks the peptide link joining the amino acids of the collagen causing breakdown, it seems that its inertness in the case of chrome tanned leather may be due to a combination at this point with the chromium molecule.

It is interesting to note that certain acids, notably oxalic acid, can partially reverse the chrome tanning process. This partially dechromed leather loses its resistance to boiling water.

4. Many theories of chrome tanning have been built around the changes which take place when the acid and chrome tanning salt diffuse into the hide substance, the fixing of the acid by certain groups in the collagen leading to changes in the chromium. Particular mention may be made of the suggestion that the withdrawal of acid from the tanning liquor which has diffused into the hide by the hide substance brings about a precipitation of an insoluble chromium salt.

According to this particular theory, chrome tanning consists of a deposition of chromium hydroxide or strongly basic chromium salts on the surface of the fibers. This thus coats the fibers with water resisting materials, which prevent swelling and putrefaction. Another factor which might lend some support to this theory is the absence of stochiometric proportions between hide and tanning material.

A variation of this theory was offered by the British Leather Manufacturers Research Association, namely, that chrome tanning consists of a deposition of the basic chromium sulfate $[(H_2O)_4.Cr.(OH)_2]_2SO_4$, in and around the fibers. Part of this basic salt combines chemically with the collagen, possibly by an interaction involving the NH_2 groups of the collagen and the OH groups in the basic chrome salts. Chrome leather in the blue was thus regarded as consisting of a deposited basic salt and a compound of this with collagen.

In closing it can be said that for tannage to occur, the active centers (electrically charged or hydrated) of the collagen molecules must be depolarized or inactivated by loss of electric charge or elimination of water. It is quite interesting to note that a skin or hide has an affinity for water, or at least certain groups in the collagen molecule have this affinity. We have seen that when we remove the water from a hide it can be preserved. Likewise, it must re-absorb this water in order to regain its original state. Moreover in liming, bating and pickling the ability of the hide to hold water varies to a great degree with pH. We found out that in a limed skin certain of the contained water is bound water and is resistant to great pressing pressures. We have seen how the chromium molecule can coordinate six water molecules around it into a stable configuration, also we know that other groups such as the OH and NH_2 groups have this ability. Thus it is not too far-fetched to have a theory which is evolved around the idea that the chromium molecule displaces the coordinated water molecules around OH and NH_2 groups in the collagen molecule and possibly has its own coordinated water molecules displaced also. This would mean that the chromium molecule was now coordinated with these groups, making them inert to water molecules from there on.

This might in some way explain the phenomena that every research chemist in a laboratory has experienced, namely, the difference in feel - immediately apparent when a piece of hide has been treated with a chemical which has the property of tanning it. This is even evident in degrees when one uses a chemical which does not have very good tanning action.

Emulsions and Fatliquors

An emulsion is a system containing two liquid phases, one of which is dispersed as globules in the other. That liquid which is broken up into globules is termed the dispersed phase, whilst the liquid surrounding the globules is known as the continuous phase or dispersing medium.

Two pure immiscible liquids, such as an oil and water, when shaken together or otherwise agitated will temporarily produce an emulsion, but as soon as agitation ceases, the drops of the respective liquids region and the liquids separate into two distinct layers. By suitable treatment fairly stable emulsions of a pure oil in water may be obtained, but the concentration of the oil is very low. If a little oil is boiled with water under a reflex condenser, such an emulsion is obtained wherein the concentration of oil in water is about 1 in 10,000. Without the presence of an emulsifying agent the maximum concentration of oil in water obtained is about 2%. The oil golbules in pur oil-in-water emulsions have diameters of the order of 10^{-5} cm., as compared with 10^{-3} cm. for colloidal suspensions.

It has been remarked that theoretically, if the oil globules be considered rigid spheres of equal diameter, it should be possible to pack them together in such a way that each sphere will touch twelve others. This maximum packing, that is concentration, occurs when about 74% of the total available space is occupied by the spheres. Hence approximately 74% of oil can theoretically be dispersed in about 26% of water. Such concentrated emulsions, however, demand the presence of a third substance capable of forming an adsorbed film at the oil-water boundary. This third substance is termed an emulsifying agent.

Most of the early work on emulsions dealt with systems in which various oils were dispersed in water, this type of emulsion being known as the oil-in-water (or O/W) type. Ostwald, in 1910, first drew attention to the existence of another type of emulsion, namely, water-in-oil (or W/O). He also pointed out that emulsions of equal volume concentrations but of opposite types, that is, oil-in-water and water-in-oil would have quite different properties. Emulsions of both types are quite common.

Water-soluble colloidal substances promote emulsions of the O/W type, whilst oil-soluble colloids promote the reverse type. In making an emulsion the primary question may concern the choice of the emulsifying agent, on the grounds of cost, liability to fermentation, or resistance to freezing, boiling, acids or alkalies.

The hydrophilic colloids (water loving) - proteins, gums, carbohydrates - have long been recognized as efficient agents for promoting emulsification of oils and fats in water. Gelatin is an emulsifying agent for oils of both glyceride and hydrocarbon character. For some time alkalies were considered good emulsifying agents for oils and fats, and patents were even issued to cover their use, such as Na_2CO_3 for emulsifying fats, and soluble silicates for preparing cod-liver oil emulsions up to 50% volume concentration. However, it was eventually shown that alkalies are efficient only when they form soaps with the free fatty acids present in the oils or fats. Soaps are excellent emulsifiers for all kinds of oils and fats.

Soap emulsions are used in some special cases for fatliquoring leather because they have advantages when applied to certain types of leather. The oil dispersion in a soap emulsion is usually much coarser, and is also broken more readily by chrome leather acids or by stripped vegetable tannins. Therefore, soap emulsions do not always penetrate as deep into the leather and do not give the same degree of softness as sulfated oils. This can mean that slightly more oil can be applied to such leather in a soap emulsion without bringing about too great softness and raggedness. This is said to also give a greater stitch-tear strength than could be accomplished with a smaller amount of sulfated oil.

Soap emulsions can, of course, simultaneously fatliquor and neutralize chrome liquor, but in doing so they may give a harsher surface feel and a poorer break. The proportion of soap to oil in various alkaline fatliquors can vary from 1:2 to 1:15. A common proportion used is 1 part of soap to 5 parts of oil. The hard soaps, like the soda soaps (castile soap) etc., can form a spue on leather, especially chrome-tanned leather. It is claimed that in tanneries a change to the soft potash soaps eliminated the spue. Potassium soaps are better emulsifiers than are sodium soaps.

FATLIQUORING - STUFFING AND EMULSIONS

Second Year - Lecture #19

Oils and greases are used in leather manufacture chiefly for the purpose of rendering leather either more waterproof or more soft and pliable. The beamhouse operations and the tanning processes have removed or modified much of the natural fats and oils which were inherent in the skin. Moreover we know that these were present mainly to serve purposes necessary to the function of the skin as a living organ.

The astringency of the various vegetable or mineral tannages employed has rendered the fibers quite brittle and resistant to flexing. That is, they are hindered in sliding by each other smoothly as is necessary in any material which must flex or stretch. The addition of various oils, fats or fatty emulsions must be resorted to in order to render the fibers soft and pliable and also free to stretch and contract independently of each other. This latter point is quite sharply brought out in industrial type leathers, for a belting leather in the rough (tanned and dried) will have a tensile strength of about 2500 to 3000 lbs./sq. in. and after currying the same leather will have a tensile strength of from 5500 to 6500 lbs./sq. in.

Oils are used in oil tannages such as the manufacture of chamois leather, and also for some miscellaneous purposes such as "oiling off" before drying. The more important processes involving oils and fats may be classified under four types:

1. Oil tannages
2. Impregnation
3. Currying
4. Fatliquoring.

1) The first type of oil treatment is oil tannage in which the oil or fat is not merely a lubricating or waterproofing agent, but actually the tanning material which converts the collagen of the hide or skin into leather. Many theories have been put forward to explain this process. The most likely hypothesis is that the amino groups of the skin protein combine chemically either with oxidized fatty acids produced from the oils, or with aldehydes also formed as a result of the oxidation of unsaturated oils. We know that the fats and oils used in treating leather are esters of various fatty acids, many of which have unsaturated bonds in their chain of carbon atoms. Also, these esters can be hydrolyzed in the skin as the correct acid catalyst is present in practically all skins. This has been quite clearly demonstrated by many degreasing experiments on curried leather. For while certain percentages of fats and oils were introduced into the leather, subsequent degreasing with various fatty solvents failed to remove a substantial fraction. This fraction of oxidized and combined fats becomes larger as the age of the leather increases.

It is claimed by Clayton that the unsaturated acids of the oily material apparently undergo oxidation under the influence of water to yield dihydroxy fatty acids which have a tanning action. He further claims that the main oil adsorption is not from the flesh side, but through the grain. Several researchers have pointed out that the center of the skin may be free from oil, as a matter of fact they claim that an unlubricated middle stratum ensures firmness, a soft and raggy leather following oil adsorption to the center strata.

2) The second manner of applying grease to leather is the process of impregnation. The leather, absolutely dry, is immersed in hot melted greases or waxes. The grease is quickly absorbed and the final product may contain 40 or 50% of fatty matter. This is a method of waterproofing leather and has been much used for chrome sole leather and occasionally for vegetable tanned sole leather also. Great care must be used in this latter case, since vegetable tanned leather is exceedingly sensitive to heat in the moist or damp state. Rosin is sometimes incorporated in this grease mixture for the purpose of preventing the soles from being slippery in wet weather.

3) Currying is very widely practiced and may be carried out by two methods: hand stuffing and drum stuffing. In the first process the leather is warmed to about 125°F. and the warm mixture of fats and oils is applied to the flesh side. The leather is immediately returned to the 125°F. atmosphere and left to hang about 12 to 18 hours, at which time the mixture is dispersed into the leather. In drum stuffing the drum is heated to the desired temperature and the leather placed in the drum. Immediately afterwards the hot grease mixture is introduced and the drum turned until all of the grease has been pounded into the leather. There are certain chemical complexities to be considered, both in the constitution of the materials used and in the chemical changes which take place after the grease mixture has been incorporated into the leather.

To the layman the most striking feature of the currying process is the indispensable necessity for having the leather damp. The exact degree of dampness is very important and a matter for experienced judgment, just as in the case of the proper amount of moisture in a skin for good shaving. However, it is this necessity for moisture which gives the clue to what really happens in currying, and this might just as well point out the reason that a water oil emulsion, or fatliquor gives satisfactory penetration.

A dry leather fiber does not possess a surface over which oil can readily spread. However, the oils used in currying will spread over a water surface and, also, though sometimes a little less readily, over the surface of a tannin solution. If a leather fiber, therefore, is sufficiently wet, so wet as to have what is essentially a water surface, oil will spread over it easily. It might be well to mention the old controversy of mineral oil versus vegetable and animal oil at this point, for in addition to variations in chemical structure and behaviour they are claimed to have much poorer spreading qualities. We can readily see that this would offer considerable variation from an animal oil if the theory of the oil spreading over the water film on the leather fiber is valid.

However, if the leather is too wet, the penetration of the oil will not be good. Under such circumstances, not only are the fibers wet, but the spaces between the fibers are filled with water, and the oil will tend to spread over the water-air surface on the exterior of the leather, rather than penetrate by spreading over each individual fiber. This means that currying does not begin until the water-content of the leather is reduced by evaporation and as the oil does not evaporate it is left behind on the surface of the fibers. Emulsifying agents such as sulfated oils appear to assist penetration very materially.

4) The fourth type of application of grease is by drumming the leather in the wet or damp state in a dilute oil-in-water emulsion, which is technically known as a "fatliquor". The process of fatliquoring has become more and more extensively used with the development of chrome tanning. Actually the process precedes the chrome tanning process as history indicates that an early American tanner, James Kent, first used this process in which he treated leather tanned by a combination tannage of alum and vegetable tannin with the alkaline liquor obtained by washing the surplus oil from chamois leather. As a matter of fact, there was even earlier use of egg yolk in the manufacture of alum tanned leather. The egg yolk is, of course, a natural fatliquor or emulsion in which the emulsifying agents are the proteins and lecithin present in the egg yolk. The usual fatliquors are oil-in-water emulsions in which the oils employed are triglyceride oils, mineral oils, or mixtures of these, emulsified either by soaps or sulfated oils and in recent years a great deal of progress has been made in the field of emulsions to yield a very impressive number of emulsifying agents, some belonging to entirely new classes of compounds. However, the theories of emulsification are still far from complete and the technical progress has been far ahead of the theoretical considerations.

Nothing is included in the literature at the present time relative to the effect of these various emulsifying agents upon the leather. Every one concerned considers the emulsifying agent as an inert catalyst which is necessary to aid the formation of small globules of oil in a water medium without itself having any effect upon the leather. This may be true in many cases as well as the fact that some of these agents may have a lubricating value of their own. However, out of the large number of emulsifying agents in use today, some have been shown to have an adverse affect upon the leather fibers. Some even have a tanning ability and can increase the degree of tannage. This has been particularly true of the emulsifying agents used in wool scouring oils and their deleterious affect has been quickly noted on leathers used on woolen cards of the condenser type. A change to a different scouring oil in a mill is often followed by rapid failure of these leather parts as the oil containing this particular emulsifying agent is transferred to the leather by the woolen fibers in the normal operation of the machine. Histological examination (thin sections viewed under the microscope) has shown that the emulsifying agent replaces the oil around the fibers by a sort of leaching action.

There is more than one theory to explain the fatliquoring operation, but the following is quite generally offered to explain the absorption of the oil. It is based upon the attraction or neutralization of opposite

electrical charges. Chrome tanned leather has a basic chromium salt combined with the free carboxyl groups of the hide, which also possesses amino groups that have already combined with the acid produced in the chroming liquors by hydrolysis. Thus the chrome leather possesses positive charges due to $-NH_3^+$ groupings. These have an affinity for the negatively charged droplets - the droplets of oil being surrounded by a film comprising the emulsifying agent, so that the charge upon the oil droplet is due to the film and not the oil. This theory is sufficient to account for the initial rapid absorption of the oil.

Neutralization and a thorough washing after tannage are essential if soap is to be used as an emulsifying agent, for if soluble chromium compounds are left in the leather, chromium soaps will be formed, leaving sticky messes on the skins. Also, the emulsion will break, causing greasy patches. Fatliquoring should follow fairly closely after neutralization for further acidity may develop on standing, due to hydrolysis of the chromium compounds combined with the hide. These dangers of soap fatliquors have been in part obviated by the use of sulfated oils which are capable of emulsifying even in slightly acid solutions.

The reason for piling up of grease in the outer layers of the skins or hides is that the emulsion is broken after relatively little penetration of the leather. According to Atkin and Thompson this is due to two (2) factors:

a. The acidity of the leather or if well neutralized, delayed hydrolysis and olation, (as noted above).

b. The absorption by the basic chromium salt combined with the leather, of either fatty acid anions of soap or of the negatively charged sulfated oils which owe their charge to the sulfate group.

We have already seen that chromium salts can and do coordinate around themselves a sphere of six molecules or ions of various types. It is claimed here that the emulsifying group may enter into this complex, displacing a water molecule or some other group present in the molecule. Thus, if the stabilizing emulsifying agent is absorbed into the chromium complex the emulsion is broken, unless a large amount of emulsifying agent has been used.

Fatliquoring may also be carried out on vegetable tanned leather, although the splitting of the fatliquor is not so easily brought about. The emulsifying agent in this case apparently combines with the free amino groups present in the leather and this may be facilitated by the usually acid condition of such leathers. Usually, when vegetable tanned leather is fatliquored, the proportion of grease in the middle layers is definitely higher than with chrome leather.

EMULSION THEORIES

Second Year - Lecture #20

Emulsions were made and used long before there was any attempt to explain their formation and behavior. Up to the middle of the 19th century, the concepts of what emulsions actually are, were quite hazy.

Two reasons may explain why the theoretical knowledge of emulsions is of comparatively recent date. First, emulsions in the early days were rather unimportant, aside from small quantities of salves and unguents made by hand in pharmacies according to carefully guarded secret formulas. Second, and more important, the early investigations concentrated on chemical studies of these structures and it was not until relatively recently that it was found that emulsions are essentially physical phenomena.

As a result of studies of surface tension, absorption, dispersions and many other side lines, formulating a theory of emulsions became possible.

For the time being, there is no equally satisfactory theory of emulsions. There are a number of valuable special theories covering particular phenomena, such as the formation of the emulsion or the reversal of the phases (de-emulsification), but a single general theory of emulsions, which can be relied upon to answer all the questions is still lacking.

That there is still some uncertainty concerning emulsions is evidenced by the lack of a clean-cut definition. The following are definitions taken at random which, although not identical, generally coincide.

1) An emulsion is a very fine dispersion of one liquid in another with which it si immiscible.

2) An emulsion is a system containing two liquids, one of which is dispersed as globules in the other.

3) Emulsions are mechanical mixtures of liquids that are immiscible under ordinary conditions, and which may be separated into layers on standing, heating, freezing, by agitation, or the addition of other chemicals.

If we consider an emulsion as a dispersion of one material in another we must seriously consider certain qualifications, particularly the degree of dispersion, or the particle size. For we know that there are several classifications of dispersion ranging from coarse to colloidal to molecular. A solution of salt (NaCl) in water may be considered a molecular dispersion wherein the sizes of the particles are the dimensions of the molecule itself. However, in the case of milk we have particles or globules of fat which are relatively large, being made up of many molecules massed together.

It is generally agreed upon to refer to dispersions as coarse, if the dispersed particles are of larger diameter than 0.1μ, to call a dispersion colloidal if the particles are in the range of 0.1 - 1μ, whereas any particle whose diameter is smaller than 1$\mu\mu$ will be classified as molecularly dispersed. A micron (μ) is defined as 0.001 m.m. or 10^{-3} m.m. and $\mu\mu$ is 0.001μ or 10^{-6} m.m. Finally, to get a comparison in terms of inches a millimeter (m.m.) is .0394 inches. These are merely ranges of sizes and there are bound to be borderline cases. For instance, the properties which are called colloidal will prevail within the colloidal range; they are most accentuated in the center of that range and vanish gradually towards both ends.

The particles in most of the commonly used emulsions are in the coarse range. Particles as large as 25μ are quite often found, yet the bulk of globules in good emulsions is in the 1-5μ range. Still smaller particles occur in emulsions treated by special homogenizing machinery. Thus emulsions are found to be coarse dispersions, where the word coarse is now no longer to be taken as a vague description, but quite precisely as above 0.1μ. That emulsions are coarse dispersions is an accepted fact. But within the particle range for emulsions, there are coarser and finer particles, so it is perfectly correct to call an emulsion having predominantly fine particles, a fine emulsion, and one having predominantly coarse particles, a coarse emulsion.

Theories of Emulsion

The solid particle Theory:

One of the early theories extended to explain emulsions formed by such materials as colloidal silica, metal hydroxides, carbonates and sulfides as well as specific basic salts was the solid particle theory. The writer states: "When the oil is broken up into globules and these globules find themselves in the presence of a number of very much more minute solid particles, the latter will be attracted by the globules and will form a coating or pellicle over the globules preventing them from coming into contact and coalescing (joining) with their neighbors." It is claimed that the solid particles do congregate closely around the globules, and that they can often be seen under a powerful microscope.

The Oriented Wedge Theory:

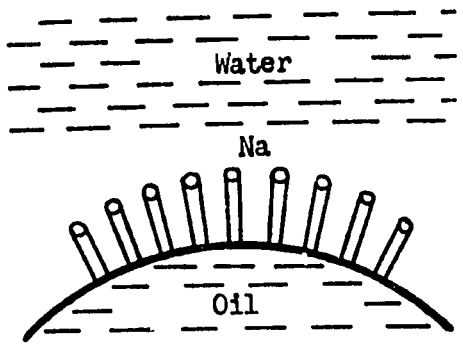
The oriented wedge is essentially a theory for a special group of emulsifying agents, the soaps. This is based on the theory that soaps are long chain molecules, rod-like in shape, having at one end an alkali ion such as Na or K. An alkali soap, for example, is represented by the general formula:

$$R\ COOM_1$$

Where R stands for a long hydrocarbon chain and M_1 for a monovalent cation such as Na^+, K^+ or NH_4^+, the $COOM_1$ group is assumed to be polar and to have a larger cross section than the non-polar hydrocarbon chain. If this is true the soap molecule is wedge shaped having the R $COOM_1$ group at the larger end of the wedge. Thus, if an alkali soap molecule becomes adsorbed at the interface or boundary between the oil and the water, the

alkali end will be attracted to the water phase and the hydrocarbon end will be more soluble in the oil phase and thus attracted to it. Now, as the alkali end is larger or bulkier at the water side the film will tend to curve concavely toward the oil and promote the formation of O/W emulsions.

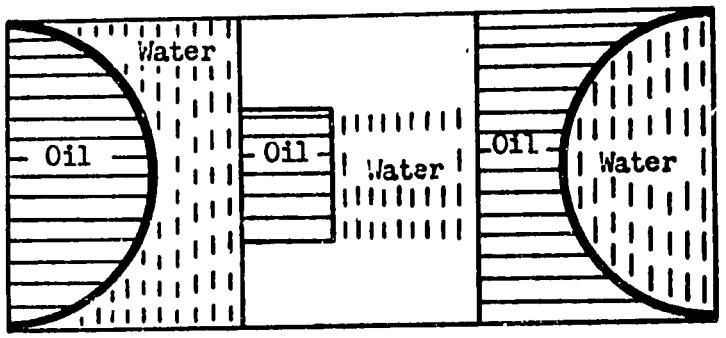
This may be expressed diagrammatically as follows:



Where the soap molecules are closely attached (by solution or attraction of their hydrocarbon ends to the oil) the greater size of the alkali end causes the film of oil to curve into a droplet.

Adsorbed Film Theory of Emulsions:

This theory is based on the concept that the emulsifying agent forms a film between the liquid and oil phases. The type of emulsion formed depends on the relative magnitudes of the surface tensions on each side of this film. Both the oil and water phase are considered to wet the film and to be adsorbed by it, so that in general, there will exist a difference in the surface tensions on the two sides. Due to this difference, the film will bend, the side with the higher surface tension becoming concave, consequently tending to envelop liquid on that side.



The emulsifying agent in this theory concentrates at the interface between the oil and the water and forms a coherent film. If the film is more readily wetted by the water than the oil, the surface tension is lower on the water side than on the oil side. Since the area of the inside face of a film surrounding a sphere is smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this

manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. This is shown in #1 above. Thus, if the wetting is greater or surface tension is lower on the oil than the water side, the film tends to curve so as to enclose the globules of water in an outer or continuous oil phase, the condition shown in #3 above.

The Adsorption Theory:

Adsorption is a very common occurrence in nature. It is in its widest meaning, the accumulation of particles at a surface. The adsorption at liquid surfaces, which is the most interesting case in dealing with emulsions, is just a special case of adsorption.

Particles, originally dissolved or dispersed in the liquid may migrate toward the surface from the inside and become adsorbed at the surface. Most of the emulsions are prepared by dispersing the emulsifying agent in one of the phases before emulsification. Then the adsorptive forces will accumulate the particles at the interface. Particles that accumulate at the liquid surface invariably act as reducers of the surface tension. The process is usually called positive adsorption. The inverse phenomena, namely that of thinning out at the surface and accumulating in the interior o the liquid is called negative adsorption, and causes an increase of the surface tension.

Many of the inorganic salts, acids and bases and some of the lower organic compounds are readily soluble in water and negatively adsorbed; in fact, they usually increase the surface tension of the water.

Some of the organic compounds such as soaps, certain proteins and esters, on the other hand are positively adsorbed and thus reduce the surface tension of the water. They are generally called surface active agents and emulsifying agents belong to this group. Positive adsorption at the interface is the explanation given by the adsorption theory for the reduction of the interfacial tension and for the formation of the interfacial film.

The Hydration Theory:

The basic difference between the hydration theory and all the previous theories lies in the assumption that substances are capable of acting as emulsifying agents only because they bind the dispersion medium with formation of colloidal hydrates in water and not because these substance reduce the interfacial tension and form protecting films around the droplets (adsorption theory).

The existence of hydrated or solvated compounds is now generally accepted. They are responsible for the high viscosity of many colloidal solutions and the formation of gels. It is assumed that a specific class of substances, called lyophilic colloids, i.e. 'solvent loving' colloids, form voluminous structures with their dispersion medium, which must be regarded as intermediates between physical mixtures and chemical compounds.

There is no doubt that many of the substances used as emulsifying agents do produce hydrated or solvated complexes. Agents such as soap, casein and other proteins, starch, egg yolk, etc. belong to this class.

It is likely that the hydrated or solvated colloids, whenever they occur in sufficient quantity in emulsions, will become partly adsorbed at the interface, where they will act according to the adsorption theory; the balance of these colloids will remain in the external phase, increasing the viscosity and so improving the stability.

Emulsifying Agents

The commercially available emulsifying agents aave been classified into eight groups with some subdivisions, as follows:

Anion Active Agents

Group 1. Soaps
- a. Alkalai soaps
- b. Metallic soaps

Group 2. Organic amino compounds producing soap with Fatty Acids.

Group 3. Sulfated compounds
- a. Sulfated oils
- b. Sulfated alcohols

Group 4. Sulfonated compounds
- a. Aliphatic sulfonates
- b. Aromatic sulfonates

Cation-Active Agents

Group 5. Cation-active agents

Non-Ionic Agents

Group 6. Esters and Ethers
- a. Hydrophobic esters
- b. Hydrophilic esters

Miscellaneous Agents

Group 7. Natural and modified Natural Agents

Group 8. Fine-Dispersed Solids

SURFACE CHEMISTRY

Second Year - Lecture #21

Tests conducted on side leather towards the end of the recent war indicated that the leathers, which had a uniform distribution of grease through the leather's thickness and a grease which was still retained by the leather under wet wear, were the best as to water resistance.

The raw castor oil-sulfated oil mixtures appeared to be best as to resisting water under flexing conditions. The rate of penetration is decreased as the raw oil content of the fat liquor is increased. When a potassium soap is used instead of a sulfated oil as the carrier or emulsifying agent for the raw oil, the uptake is about the same but a leather is obtained which is more permeable to water. This is no doubt due to the hydrophilic or water loving nature of the potassium soap when used as an emulsifier. Another interesting observation was made as regards water absorption, that the water absorbed increased as the mineral oil content increased. Sperm oil has been found to have unfavorable characteristics as the amount of water absorbed as well as passed through is quite large when it is used.

These same experiments showed that while fatliquored leather which has been then stuffed absorbs less water than fatliquored leather, the fatliquored leather dries more rapidly. Evidently water enters and leaves fatliquored leather readily, no doubt due to the fact that the oils are spread out on the fibers, leaving the voids between open.

Cross-sections of the fatliquored leathers showed that the blood vessel system serves as channel or road for the fatliquor. It seems moreover that the sulfated oil readily penetrates through the leather from the blood vessels, but the raw oil is stopped at the walls of the blood vessels. Subsequent drying allows for migration of the raw oil into the voids. This penetration of the fatliquor under special conditions was shown to take place from one surface of a piece of leather to the other withing one hour.

One of the interesting results of this experiment was the conclusion that while more fatliquor will pass through from the flesh side to the grain side than from the grain side to the flesh side (more being taken up by the leather in this manner) the amount in the grain side is about the same regardless of the side that it has entered. This seems to be a fundamental factor.

Sulfated oil when used alone gives a leather which absorbs water readily and the least amount necessary should be used in fatliquoring a leather such as chrome-vegetable retanned leather if it is desirable to avoid water penetration. This increase in water absorption was noted even with leathers which were subsequently stuffed.

Surface Tension

The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced force. The molecules at the surface are pulled inward by the other molecules of the liquid and the liquid tends to adjust itself to give the minimum surface area. This fact explains many common phenomena including the spherical shape of raindrops, the rise of water in a capillary tube, and the movement of water in a llotting paper or in the soil.

Surface Active Agents

During the past twenty-five years, the chemical industry has developed the manufacture and sales of a group of compounds which because of their effect on surface tensions of liquids are termed surface active agents. This large field developed from two materials, soap and sulfonated oils. Today it is estimated that there is over one thousand of these products termed surface active agents. Moreover, they are classified into three groups: wetting agents, detergents, and emulsifiers.

By definition:

1. A wetting agent is a material which has the property of speeding up the rate at which anaqueous solution soaks through or penetrates a fibrous material or spreads over a smooth surface.

2. A detergent is a material which has the ability to loosen and remove soils (dirt, grease, etc.) from fibrous materials and non-fibrous surfaces, such as metals, paint, etc.

3. An emulsifying agent must be able to cause two non-miscible liquids such as oil and water to become intimately and stably mixed or emulsified together.

   A dispersing agent should have the ability to cause an insoluble solid material, such as a dye or carbon black, to become uniformly distributed through an aqueous solution. It is this property of a surface active agent in combination with wetting ability which causes level dyeing. Some products have such a strong dispersing action that the dyeing is partially prevented.

5. Re-wetting: a good re-wetting agent is one which enables treated fibrous materials, after being dried, to rapidly absorb moisture.

The conditions under which the ideal surface active agent will be stable are four:

a) alkaline solution
b) acid solution
c) hard water
d) salt solution

A surface active agent is a chemical product which tends to break down the forces which are active between surfaces. In a great many applications, we are interested in the forces which exist between an oil, or a greasy surface and water solution.

If you examine a drop of water, you will note that it has, in general, a round or spherical shape. Why isn't it flat? The reason is that the molecules in the surface of the drop arrange themselves in a way which gives the drop of water the smallest possible surface area. These surface molecules actually form a "skin" around the rest of the drop and this "skin" is contracted just as much as possible and since a sphere has the smallest possible ratio of area to cubic content the drop is spherical in shape. The force that makes this drop round is called surface tension.

All liquids exhibit surface tension. The amount of surface tension of various liquids is different but in all cases, the surface tension tends to prevent two unlike liquids from mixing. Thus, if we pour into a cylinder both water and oil, oil being lighter than the water floats on top and we have a situation where there is an oil surface next to a water surface. This is a "surface between" and is, therefore, called an interface. The combined surface forces at this interface are called interfacial tension and these forces must be greatly reduced if we wish to get a stable mixture or emulsion of the oil and water.

Thus, we see that a surface active agent must reduce surface tension and interfacial tension. Oils contain, for the most part, two chemical elements, carbon and hydrogen. Water, on the other hand, contains oxygen and hydrogen. It would seem, therefore, that if one could get enough oxygen combined with an oil it might mix with water. If one could get enough carbon into combination with the elements of water-oxygen and hydrogen we might have a product which would be soluble in oil - such is also the case. If we then could get just the right combination of the elements in oil with the elements in water, we should have a product that would mix with both oil and water.

Thus, if we put one of these agents which contains the proper amount of the elements of water and oil into the cylinder containing the water and oil, these molecules tend to collect at the surface between the oil and the water. This upsets the normal interfacial tension forces between the oil and the water and if our proportions are right, we find that instead of having an interface, we get emulsification which with the aid of a little shaking will extend throughout the mixture.

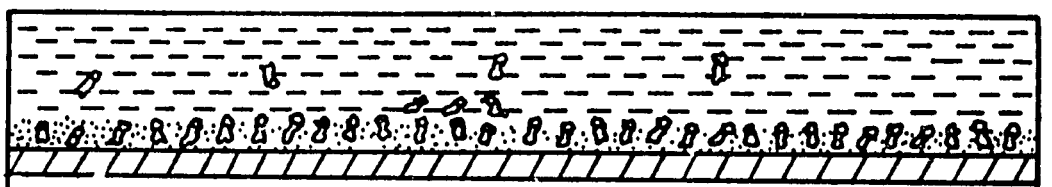
In trying to modify oil to make surface active agents, it has been found that better results are obtained if the oxygen is grouped together and fastened to the carbon chain at only one point rather than spread out along the chain. The compound should contain one oxygen for each 3 to 4 carbons in the chain. Sulfur is very commonly present in surface active agents and is present because treatment of oils with sulfuric acid is often the cheapest and simplest method of combining oxygen with a carbon chain. The common ones are the sulfates (SO_4^-) and the sulfonates (SO_3^-).

Thus, we see that a surface active agent consists of two parts, the hydrophile or water loving part and the hydrophobe or lipophile - the oil loving part.

The lipophilic groups come either from petroleums or from fats. Those which come from fats always have a straight carbon chain structure, while those coming from petroleum nearly always have a branched chain or cyclic structure or both.

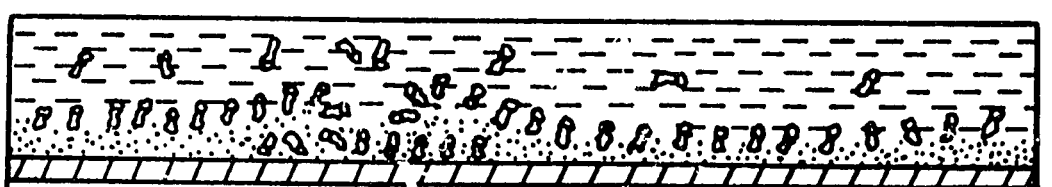
The more common hydrophilic groups are the following:

carboxylate	$-COO^-$	(anionic)
sulfate	$-SO_4^-$	(anionic)
sulfonate	$-SO_3^-$	(anionic)
phosphate	$-HPO_4^-$	(anionic)
ammonium	$-NH_3^+$	(cationic)
trimethyl ammonium	$-N(CH_3)_3^+$	(cationic)
triethyl ammonium	$-N(C_2H_5)_3^+$	(cationic)
benzyl dimethyl ammonium	$-N(CH_3)2(C_7H_7)^+$	(cationic)
sorbitan	$-C_6H_{12}O_5$	(non-ionic)
polyoxyethylene	$-C_{18}H_{36}O_9$ to $-C_{28}H_{56}O_{14}$	(non-ionic)



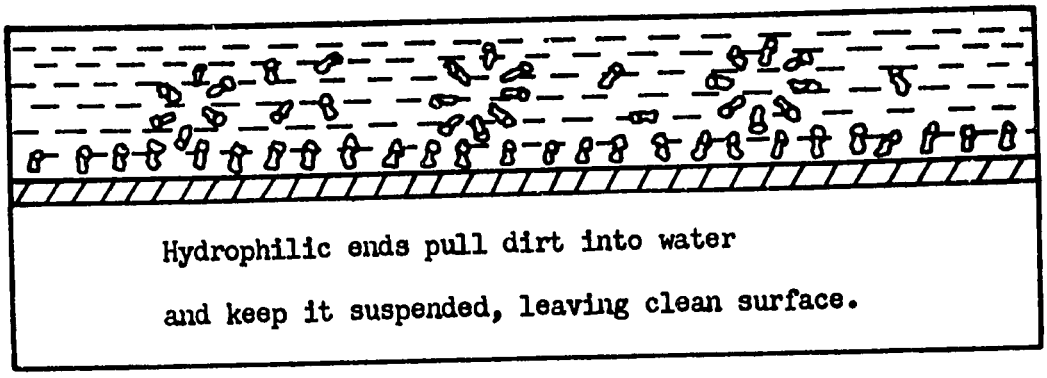
Addition of detergent to water results in a scurry of the lipophilic molecules to the greasy dirt.

The hydrophilic end of the surface active end of the molecules is represented by the round knob and the lipophilic portion is represented by the rod. The surface active agent is attracted through the lipophilic group to the dirty surface.



Surface active molecules arrange themselves with the lipophilic ends tied.

The hydrophilic (round ends) pull and begin to loosen the dirt.



The cleaned surface is wetted because of low surface tension. The surface active agents group around the greasy particles with the hydrophilic groups protuding. The surface is covered with a layer of surface active agents with the lipophilic portion of the molecule contacting the surface and the hydrophilic portion of the molecule directed toward the water solution.

DYEING AND COLORING

Second Year - Lecture #22

In the last 75 years there have been many attempts to explain the mechanism or nature of dyeing. Listed below are a few of the theories which have been considered:

1. Mechanical Theory
   Absorption of dye particles by pores of fibers.

2. Chemical Theory
   Chemical combination between fiber and dye, viz: between acid group of dye and basic group of fiber.

3. Solution Theory
   Dye exists within fiber in a state of solution. (Certain dyes have different color on fiber than in the dry or solid state.)

4. Adsorption Theory
   The dye taken up is concentrated at the surface of the fiber or absorbing medium.

5. Colloidal Theory
   Considers that the dye is precipitated as a colloidal substance on the fiber.

6. The Electrical Theory
   Electrical attraction between oppositely charged dye and fiber, just as a magnet attracts iron filings,

Summary

The electrical theory has become generally accepted as it best answers the various conditions found. The manner in which the fiber or other material acquires its charge is immaterial - it may be due to its chemical character, the presence of certain impurities, the adsorption of a particular kind of ion, contact electrification or the addition of a new properly charged surface, such being called a mordant.

The composite nature of dyeing

We have just considered how a dye is taken up by a fiber, but it does not follow that the process is at an end when this stage has been reached; before a material can be regarded as dyed it is necessary that the dye should be in such a condition that it cannot be readily removed by washing.

The two stages may be described as the adsorption and fixation stages respectively. Probably in many cases of dyeing the two stages of the process take place simultaneously, but this is not always so. Viz:

When a dilute colloidal solution of the blue color acid of Congo Red is mixed with well-washed aluminum hydroxide, the latter takes up the color acid and acquires a blue color, the process being one of absorption. On suspending the blue precipitate in water and warming the mixture, the color changed to red owing to the formation of an aluminum salt of the acid.

Chemical action between the previously absorbed dye and the fiber probably occurs in many cases, thus leading to the fixation of the color. The application of the mordant dyes certainly involves the formation of a compound between the mordant and the dyestuff, for the color obtained varied according to the mordant used. (Morgan considers that the resulting color is a co-ordination compound which can be formulated in accordance with Werner's co-ordination theory.)

THE DYEING OF LEATHER

There are several kinds of dyestuffs for coloring leather, but the following are the most important:

Basic Dyestuffs
Acid "
Direct "

Basic Dyestuffs:

These are hydrochloric acid salts of dyestuff bases and can be used only on vegetable tanned leather or on a mineral tanned leather treated with a vegetable tanning extract, or a suitable syntan. If an alkali is added to a solution of basic colors the dyestuff base is precipitated and the liquor cannot be used for coloring purposes. It is important that the water used for dissolving basic dyestuffs and for the coloring process itself does not contain any alkali. If hard water or water which has been softened by the permutit process must be used, it is necessary to correct the alkalinity by adding a sufficient amount of an organic acid, such as acetic or formic acid. Acetic acid is generally used and a small amount of free acetic acid helps to produce level and uniform shades.

Basic dyestuffs are readily precipitated by tannin if the dye solution comes in contact with vegetable tanned leather or with chrome tanned leather mordanted with tannin or one of the syntans. The quick exhaustion of the dye bath can be retarded by the addition of acetic acid, which tends to produce level and uniform shades.

Basic colors give very full and level shades if the right selection is made of each dye as well as of a combination of dyes necessary to produce a given shade. These dyes are generally not as fast to light as most dyes belonging to other classes.

There are a large number of basic colors which we can use, but a comparatively few only are necessary for the production of the principal shades.

The Phosphines produce a yellow shade, and with the straight Leather Browns give full, level, and clear shades, and exhaust at the same ratio when used together.

Bismark Brown has been and is one of the principal dyes used to produce brown shades. It does not dye as level nor is it as fast to light as some of the new Leather Browns.

Basic Navy Blue or Naphthol Blue type is a good self color. It is a very important dye when used in small quantities as a shading color for the production of tan and brown shades. In contrast to other basic blues it colors very level and exhausts in the same ratio as the Phosphines and basic leather browns.

We can use Brilliant Green Crystals, Methyl Violet, Rhodamine and Basic Black also for a variety of colors.

Acid Dyestuffs:

These dyes are mostly sodium salts of organic compounds containing one or more sulpho groups. In an acidified water solution the dyestuff acts like an acid and this acid combines with the basic groups of the skin.

To obtain level dyeings, the leather is run 15 minutes in the dye-bath and then formic acid is added. The acid will develop and fix the dyestuff and will also accelerate the exhaustion of the dyebath. While acid dyestuffs are not affected by weak alkaline solutions, the coloring process is retarded and the dyestuffs are not fixed until a sufficient amount of acid has been added. This fact has been used at times to obtain level dyeings when small amounts of dyes were used for pastel shades or when particularly good penetration was required. Ammonia, Borax or Disodium Phosphate were the alkalies most commonly used. They should be used with care to prevent affecting the basicity of chrome tannage.

The fact that not all acid dyes are affected by weak alkaline solutions makes some of these dyes suitable for coloring finishes.

When chrome tanned leathers are colored with a combination of acid and basic colors, they should first be dyed with the acid colors. After the dye-bath is exhausted, the extracts are added and the leather is run for 20 minutes.

If a striker is used (that is, Tartar Emetic or Titanium Potassium Oxalate) it should be added now and the leather run for another 15 minutes. The bath is now drained, the leather is rinsed and the basic colors added.

The extracts can be added first, then the acid colors and then the basic colors. If the amount of dye is not too great, it may not be necessary to wash after the acid dyes.

Acid dyes yield clearer and more brilliant shades than basic dyes. The shades obtained are not as full and do not cover and fill as well as if produced with Basic dyes. For the production of fancy shades such as Pastels or bright Oranges, Reds, Greens, Blues, the acid dyes are indispensable. Many acid dyestuffs glaze either dark or very reddish and are, therefore, not suitable for the production of tan or brown shades on glazed leathers. The newer Acid Leather Browns which are straight products are level dyeing and glaze true to shade.

Since weak alkaline solutions may redissolve the acid dyes, one must be careful about using any soap or alkaline fatliquor. Acid dyes which have been topped with Basic dyes are much less sensitive to alkaline fatliquors and rarely bleed.

Acid dyes may be mixed and used in combination with any other class of dyestuffs except with basic colors. There is one Acid Dye that should rarely be used, and then only on a neutral leather. Metanil Yellow is very sensitive to weak acid and if used on a leather containing only a trace of acid it will change from yellow to a reddish color.

Direct Dyestuffs:

Direct colors, with few exceptions, have no affinity for vegetable tanned leather. It has been customary when coloring chrome tanned leather to apply the direct dyes right on the chrome surface, and then if extracts are used they are added after the dyebath is exhausted. However, we some times use acid and direct dyes together and they may be added after an extract bath.

Direct colors are more or less sensitive to acids. If the leather is too acid these dyes may be deposited unevenly on the leather with a mottled effect. Leather which is dyed with direct colors should not show less than pH 5.

Alkali added to the dyebath will affect these colors. The bath is exhausted more slowly and the color penetrates batter. We must be careful that alkali does not raise the pH of the leather too much with harmful effects on the leather.

Direct dyes are used because they give a strong, full color; they may be dyed level and have good covering value. Direct dyes are not as bright as acid colors.

Coloring of Leather

A large proportion of sheepskins are tanned with Quebracho extract. Such leather will color better and more even if it is given a bath of fresh tannin such as Sumac extract or a selected syntan. Leukanol or Tanac C as well as some other syntans act as a good mordant for basic dyes. Sheepskins are usually colored with an acid dye to give a level bottom and then given a bath of Basic dyes to give strength and fullness to the color.

For light or pastel shades, acid dyes are used to give a level and bright color.

A black color on vegetable tanned skins is made with Hematine Crystals (Logwood) followed by a bath of Copperas to develop the Hematine. Then a bath of Nigrosene. This makes a good black bottom, but requires a bath of Basic Black dye to give a good full black color.

Quebracho tanned side leather (hides) may be hand colored with a brush on the grain side or it may be sprayed with a pressure gun. Some side leather is also colored in a wheel the same as sheepskins.

Chrome Tanned Leather

Most all chrome tanned leather receives a first bath of vegetable tannin such as Quebracho, Sumac or Gambier. This serves two purposes. It gives a mordant for any basic dyes that may be used: If the leather is to be glazed in the finishing process it must have this vegetable treatment on the grain. A straight chrome leather will not produce a clear highly-glazed surface by friction glazing.

Following the vegetable extract, the acid dyes or a mixture of acid and direct dyes may be given; then another bath of basic dyes, to build up the color and make it easier to obtain a clear color in the finishing room.

Dissolving Dyestuffs

Acid and Direct dyes should be added to water at or near the boiling temperature - 180 to 212°F.

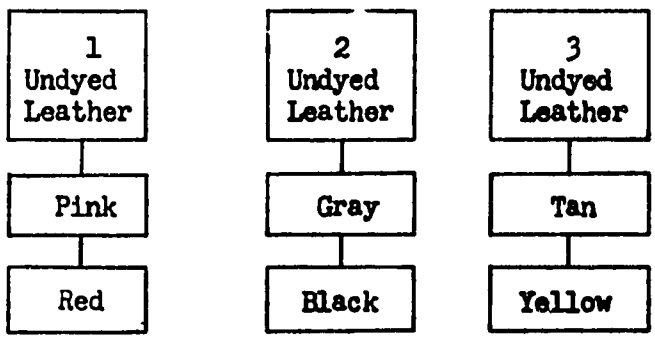
Basic dyes should not be put into boiling water. A temperature of 175 to 180°F. is better as some of the basic dyes undergo decomposition at the temperature of boiling water. It is good practice to filter all dye solutions before adding to the color wheel. Some of the basic dyes are difficult to dissolve in water, such as Methyl Violet or Fuschine. These should first be made into a paste with acetic acid and the paste added to hot water.

Acid dyes require 15 to 20 times their own weight of boiling water to dissolve them; 5 lbs. of dye will require about 10 gallons of water.

Basic dyes are less soluble and need 20 to 40 times their own weight of hot water to dissolve them; 2½ to 5 lbs. dyestuff will require about 10 gals. of water.

Color Differences

One of the important aspects of color is strength. In considering strength, a value of 0 is always used to represent the undyed leather. Viz:



When 1/10th of one percent (0.1%) of a red dye is added to a chrome tanned leather, the resulting color is rather light and may be called pink. If, however, a one percent (1%) dyeing is made, it becomes red in color. The difference between the three stages is a matter of concentration.

The same is also true in Number 2, a black, and #3 an orange. It is seen that an increase in the amount of dye used introduces variations in color towards stronger deeper colors.

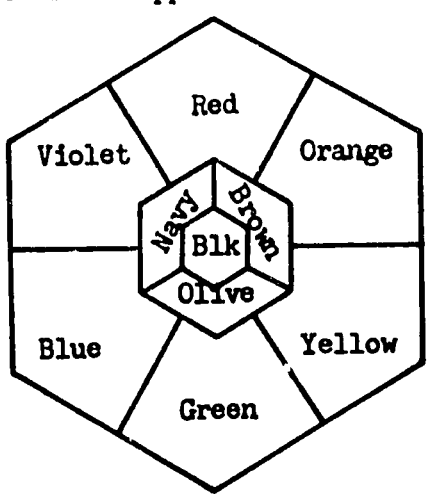
A strength difference is any difference in color of two samples which can be accounted for by a variation in concentration of the dyes in the formula. In a formula involving a single dye, a strength difference is a percentage variation of that dye. In a formulation involving several dyes is a change in the total concentration of all the dyes, maintaining constant the percentage ratio of each dye in the total.

A second important variation is shade. By shade is meant a difference in hue or a difference in dullness. Viz:

Color	Variation in Hue
Red	Yellower or bluer
Orange	Yellower or redder
Yellow	Greener or redder
Green	Bluer or yellower
Blue	Redder or greener
Violet	Redder or bluer
Brown	Redder or yellower
Olive	Yellower or bluer
Navy	Bluer or redder
Black	Redder, yellower, greener or bluer
White	Redder, yellower, greener or bluer

In addition to the hue changes shown in the above table, all of the colors in the first column, except white and black, may also be duller or brighter. Duller means that they tend towards a gray, and brighter means that they appear less gray.

A color diagram will exemplify color differences which can occur, as for instance when one green almost appears blue and another almost yellow.



Moving towards the center we can see that green can vary to an olive and finally to a black. As it deviates toward olive and black it becomes duller and in the other direction it becomes brighter.

Red, blue and yellow are considered to be the three main colors from which all of the others are made. Thus yellow is described as being redder if it deviates toward an orange. Thus a shade difference may be defined as a difference in color which cannot be corrected by varying the total concentration of the dyes employed. In order to correct this shade difference it is necessary to vary the concentration of only part of the total number of dyes being used, keeping the total strength of the mixture about the same.

Lastly this same color map can be drawn so that various dyes are located in their respective areas according to their shades. For example, in the yellow area different yellows will be located at definite points according to whether they vary towards red or blue, and whether they are bright or dull. If the diagram is laid out quantitatively the relative amount of two dyes may be calculated to arrive at any shade which lies on a line drawn between them.

PROTECTIVE AND DECORATIVE COATINGS

Second Year - Lecture #23

The finishing of light leathers has for its object making the leather more pleasing to the eye. Moreover, finishing is the last operation, yet the leather is judged largely on the manner by which it was performed.

Most methods of finishing involve coating the exposed surface with plastic materials and then treating the leather mechanically in various ways. The plastic materials and combinations of them are usually referred to as finishes. In the early days of finishing the materials used were mainly natural products and it was necessary to go all over the world to obtain them: India for shellac, Persia for gum, Brazil and Mexico for waxes, Argentina for casein, Italy for soap, and the East Indies for natural latex. Also, it can be seen that these materials were found in the animal, vegetable and mineral kingdoms and thus their availability and purity varied considerably due to wars, famines, etc.

In leather finishing today, chemistry through the magic of molecule building is replacing many of these natural materials. It is now possible to obtain most of our materials in this country, also we can obtain them in a uniform condition, from lot to lot. Another important aspect is that we may "tailor" these synthetic molecules to obtain desirable properties and to suppress undesirable properties or effects.

Synthetic Resins

Resins are the main ingredient of both the solvent or lacquer finishes and of the aqueous or dispersed finishes. Natural resins, such as shellac, were formerly used, but about twenty-five years ago synthetic resins pioneered by polymers of acrylic resins began to play a larger part. Since the recent war a flood of new synthetic resins have been made available. There are two types of resins, thermosetting and thermoplastic. Thermosetting materials set or harden when subjected to heat; this is an irreversible process and further application of heat will not soften them. The effect that is obtained when egg is hard-boiled is a good example. Thermoplastic resins, the most commonly used on leather, softens on heating and hardens on cooling. This cycle may be repeated any number of times.

Lacquers

Resins dissolved in solvents of the organic type are used in lacquers. The most common are the nitro-cellulose and cellulose finishes which consist of nitrated cotton dissolved in solvents such as butyl acetate, cyclohexanone or methyl cyclohexanone. With a lacquer of this type the mixture approaches more that of a true solution and the choice of solvent is important since it affects the nature of the film produced on the leather. A low boiling point solvent will evaporate off so rapidly that moisture will be deposited from the rapidly cooled air between the film and the leather. This will produce an opaque film and prevent adhesion of the film to the leather. A high boiling point solvent, however, evaporates off slowly and sufficient time

is afforded for the solution to penetrate the grain surface slightly and so provide for good adhesion to the leather; also a higher gloss is obtained.

The films obtained are brittle or develop brittleness unless some suitable softening agent (plasticizer) is incorporated in the solution of the nitrated cotton. Among the plasticizers most used are castor oil, tricresyl phosphate, amyl tartrate and methyl cyclohexanone acetate. These agents, as a rule, will also dissolve the nitrated cotton, and possess such a high boiling point that they remain in the lacquer film on the leather after the ordinary solvent has evaporated off. Leathers treated with lacquers are usually fast to wet rubbing on the grain side.

Today lacquers are usually confined to specialty items. They are often furnished for flash coating or toppings on other finishes and may be or not be plated as the needs may call for. Their main disadvantages are considerable fire hazard from the solvents used as well as some toxicity, increased cost and difficulty of recovery.

Aqueous Dispersions of Resins

By far the greatest quantity of finishes used on leather today are of the aqueous dispersion type. These are obtained in emulsion form and can be readily mixed with any protein-wax type of leather finish.

The acrylics such as methyl methacrylate (the Primals of Rohm & Haas) can be obtained so as to yield films of varying hardness, also they may be blended. They give excellent adhesion to the leather, high luster and clarity. They are particularly good in ageing and holding colors, especially white. However, they are quite sensitive to temperature changes and may crack at low temperatures. Waxes may be added to protect them against higher temperatures. The best surface appearance is obtained with plating.

Vinyl resins appear in many forms:

1. Polyvinyl acetate
2. Polyvinyl alcohol
3. Polyvinyl chloride
4. Co-polymers of polyvinyl acetate and polyvinyl chloride
5. Polyvinyl butyral
6. Polyvinylidene co-polymers.

Vinyl resins usually require comparatively high temperatures in order to form a continuous film. However, as techniques for forming films when air dried continue to improve, more and more vinyls will find their place in formulations.

Polyvinyls (such as the Geons of B. F. Goodrich Co.) have a range of hardness like the acrylics and are plasticized with esters in order to control the film brittleness. Dioctylphthalate is most commonly used for this purpose. However, care must be exercised as the plasticizer may migrate to the leather. From this it is easy to see that they are susceptible to change with ageing. A good means of obviating this difficulty is to use one plastic as the plasticizer, or softening agent, for another. These are termed polymeric plasticizers and a good example is a mixture of polyvinylchloride plus

vinylidene. These do not have a tendency to separate from each other and the film forms at room temperature. A high drying temperature is not necessary nor is plating; however, they will yellow upon ageing.

Sometimes two types of monomers are reacted together to form what is known as a copolymer. Butadiene-styrene (water paints of Glidden) is a typical example. Protective colloids like casein are usually added to control the viscosity and thus the brushability and flow-out. The styrene adds luster and the butadiene yields viscosity and tackiness. Butadiene-acrylonitrile copolymers (Hycars) are resistant to oils and natural fats and are harder and tougher. Likewise it is thus easy to deduce that they are liable to crack at lower temperatures.

Rubber latex dispersions such as chloroprene are also used and they possess good sealing properties and when dried at a high temperature are sufficiently hard and resistant to abrasion. However, chloroprene, unless stabilized properly will deteriorate on standing and form acids.

There are several resins being used in small quantities which will probably be developed to a greater extent. Phenolic formaldehyde resins are being used; nylon or, in general, polyamides have fairly good ageing properties. Silicone rubbers show a marked water-repellent property. Oils treated with urea have been used in coat leather.

Binders

A binder can be simple or it can be made up of one or more resins plus pigments plus waxes and shellac. Stock solutions of casein, shellac, egg and blood albumin, carnauba and beeswax dispersed in soap solution, Irish moss, flaxseed, and gum tragacanth, usually are prepared in a concentration of one pound to the gallon. These stock solutions are used to make the final binder. Egg and blood albumin are used to promote high glazing. Shellac is an excellent binding or adhesive material and provides a natural brilliance, but it is brittle and not readily plasticized. Waxes are used for their relative softness and tendency to maintain the "leathery feel" as well as to provide luster when the finish cannot be glazed. Irish moss, flaxseed and gum tragacanth are good fillers, that is, they tend to penetrate farther into the leather; being softer than some of the others they help make the film more flexible. Flaxseed especially gives the leather a soft feel. Gelatin is an adhesive, a protective colloid, and a good glazing and filling material. Casein in pigment finishes serves in the important capacity of dispersing the pigments, acting as a protective colloid to prevent agglomeration of the pigment particles, and stabilizing the product. Its relatively high viscosity makes it an especially valuable agent in preventing settling of the pigment.

The following shows typical composition of a binder:

	Percentage by volume of stock solution		
Stock Solution	Hard binder	Medium binder	Soft binder
Casein	40.0	30.0	20.0
Shellac	15.5	30.0	20.0
Carnauba Wax (dispersed in soap sol.)	19.5	30.0	40.0
Blood Albumin	9.0	-	-
Gelatin	9.0	-	-
Sulfonated Castor Oil	7.0	10.0	10.0
Irish Moss	-	-	10.0
	100.0	100.0	100.0

Note: The stock solutions contain (1) one pound of solute per gallon of water except that the gelatin solution contains (5) five pounds of gelatin in (9) nine gallons of water. The gelatin solution is added while hot.

The binder can be made hard or soft by varying the relative proportions of casein and waxes. Casein is also good with rubber latex, giving good flow. It increases the viscosity so that it will not run or puddle. Methyl cellulose or carboxy methylcellulose can also be used for this purpose as they have body, luster, strength and affinity for the leather. They will stand high temperatures and are hardening agents for rubber latex; also they cut the tackiness.

Pigments

The selection of the pigments, primary requisites being high opacity, chemical inactivity, resistance to acids and alkalies, small particle size, freedom from abrasive material and water soluble matter, and fastness to light.

There are three classes of materials used for this purpose:

1. Inorganic pigments - salts, usually oxides of metallic elements such as yellow and red iron oxides, chromium oxide and zinc yellows. Some are manufactured and some are found in the natural state.

2. Organic pigments - sometimes referred to as toners. These are dyes such as the azo dyes, the triphenylmethane dyes, the thiazole dyes, the phthalocyanines, etc. which have been precipitated from aqueous solution by several means such as with tartar emetic or tannic acid. Among these are the lithol reds, the toluidine reds, the phthalocyanine blues and the benzidene yellows.

3. Lakes - these are toners or organic dyes which have been precipitated onto bases, such as clay and alumina or barium carbonate.

The inorganic pigments are quite stable to light and heat and possess good hiding powers. The toners tend to bleed into the solvents used in lacquers used in the top coats and their light fastness is fair in large concentrations. However, in the amounts used in the pastel shades many are not resistant to the alkaline nature of the resin emulsions.

The pigments and toners are mixed and ground in either pebble mills or colloidal mills. A dispersing or grinding vehicle is added to aid the work. Different manufacturers have different procedures for grinding, some preferring to grind the pigment in an oil and wax mixture and then stirring in the remaining ingredients. Others prefer to grind the pigment in the completed binder, such as one of those listed in the table above. It is customary for the manufacturer of pigment finishes to make stock finishes of the primary colors and then to blend them to produce the desired colors, tints, and shades. When any special color is to be made in large volume, however, it saves time to use a dry color formula and to grind this color rather than to mix the primary stock colors each time.

The amount of pigment used per gallon varies from (1) one pound to roughly ($2\frac{1}{2}$) two and one-half pounds for the colors, and from (2) two to (4) four pounds for the whites. A sulfonated oil is used to wet or disperse the pigment in the water resin emulsion. Casein is also used for viscosity control. The usual procedure is to charge the mill with the binder to the extent of one-half to three-quarters of the final volume desired, followed by all the pigment, after which the door is put on and the ball or pebble mill rotated for about (16) sixteen hours. After removal the batch is then made up to the desired volume with water or binder according to the individual requirements.

In practice finishes are applied in one or more coats. Bottom coats are applied to bind the succeeding coats to the leather, to act as a filler, a base for lacquers and a leveler for stain coats. Intermediate coats are added to bind the pigments and enhance the color. Top coats are added to improve the plating, feel, water resistance and toughness. Very often the top coats are clear coats.