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LEATHER CHEMISTRY FOR FOREMEN

Third Year Course

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PRACTICAL BASIC CHEMISTRY FOR FOREMEN

3rd Year

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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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WEIGHING - MEASURING - STANDARD SOLUTIONS

Third Year - Lecture #1

The Analytical Balance

The analytical balance by which all weighings are made is the most important piece of apparatus in the quantitative laboratory. Balances differ a great deal in details of construction and in sensitiveness depending upon the use to which they are to be put. In general, this type of balance weighs to the fourth place, that is to 0.0001 of a gram.

Mechanical Features

The balance operates on the principle of the lever. A beam, to the center of which is attached an agate knife-edge, rests upon an agate plate. The beam carries at each end a stirrup with a knife-edge, the two stirrups supporting the pans upon which the weights and object are placed.

A good balance in order to give accurate and satisfactory service must have the central knife-edge and the terminal knife edges in the same horizontal plane.

The knife edges must remain true and not be blunted by rough treatment. The center of gravity must lie slightly below the central knife edge. The balance must oscillate fairly rapidly.

Before attempting weighings examine the balance, study its construction and then check the following points:

1. See that the balance is level as indicated by the spirit level. If it is not, adjust it by means of the screw supports on the base.

2. Test the beam support and the pan arrests for smooth operation.

3. Check over the weights in the weight box and familiarize yourself with the units. Also check the rider.

4. With the balance door closed, release the beam and pans and start with the pointer to swinging. If the balance is properly adjusted the pointer should swing equal distances on either side of the zero mark on the pointer scale.

Point of Rest

Set the pans in motion with no load in either pan, so that the pointer traverses at least five scale divisions on either side of the zero point. When the pointer is swinging freely, take four successive readings of the pointer position at the end of the right and left swings. Average each set; take the difference and divide by 2 - viz;

	Left		Right
	6.1		5.4
	6.0		5.3
	5.9		5.2
	5.8	Ave.	5.3
Ave.	5.95		

$$\frac{5.95 - 5.3}{2} = 0.3 \text{ scale divisions to the left of zero.}$$

If it is off by more than one whole scale division, ask the instructor to adjust the balance. This is done by moving the small thumb nut on the extremity of the beam, thereby adding or subtracting weight from one of the pans.

Rules for Weighing

1. Place the object to be weighed on the left hand pan. Samples of dry material are weighed on a weighed watch glass of in a weighing tube.

2. Always use the forceps for handling objects and weights — never touch them with the fingers.

3. Whole and fractional weights are added to the right hand pan starting with the largest weight. Never change weights or remove the object being weighed without first arresting the pans and placing the beam on its support.

4. Close the door and adjust the rider until the swings of the pointer are equal on both sides of the zero position. Never move the rider while the beam is suspended on the knife edges.

5. Hot or recently rubbed objects are never weighed. Hot air currents, varying humidity and electrical effects will introduce large errors.

6. Make sure that the beam and pan arrests are restored before leaving the balance.

Measuring

The measurement of solutions in volumetric analysis is made by means of flasks, burettes and pipettes. The greatest care must be exercised in the use of volumetric apparatus.

The Liter

A true liter is the volume occupied by one kilogram of water at the temperature of its greatest density, which is approximately 4°C. A milliliter is one one-thousandth of a liter. The standard temperature at which measuring vessels are used has been fixed by the Bureau of Standards at 20°C. A liter flask for example is usually marked to contain or to deliver at 20°C. A volume of water which at 4°C will weigh 1000 grams in vacuo.

Flasks are made in capacities from 10 ml. up to 1000 ml. They are marked with an etched ring around the neck.

Burettes are graduated tubes used for measuring volume of solutions in titrations. The burette should be clean so that a uniform film of liquid remains on the walls when the liquid is withdrawn. Care must be exercised in reading a burette to place the eye on a level with the lower meniscus of the solution so that parallax will not introduce serious error. Estimate the reading to one-hundreth of a ml. In measuring liquid levels in a burette always allow one minute to elapse before taking a reading. This allows time for drainage from the walls of the burette.

Pipettes

Measuring pipettes are used in much the same way as burettes. Transfer pipettes are used to transfer single volumes of liquids.

STANDARD SOLUTIONS

Third Year - Lecture #2

Since chemical reactions take place between weights of reacting components, the general principle involved in calculation is in conformity with the Law of Combining Weights, viz "Reactions take place between weights of chemical substances which are proportional to the atomic or molecular weights of the reacting elements or compounds." In gravimetric analysis the weight of a precipitate is determined. In volumetric analysis the weight of reacting constituent is determined from the volume and strength of the solution used in titration, and its equivalent in terms of the substance being analyzed is readily calculated from the equation for the reaction. This is really a simple method of indirect weighing.

The strength of the reagent used must be carefully determined prior to its use as the titrating solution. The actual strength must be ascertained by causing an accurately known amount of a pure substance to react with the requisite volume of solution by a separate titration. This procedure is known as standardization, and, after the strength of the solution is thus determined, the reagent is spoken of as a Standard Solution.

Preparation and Standardization of Approximately 0.1N Solutions of Hydrochloric Acid and Sodium Hydroxide.

A normal solution of an acid contains 1.008 grams of replaceable hydrogen per liter of solution. For hydrochloric acid a liter of normal solution contains 36.465 grams of pure hydrogen chloride. Since a solution of approximately 0.1 normal strength is best suited for the following procedures, 0.1 of a gram molecule of HCl must be used. This requires 0.1 x 36.465 or 3.6465 grams. The reagent from which this is obtained is concentrated hydrochloric acid, of a specific gravity of 1.19 or containing 37.23 percent of pure HCl. Therefore, the volume of concentrated HCl to use is:

$$3.6465 \div (1.19 \times 0.3723) = 8.25 \text{ c.c.}$$

For the solution measure out about 8.5 c.c. of concentrated hydrochloric acid, dilute with about 200 c.c. of distilled water, transfer to a liter measuring flask and fill up to the mark with distilled water. Keep the solution in a labeled liter bottle.

A normal solution of NaOH should contain 17.008 grams of replaceable hydroxyl ion per liter and this amount is contained in a gram-molecular weight of 40.005 grams.

For an exactly 0.1N solution one-tenth of a gram-mole is required, that is, 4.0005 grams per liter. Take about 4.4 grams of NaOH and dissolve it in about 200 c.c. of distilled water. Pour this solution into a liter measuring flask.

Add distilled water until about half full; shake well and then fill the flask to the mark with distilled water. Transfer the NaOH solution to a liter bottle provided with a rubber stopper.

Standardization

Weigh accurately into two numbered 200 c.c. beakers two samples of Na_2CO_3 of about 0.2 grams each. Dissolve each sample in 80 c.c. of water and add 2 drops of methyl orange solution. Fill a clean burette with the 0.1N HCl and take the initial reading. Be sure that no air bubbles are present. Run in HCl with constant stirring until a color change takes place. The end point is reached when one drop of HCl will change the color of the solution from a faint yellow to a faint pink.

Calculate the Na_2CO_3 titre of the HCl by dividing the number of grams of Na_2CO_3 neutralized by the net volume, in cubic centimeters, of HCl used. From the titre calculate the normality of the HCl by dividing by the number of grams equivalent to 1 c.c. of normal HCl.

pH MEASUREMENT AND INDICATORS

Third Year - Lecture #3

During the early decades of this century accurate hydrogen ion concentrations were determined by the use of a hydrogen electrode. A stream of hydrogen was passed over a small square platinum electrode and when this was immersed in a solution the hydrogen is adsorbed on the surface of the platinum and it behaves just as if it were a metallic electrode.

A second electrode was immersed in the solution for the purpose of measuring the difference in potential or electromotive force which was generated. This electrode is known as a calomel electrode. It consists of a small tube containing a paste of mercury and mercurous chloride within a second tube filled with saturated potassium chloride. This second tube has a ground glass joint or a porous tip by means of which contact is made with the solution.

This combination proved satisfactory for some solutions, but certain materials affected the platinum black coating on the hydrogen electrode so that it became inoperative. This was known as "poisoning". This was a condition particularly prevalent with tanning solutions and the invention of the glass electrode was a happy solution to this problem.

The glass electrode has a very thin glass membrane separating it from the solution being measured. This electrode is not affected by oxidizing solutions and it can be used in non-aqueous solutions.

In theory now when the reference electrode and the glass electrode are immersed in a solution we have an electrical current generated, thus we actually have a battery. In effect it is similar to the battery in your car. And when you place an ammeter or voltmeter on to the two poles of your battery you measure the current which flows out of it. In a similar manner if we place an electrical measuring device into our circuit we can measure the E.M.F. generated, this force being proportional to the concentration of the hydrogen ions in the solution. This electromotive force is very weak, partly due to the glass membrane of the glass cell and it cannot be measured directly by a voltmeter which would require too much energy merely to operate it. The scientist devised a means whereby the force is measured when no current flows. He opposes a second current to the one being measured. This current is from a battery and when the two currents are equal a galvonometer in the unit will rest a zero deflection showing equality.

He then measures the magnitude of this balancing current through an electrical measuring circuit known as a wheatstone bridge. This circuit measures the unknown voltage against a standard known voltage in a way similar to that employed when we weigh a substance on an analytical balance and compare it to a set of predetermined weights. The electrical resistor is calibrated directly in pH units or in other machines proper circuits balance the system so that a

a needle deflects across a scale giving a direct reading.

By the above means exact pH measurements can be made of any concentrations. However, simpler means are available to measure approximate ranges in the pH scale and do not require expensive or cumbersome equipment. We know that certain chemical substances can change color at certain pH values and by the proper selection of these compounds we can select a number which represent exact points across the pH scale. Thus, by adding a drop of any of these to a solution to be measured we can arrive at the approximate pH value by observing which side of the color range we arrive at.

These color changes can be observed by the use of comparator sets wherein an indicator is added to the unknown solution and the color generated in the solution is compared to color standards in tubes by transmitted light.

However, all color change methods work only with colorless solutions and E.M.F. or pH meter methods must be used in those cases where the solution is colored.

Experimental

Using the Model G and the Model N meters:

1. Calibrate the buffer solution.
2. Wash the electrodes and
3. Check the pH of the following:
   .1 N HCl .1 N acetic acid
4. Dilute the above ten times and measure.
5. Dilute again ten times and measure.
6. Titrate a standard solution of HCl with a standard solution of NaOH using the pH meter to follow the titration. Also use an indicator and observe the end point as shown by the meter and by the color change.

Using the indicator set check some of the above solutions as well.

VOLUMETRIC ANALYSIS

Third Year - Lecture #4

Analysis of a spent pickle liquor.

The usual constituents of a spent liquor that are analysed for routine factory control are salt, sulfuric acid, and pH.

1. Sulfuric acid: The amount of H_2SO_4 left in the spent pickle must be known if the liquor is to be strengthened for following packs. It is also an indirect measure of the lime left in the stock from the preceding operations, and therefore, a valuable check on the uniformity of those operations.

Filter the pickle liquor and pipette 100 m.l. into a suitable beaker or erlenmyer flask. Titrate with standard NaOH solution using phenol phthalein as an indicator. If the NaOH is exactly 0.2785 normal, each c.c. of NaOH consumed is equal to 1 fluid ounce of sulfuric acid in 100 gallons.

2. Salt is almost always determined in a spent pickle liquor by determining the specific gravity by use of a hydrometer. Special hydrometers known as salometers are used for this purpose. But any hydrometer, or as they are commonly known barkometer or baume sticks, may be used and the salt concentration looked up in prepared tables.

However, for this lesson, we will determine the percentage of sodium chloride by methods of volumetric analysis.

Take an aliquot of the filtered liquor containing from .25 to .50 gms. of salt. Titrate with tenth normal silver nitrate solution, using potassium chromate as the indicator. Titrate to first permanent redness which is the end point.

Take 5 cc of the filtered liquor--add 25 cc of distilled water and a few drops of 10% potassium chromate solution. Titrate with N/10 $AgNO_3$ to end point.

lbs. of NaCl per 100 gallons = c.c. $AgNO_3$ x 0.975500

2a. Determine specific gravity and calculate % of NaCl.

3. pH - Determine by use of electric pH meter or suitable colorimetric method.

VOLUMETRIC ANALYSIS

Third Year - Lecture #5

Spent Lime Liquors

The methods of volumetric analysis may be applied to a limited extent to the factory control of lime liquors especially when such liquors are to be used over again and, therefore, must be reinforced.

Also of considerable interest is the determination of nitrogenous matter in its various stages of degredation from protein to ammonia.

Taking sample: Make sure liquor is thoroughly agitated before taking samples and that sample is thoroughly shaken before pipetting.

Total Lime

Pipette 50 cc into a beaker and add enough hydrochloric acid to make solution slightly acid. Filter through a folded filter paper, returning the filtrate till it comes through clear. Wash the filter paper with distilled water until free of chlorides, adding the wash water to the filtrate.

Make slightly alkaline with ammonia, heat to boiling, add 35 ml of a saturated solution of ammonium oxalate, and continue boiling until the precipitated calcium oxalate becomes granular. Let stand until the precipitate has settled. Filter through fine filter paper and wash thoroughly with dilute (2%) ammonium hydroxide. Redissolve the precipitate (why ?) in a little dilute hydrochloric acid, receiving the solution in the beaker in which the original precipitation was made and washing the paper thoroughly with hot water.

Reprecipitate with ammonia and ammonium oxalate as above described, filter and wash free from chlorides.

Break the point of the filter paper with a glass rod and wash the precipitate into the beaker using hot sulfuric acid (1:1) and hot water. Wash the paper in the funnel with successive portions of hot acid and hot water until all the precipitate is dissolved, and titrate while hot with N/10 $KMnO_4$ until one drop produces a permanent pink. Finally add the filter paper to the beaker and complete the titration of additional $KMnO_4$ is necessary.

Calculation:

Lbs. $Ca(OH)_2$ per 100 gallons = cc N/10 $KMnO_4$ x .1235

Sulfide

Pipette 25 ml of filtered lime liquor into a beaker and titrate with 0.1 M Zinc Sulfate solution.

A freshly prepared sodium nitroprusside solution 0.1% is used as an external indicator on a spot plate, and zinc sulfate solution is added until a drop of the mixture added to a drop of the indicator on the spot plate produces only a faint blue color, which does not change with further addition of zinc sulfate. If the volume of zinc sulfate consumed is less than 6.5 cc, the figure is used to calculate the sulfide content. If the volume exceeds 6.5 cc, repeat the titration as follows: Pipette a second 25 ml portion of lime liquor into a 250 cc volumetric flask, add an accurately measured volume of 0.1M zinc sulfate, slightly less than that required in the first titration, make up to the mark with distilled water, and filter through a dry filter paper. Discard the first 25 ml of filtrate.

Pipette a 50 cc aliquot of the filtrate into a beaker and add 0.1 M zinc sulfate drop by drop, spotting as before after each addition, until the blue color is no longer produced.

If A = the ml 0.1 M zinc sulfate added before filtering, and B the ml added to the aliquot after filtering:

$$Na_2S \text{ per 25 ml lime liquor} = (A + 5B) \times 0.0078$$

WATER ANALYSIS

Third Year - Lecture #6

The complete mineral analysis of water involves many procedures which, although important, are too time-consuming for the purposes of this lesson. The student is referred to the standard books in this field, especially the methods of the American Public Health Association.

We have selected a few which we hope can be performed during the time allotted to this lesson.

(1) Soap Hardness:

Measure 50 ml of the water into a glass shaking bottle and run in the standard soap solution from a burette. Ad 1/2 ml at a time and shake the bottle well after each addition of soap solution, laying the bottle on its side to observe the condition of the lather. When the lather does not break on the surface of the liquid for at least 5 minutes, the end point has been reached.

To make certain that the end point has been reached, 1/2 ml of soap solution should be added after the burette reading has been noted. If the lather is still stable, the final end point was reached before the last addition. If the lather breaks, more soap solution should be added until a permanent lather is obtained.

The number of c.c. used minus the lather factor for distilled water multiplied by 20 equals the hardness in parts per million (p.p.m.) of Calcium Carbonate.

(2) Determination of Free Mineral Acid:

If the water is acid to Brom Phenol Blue, titrate 100 c.c. with 0.02N Na_2CO_3 to the Brom Phenol Blue end point.

The ml. of Na_2CO_3 required, multiplied by 10, equals the p.p.m. of $CaCO_3$. This may be regarded as negative alkalinity.

(3) Determination of Alkalinity:

Titrate 100 c.c. of the water in the cold using Brom Phenol Blue as indicator with .02N HCl.

Each c.c. of .02N HCl is equivalent to 10 p.p.m. of $CaCO_3$ at alkalinity.

(4) Carbonate Hardness:

Since natural alkaline waters contain no hydroxides of alkalies or alkaline earths, the alkalinity is actually the carbonate hardness, if the total hardness is equal to or greater than the alkalinity and the difference is non carbonate hardness. If the total hardness is less than the alkalinity, the difference is sodium carbonate, and all of the hardness is then carbonate hardness.

If the water is acid, all of the hardness is non-carbonate hardness.

In addition to the above, tests for the presence of iron, sulfates, and chlorides are very important. Presence of amounts of ammonia above a very small figure will indicate contamination with sewage. Bacteria counts may be very significant along this line

DETERMINATION OF HIDE SUBSTANCE

Third Year - Lecture #7

Hide Substance: This is the determination of nitrogen in the protein or protein degredation products present in leather; rawskin. With modifications the method may be used on almost all tannery liquors and then will measure the amount of protein present in the liquor.

Nitrogen: Kjeldahl Method.

Standard Acid: For ordinary purposes .5N acid is recommended. For determining very small quantities of nitrogen 0.1N acid is recommended. Determine accurately the strength of the standard acid, either hydrochloric or sulfuric.

Standard Alkali: A 0.1N solution is recommended. Determine accurately its strength with respect to the standard acid.

Concentrated Sulfuric Acid: Use sulfuric acid of specific gravity 1.84 and free from nitrates and ammonium sulfate.

Sodium Hydroxide Solution: Use a solution made in the proportion of 450 gms. of sodium hydroxide, free from nitrates, dissolved in one liter of water.

Blank Test on Reagents: Previous to use, test all reagents by a blank determination with sugar which will partially reduce any nitrates present that may otherwise escape notice.

Determination: Place 1.4 g. of sample in a digestion flask, add 10 gms. of pulverized anhydrous sodium sulfate and two or three Hengar granules, or 1 gm. of copper sulfate of 0.1 gm. of Selenium and 25 to 35 ml. of concentrated sulfuric acid.

Place the flask in an inclined position, boil until the liquid is clear and nearly colorless and continue boiling for 10 minutes. Digestion normally takes about one hour (a small piece of paraffin may be added to prevent foaming, and in cases of extreme foaming a preliminary heating at lower temperatures may be required. A few glass beads will prevent bumping. Do not let the bare flame touch the sides of the flask above the level of the solution at any time during the digestion.).

Cool, dilute with about 200 ml of water, and add enough sodium hydroxide solution to make the solution strongly alkaline, pouring it down the side of the flask so that it does not mix at once.

Immediately connect the flask to a bulb trap and condenser, mix its contents by shaking, and distill until all ammonia has passed over into 125 ml of boric acid solution (45 g/liter) to which methyl orange has been added as an indicator. The distillation usually requires from 40 to 90 minutes and the

first 150 ml will generally contain all the ammonia. Titrate with .5N sulfuric acid.

Calculate percent of nitrogen - each c.c. of .5N = 7.0 mg of nitrogen.

Multiply % of nitrogen by 5.62 to get percentage of hide substance.

DETERMINATION OF CHROMIC OXIDE IN LEATHER

Third Year - Lecture #8

(1) Weigh a two gram sample and transfer to an Erlenmeyer flask and oxidize with 10 ml of an equal volume of 80% sulfuric acid and nitric acid until charring is complete. Cool. Add 10 ml of 70-72% perchloric acid. Heat under reflux conditions, using a small funnel as a condenser, until the color changes to a reddish orange. Continue heating for two minutes after the color change to insure complete oxidation. Dilute the hot oxidized solution as rapidly as possible, diluting to approximately 225 ml. Bring to a boil for a few minutes to liberate free chlorine and cool.

(2) Titration of Chromium Oxide: To the boiled oxidized solution, add 30 ml of a diluted phosphoric acid (1:1). Add 10 cc of 10% sodium iodide solution, and titrate the released iodine with 0.1N sodium thiosulfate solution, using starch as the indicator.

Calculate % Chromic Oxide:

$$\frac{\text{c.c. sodium thiosulfate} \times 0.002533}{\text{wt. of leather}} \times 100$$

ANALYSIS OF LEATHER

Moisture & Grease Content

Third Year - Lecture #9

Preparation of Sample for Analysis:

Reduce composite sample to small pieces convenient for grinding, mix well and grind through a Wiley mill using a four mm screen. Mix ground sample thoroughly and place in a clean, dry, airtight container.

Moisture:

Place from 5 to 10 g. of the prepared leather in a weighing bottle or similar vessel, that can be covered tightly. Dry for sixteen hours at 95°-100°C., cover the container, cool in a desiccator and weigh. Loss of weight is taken as moisture.

Chloroform Extract:

Extract from 5 to 30 g. of prepared leather in a Soxhlet type extractor until free from chloroform extractable matter. Evaporate and dry to approximately constant weight.

ANALYSIS OF VEGETABLE TANNING MATERIALS

Third Year - Lecture #10

Procedure

Vegetable Tanning Materials

The material must be sampled according to the standard methods to insure that it is representative.

(1) Weigh such quantity as will give as nearly as possible .4 gm. of tannin to 100 ml. - Precautions must be taken to prevent loss of moisture during weighing.

Pour approximately 200 ml of water at 95°C. into a liter flask and immediately wash the weighed charge into the flask with water at 95°C. using sufficient water to bring the volume to approximately 900 ml.

(2) The solution prepared as above shall be allowed to stand overnight, the temperature not being permitted to go below 23°C. Test before proceeding with the analysis. The solution is brought up to 23°C. by immersing the flask in water at not less than 22°C. After adjusting the temperature of the solution, make up to the mark with water at 23°C.

(3) Total Solids: Thoroughly mix the solution. Pipette 100 ml into a tared dish, evaporate, and dry as directed and weigh.

(4) Water: The percentage of water in the extract is 100 minus the percentage of total solids.

(5) Soluble Solids: Use for filtration a single 21.5 cm C.S.&S. No. 610 filter paper, pleated so that it contains 32 creases which divide the paper into as even divisions as conveniently possible. To 2.0 g. of Kaolin in a clean glass container add 225 cc of analysis solution. Stir until thoroughly mixed, then pour onto the pleated paper set in a funnel of such size that the top of the paper is approximately 1 cm below the top of the funnel. Collect the filtrate in the blass in which the Kaolin and solution were mixed and, when approximately 40 ml have passed through, return the filtrate to the funnel. Continue this operation for one hour. At the end of the hour, syphon the solution out of the filter paper, disturbing the Kaolin film on the paper as little as possible. Refill the paper with 225 ml of analysis solution which has been kept at a temperature of 23°C. and continue the filtration.

When 40 ml have passed through, collect the next 125 ml in a clean dry glass container for pipetting. Adequate precautions must be taken to prevent evaporation during filtration. Pipette 100 ml. of the clear filtrate into a tared dish, evaporate, dry and weigh.

(6) Insolubles: The percentage of insolubles is the difference between the percentage of total solids and the percentage of soluble solids. It designates the percentage of material in the extract that will not pass through the

filtering medium described under the conditions specified.

(7) Non-Tannins: Digest the hide powder with 10 times its weight of distilled water for 30 minutes. Add 1.0 ml of the chrome alum solution for each gram of air dry powder. Agitate frequently for two hours and let stand overnight.

Squeeze and wash by digesting with four successive portions of distilled water, each portion equal in amount to 15 times the weight of the air dry powder taken. Each digestion shall last for 15 minutes and the hide powder shall be squeezed to approximately 75% water after each digestion, except the last, a press being used of necessary.

The wet hide powder used for the analysis shall contain as nearly as possible 73% of water (not less than 71 or more than 74). Determine the moisture in the wet hide powder by drying approximately 20 g.

To such quantity of the wet hide powder as represents as closely as possible 12.59 (not more than 12.8 or less than 12.2) of absolutely dry hide powder add 200 ml of the original analysis solution and shake immediately for 10 minutes.

After shaking, pour onto a linen cloth or onto a perforated plate set in a glass funnel and after the bulk of the solution has drained off squeeze lightly. To this detannized solution add 2.0 gms. of Kaolin, stir until thoroughly mixed, and then filter through a 32 crease folded filter paper as used for "Soluble Solids". Return filtrate to the funnel until perfectly clear. Pipette 100 ml of this filtrate into a tared dish, evaporate, dry and weigh.

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

(8) Tannin: The percentage of tannin is the difference between the percentage of soluble solids and the percentage of non-tannin. It represents the amount of material absorbed by the hide powder under the conditions specified.

HISTOLOGY - THE STUDY OF TISSUES

Third Year - Lecture #11

1. Cells

Cells are the structural units (like bricks in a house) in living forms. They contain carbohydrates (sugars, etc.), fats, and proteins and large amounts of water. Their activities are directed by a small body called a nucleus. They are surrounded by a membrane through which all substances that enter them must pass.

2. Tissues

A group of similar cells all specialized to do a certain job is called a tissue. Example: Muscle tissue, connective tissue (the fibers in leather), and fat tissue.

3. Organs

A group of tissues working together to carry out a certain function is called an organ. Example: sweat gland, sebaceous gland, hair, blood vessels.

Organ System

A group of organs, working together to do a certain job, is called an organ system. Although we sometimes speak of skin tissue, the skin is actually an organ system.

Leather

Leather is a product which results from the chemical conditioning of connective tissue fibers. Apart from hair or wool there is little else to skin except these fibers. Since the fibers give leather its fundamental properties, they are important. Let us consider them briefly:

1. They are not cellular but are the products of cells. This means that in the living animal they are not alive any more than milk (which is also a product of cells) is alive. Leather technologists sometimes overlook this fact.

2. Fibers do have a complex organization. Collagenous fibers, for instance, are made up of a complex hierarchy. The big ones you see under the microscope are properly called fiber bundles. Fiber bundles are made up of bundles of fibers (to use the word properly). Fibers are made up of fibrils. Fibrils, which can barely be seen under the microscope, are made up of filaments. Filaments are made up of protofibrils, which are composed of complex, oriented chains of protein (collagen) molecules.

3. The size, direction, position, number, arrangement, and individual appearance of the fiber bundles are indicative, to some extent, of the physical properties of the leather.

Identify:

1. Epithelium - Cellular. Seen only in green or fresh skins. Largely dead cells. Only the bottom cells are alive. Waterproofs the skin. Surrounds the hair follicle.

2. Corium minor - Region of hair and glands. Small fibers. The grain.

3. Corium major - Large fibers.

4. Adipose layer - Fat cells and layers of connective tissue. The flesh.

5. Hair follicle

6. Erector pili muscle - Raises hair. Squeezes sebaceous gland. Activated by temperature extremes even in the beamhouse.

7. Sebaceous gland - Oil gland, associated with hair.

8. Sweat gland - Usually only the body of the gland may be seen.

9. Blood vessels

10. Hair papilla

11. Fat cells

12. Elastic fibers - Support organs, require special stain.

HISTOLOGY - THE MICROSCOPE

Third Year - Lecture #12

This instrument allows one to view under great magnification the structures of skin or leather. It enables one to note the condition of the fibers and of other structures; to study damage done by bacteria, molds, or other organisms; to detect the presence of undesirable chemicals; and to study the extent and manner of penetration of substances used in the leather-making process.

The skin or leather is sliced into thin sections which are mounted on a glass slide. A very thin cover glass is placed over them. Since they are viewed by light passing through them, they must be very thin. The sections you will see are about 1/1200 in. thick.

Parts of the microscope

1. Stage - where the slide rests.
2. Illumination apparatus
   - (a) Iris diaphragm
   - (b) Condensor - increases intensity of light. May be omitted.
   - (c) Lamp plus mirror
     - or
   - (d) Direct Illumination.
3. Objective - lens system nearest the slide.
4. Ocular - lens system nearest the eye.
5. Coarse adjustment - primary, coarse focusing.
6. Fine adjustment - final, delicate focusing.

Magnification

Magnification is most easily expressed in diameters, represented by the symbol X. A 10X objective will magnify so that a circular body will appear to have a diameter which is 10 times its actual diameter.

The magnification of the microscope is the product of the magnifications of the ocular and objective. A 10X ocular used with a 43X objective magnifies 430 times.

Precautions

1. NEVER FOCUS DOWNWARD WITH THE COARSE ADJUSTMENT WHILE YOU ARE LOOKING INTO THE MICROSCOPE.

2. Do not scratch the lens. Clean it with lens paper.

3. Do not mount your slide on the stage upside down.

4. Use the right amount of light. A change in magnification requires a change

in lighting, which is attained by manipulating the iris diaphragm.

5. Hold the slide by the edges.

6. Carry a microscope in an upright position. If it has direct illumination, hold your hand under the bulb. Never carry a microscope with a slide on it.

7. Keep both eyes open when viewing the slide.

Oil Immersion

For magnifications approaching 1000X, the objective must come in contact with the slide. To protect the lens and to maintain the decencies of the laws of optics a film of oil is placed on the slide. A special immersion oil is used and the slide and lens are cleaned with Xylene after use.

HISTOLOGY - THE TECHNIQUE OF SLIDE MAKING

Third Year - Lecture #13

I. At any point in the leather-making process from the green skin through the pickle, sections are made most commonly by one of the two following techniques:

A. The Paraffin Technique

Fixation

The tissue is soaked for a minimum of 12 hours in 10% formalin (HCHO). This pro ess hardens and sets the structures and renders the tissue immune to decay. (Fixation bears something of a resemblance to tanning.) The tissue is then washed in water for an hour in the tumbler.

Dehydration

The tissue is next run through a series (6-12 hours in each) of increasingly concentrated alcohol solutions. Our laboratory uses ethyl alcohol 35%, 50%, 70%, 83%, 95% and absolute. These solutions remove the water from the tissues. Because of currents set up in the alcohol, the dehydration must be carried out gradually. Unless dehydration occrs, paraffin will not penetrate.

Dealcoholization

The tissue is next soaked for about 6 hours in an agent which removes the alcohol. Clove oil, phenol, cholorform, or aniline are among those ised. In this laboratory cedar wood oil has proved to be very satisfactory.

Xylene

The tissue will not be well penetrated by the paraffin unless the dealcoholizer is removed. With cedarwood oil, we soak 15 minutes in xylene, toss out the solution, and soak 15 minu'es again.

Dioxane

To save time, one may fix ard wash in the usual manner and then soak 3 hours in 1-4 dioxane, change the solution, and soak 3 hours more. This eliminates dehydration and dealcoholization. Dioxane is toxic and forms explosive peroxides upon excessive heating. It should be handled cautiously.

Paraffin

The tissue is next heated in melted paraffin. A paraffin melting between 52 and 58 degrees is desirable. The paraffin should be kept as close to the melting point as possible. Higher temperatures may cook the tissue. The paraffin bath must continue until the tissue has been thoroughly penetrated. After 72 hours, however, the tissue shows a tendency to become brittle. In the vacuum oven, from 3 to 6 hours will usually cause satisfactory penetration.

When dioxane is used, it is customary to heat the tissue in a 50-50 dioxane-paraffin bath for three hours before putting it into straight paraffin.

Embedding

A paper boat, one inch square and a half inch deep, is made to hold the tissue. A shallow layer of melted paraffin is poured into the bottom of the boat, and with great rapidity the tissue is squarely oriented in this layer. The boat is then filled with paraffin and the paraffin is quickly cooled in water.

Sectioning

Sectioning will be discussed elsewhere. It consists in cutting the tissue into very thin sections on the microtome and then affixing them to a glass slide by means of a thin film of an adhesive made of egg albumin and glycerine.

Staining

With the paraffin method, staining is commonly done in Coplin jars or special staining dishes.

One can only generalize about staining, since methods vary with the stains used.

The purpose of staining is to enable one to see structures more distinctly or to see structures that might otherwise be invisible.

Stains are generally classed into alcohol soluble stains and water soluble stains. One usually selects from one of these two classes a stain that has an affinity for certain structures; a stain of a contrasting color is selected from the other class to stain the remainder of the section. The latter is known as a counter-stain.

Hydration and dehydration are accomplished by an alcohol series (83% and absolute omitted). When going from a non-aqueous to an aqueous medium, one decreases percentages and vice versa.

Final Steps

After staining, the section is immersed in xylene to remove the alcohol. It is then washed with a few drops of clove oil to remove dirt and to make it more translucent. This process is known as "clearing". The slide is then washed in xylene; a drop of Canada balsam is placed over the section, and it is sealed with a cover glass.

A Typical Procedure

Xylene 15 min. to remove paraffin
95% alcohol 5 min.
70% alcohol 5 min.
50% alcohol 5 min.
35% alcohol 5 min.
water soluble dye (time depends on strength)

35%, 50%, 70%, 95% alcohols 1 min. ea.

alcohol soluble dye (time depends on strength)

95% alcohol 1 min.

xylene 5 min
clove oil 3 min.
xylene 5 min.
mount in balsam.

HISTOLOGY - THE TECHNIQUE OF SLIDE MAKING II

Third Year - Lecture #14

I-B The Freezing Technique

Sections cut on a freezing microtome are floated on water. They are not usually affixed to a slide. They may be transferred from solution to solution by section lifters or may be picked up on a slide and balanced precariously while solutions are applied with medicine droppers. They may be mounted in either balsam or glycerine jelly.

Balsam

Aqueous dye; 35%, 50%, 70%, 95% alcohols (3 min. each); alcohol soluble dye; xylene 3 min.; clove oil 3 min.; xylene 3 min.; mount in balsam.

Glycerine Jelly

Since glycerine jelly leaches aqueous dyes, alcohol soluble dyes must be used. Go up through (3 min. each) the alcohol series and stain. Add a drop of glycerine jelly (melt in a water bath) and seal with a cover glass.

Fat Stains

Since xylene dissolves fats and oils, the freezing microtome must be used and the sections must be mounted in glycerine jelly.

Fixation

Before sectioning skin on a freezing microtome, soak 12 hours in 10% formalin.

II - LEATHER

Freezing Technique

The leather is soaked in water for a half hour and then sectioned. The leather usually does not need to be stained, but if a stain is used the method for staining skin with the freezing technique is followed.

Paraffin Technique

This technique is uaually used only with soft leathers. If the leather has not been dried, follow the paraffin technique for skin with the exception of fixation, which is omitted. If the leather is dry, place directly in the paraffin bath. If stains are to be used, follow the paraffin technique for skin. If stains are not used, melt off paraffin in xylene, clear in clove oil, wash in sylene, and mount in balsam.

III Sectioning

With skin, it is usually desirable to cut parallel to the hairs. Before fixation the skin should be shaved. The pieces for sectioning should be about 1/4 inch by 3/8 inches. For identification, the long side should be perpendicular to the direction of the hairs for paraffin sectioning, and parallel to the direction of the hairs for freezing sectioning.

Freezing

A few drops of water are placed on the freezing platform. The piece to be sectioned is placed so as to be cut the long way, and frozen by admitting the gas in short bursts. As the sections are cut, they are transferred to the water bath by means of a pick needle.

Paraffin

The block is shaved down so that there is about a 1/16 inch margin of paraffin around the specimen. It is embedded in melted wax in the metal carrier in such a way that it will set parallel to the blade. Sections should come off the blade in a ribbon. Watch the tilt of the knife, the temperature of the room, and the sharpness of the blade.

HISTOLOGY - SPECIAL TESTS IN LEATHER MICROSCOPY

Third Year - Lecture #15

There is no all-purpose technique in microscopy that will show us all that we wish to see or tell us all that we wish to know. Accordingly, there have been developed special methods and tests which allow us access to information not available through ordinary procedures.

Nuclear Stains

Fibers are the products of cells. In order to attain a better understanding of the nature of fibers, research people have felt that they must study their origin and development. This study entails some knowledge of the fiber-producing cells.

Unfortunately these cells are very small and very difficult to see. It has been found that, if the tissue is stained with a dye which imparts a heavy, dark color to the nuclei, the cells will stand out under low magnifications. Once they are located, the cells may be easily studied under oil immersion.

Delafield's Hematoxylin is the outstanding nuclear stain. Along with eosin, it is the most widely used of all stains. It has a litmus-like action, hence its pH must be carefully controlled. Its staining properties may vary slightly from day to day since it undergoes an aging cycle, at the end of which it becomes useless.

The cells under discussion are known as fibroblasts, and the study of them is a research problem rather than a practical one. It is interesting to note, however, that scientists have been able to remove living fibroblasts from the bodies (not the skin) of animals, to feed them and keep them alive, and to make them grow fibers.

Fat Stains

The distribution of natural fats in the hide or of fats and oils introduced during the leather-making process is an important practical problem.

Fats and oils may be stained by selective dyes, such as the Sudan series (II, III, IV) Nile Blue Sulphate, or osmic acid. Nile Blue Sulphate has the advantage of giving us a clue to the nature of the fats through color variation, but has the disadvantage of being practically useless for permanent mounts because of its tendency to fade.

Fat stains cannot be prepared by any method involving a fat solvent (xylene) and the tissue is, therefore, usually cut by the freezing technique and mounted in glycerine jelly.

Penetration

The degree of penetration of colorless substances into leather may be determined by various means. Salt serves as an outstanding example. The section is treated with silver nitrate, which reacts with the salt to precipitate silver chloride. The silver chloride darkens in the presence of light to reveal the area covered by salt.

Penetration studies may be made at many points during the leather-making process.

Reticular and Elastic Tissue

For research purposes it is sometimes necessary to stain for reticular and elastic tissue.

Reticular fibers are easily seen by staining with hematoxylin after the tissue has been treated with a lime solution.

Elastic tissue is commonly stained with a mixture of resorcin and basic fuchsin.

Physical Tests

In the study of the physical properties of leather it is often desirable to measure the size and angle of weave of fibers.

Size is conveniently measured by micrometers on the fine adjustment and on the mechanical stage. Angle of weave is measured by a complex protractor.

The Polaroid Microscope

The presence of certain crystalline or oily substances in leather may be revealed (provided that these substances have the necessary optical characteristics) by the polaroid microscope, which you have seen demonstrated.

BEAM HOUSE OPERATIONS

Third Year - Lecture #16
Experiment #1

SIDE LEATHER--CALFSKIN-SHEEPSKIN

One cowhide, four calfskins and four shearlings were put into process in a series of successive steps in order that each might be seen and handled in various stages during a two and one-half hour laboratory period. The attached schedule shows how this was accomplished.

Side Leather Process

The cowhide was cut into sides before soaking.

Soak:- The sides were soaked in water at 60°F. overnight, about 20 hrs. The sides were allowed to drain for 15 minutes and were fleshed.

Unhairing:- Because only two sides were involved it was decided to unhair in a barrel.

Lime-Sulfide for sides
½ bbl. of Water
6 lbs. of Lime (15% by wt.)
4 lbs. of Sodium Sulfide (10% by wt.)

The sides were unhaired one at a time and the first side was in the unhairing solution about 20 hours, the second about 9 hours. In the first case the hair and epidermis were completely dissolved, in the second case the hair was heavily pulped and partly dissolved. Thus the second side needed but a slight scudding.

Reliming:- The sides were placed in a reliming solution to be held for the next class (1 week).

Reliming solution
25 lbs. Lime
180 gals. of Water

Sides paddled three times each day for about 15 minutes each time.

Calfskin Process

Soak:- The calfskins were soaked in a paddle at about 65-68°F. Three of the skins were soaked for 20 hours and one was soaked for 9 hours. Each skin was fleshed before unhairing.

Unhairing:- The skins were painted with a lime-sulfide paste and packed down for 20 hours.

Paint Formula
9 lbs. Lime
4½ lbs. Sodium Sulfide

Above dissolved in about 1 gal. of water to give paste.

The hair was removed on the beam and each skin was scudded clean with a slicker to remove all small hairs and pigment. All the skins were washed 20 minutes.

Reliming:- The skins were placed in the relime bath prepared for the sides.
25 lbs. Lime
180 gals. Water
Paddled fifteen minutes, three times per day.

Shearling Process

Soak:- It was intended to remove the wool from these skins before tanning, thus they were given the same process as the calfskins. Three of the skins were soaked for 20 hours at 65 68°F. and one was soaked for 9 hours. The skins were fleshed before unhairing.

Unhairing:- Each skin was painted with a lime-sulfide paste and packed down for about 20 hours. The wool was removed on the beam and a slight scudding was given to each skin. This did not seem to remove anything but wool grease. The skins were washed for about 20 minutes and placed in the relime paddle.

Reliming:- The sheepskins were placed in the same relime bath as the calfskins and the sides.
Reliming Solution
25 lbs. Lime
180 gals. Water

	Sunday	Monday	Tuesday	Wednesday	Thursday to Tuesday
Sides					
1	Soak	1. Flesh 2. Lime-Sulfide Sol.	1. Unhair) 2. Flesh)A.M. 3. Relime)	Relime	Relime
1		Soak	1. Flesh 2. Lime-Sulfide Sol.) A.M. 3. Unhair&Relime-P.M.	)Relime	Relime
Calf					
1	Soak	1. Flesh) 2. Paint) A.M.	1. Unhair) 2. Relime) A.M.	Relime	Relime
1	Soak	1. Flesh) 2. Paint) A.M.	1. Unhair) 2. Relime P.M.	Relime	Relime
1		Soak	1. Flesh) 2. Paint) P.M.	1. Unhair 2. Relime	Relime

	Sunday	Monday	Tuesday	Wednesday	Thursday to Tuesday
Calf (cont.)					
			1. Soak - A.M. 2. Flesh) 3. Paint) P.M.	1. Unhair 2. Relime	Relime Relime
Shearling					
1	Soak	1. Flesh) 2. Paint) A.M.	1. Unhair) 2. Relime) A.M.	Relime	Relime
1	Soak	1. Flesh) 2. Paint) A.M.	1. Unhair) 2. Relime) P.M.	Relime	Relime
1		Soak	1. Flesh) 2. Paint) P.M.	1. Unhair 2. Relime	Relime
1			1. Soak - A.M. 2. Flesh) 3. Paint) P.M.	1. Unhair 2. Relime	Relime

BEAM HOUSE OPERATIONS

Third Year - Lecture #16
Experiment #2

SIDE LEATHER-CALFSKIN-SHEEPSKIN

Wash

The skins and sides which had been in the relime solution for 6 to 7 days were washed for 15 to 20 minutes in water at 90°F.

Bate

170 gallons of water in paddle - temperature 92°F.
Total weight of 8 skins and 2 sides 83 lbs.
Oropon F added - 1.5 lbs (1.8% of lime wt.)
Paddle run for about 1½ hours.
In this case the volume of water to hide is rather large and an excess of Oropon up to 100% could be used without any great danger.
Note:- The sheepskins took up the effects of the bate rapidly and were quite well delimed in about 45 to 50 minutes. The calfskins were quite well delimed in about 90 minutes, but the sides were still quite swollen in this time and showed a large raw streak.

Pickle

The sheepskins were placed in the pickle after 45 minutes bating and the calfskins and sides after 90 minutes. The pickle solution was made up as follows:

Pickle:- 100 lbs. Salt
3 lbs. Sulfuric acid

At start (Tues. night)

Barkometer	54
pH	1.8

Wed.

Barkomenter	53
pH	2.2

Mon.

Barkometer	53
pH	2.35

Sufficient acid was added Monday to bring back pH to 2.0.

TANNING

Third Year - Lecture #17
Experiment #2

SIDE LEATHER-CALFSKIN-SHEEPSKIN

Drum #1 (2 Calfskins)

Tanning:- (Chrome) performed in afternoon prior to class.

Float:- 1 gal. of pickle solution
1 lb. of Tanolin R dissolved in
1 gal. of water at 212°F.

The chrome solution was added in three feeds at 70°F.

1. Add 1/3 - run 30 mins.
2. Add 1/3 - run 30 mins.
3. Add 1/3 - run 3 hrs.

Neutralization:- (during evening class)
One ounce of $NaHCO_3$ dissolved in two (2) quarts of water.
(Approximately 0.5% of hide wt.)
1. Add 1 quart, run 30 mins.
2. Add 1 quart, run 60 mins.
final pH 3.9

Skins removed and horsed up.

Drum #2 (2 sides, 1 calf, 1 degreased sheep)

Tanning:- (night class)
Pickled weight - 52 lbs.

Float:- 6 gals. pickle liquor plus
2 gals. water
Stock chrome solution 4 lbs. of Tanolin R per gallon mixed at 212°F. and cooled to 70°F.

Tanning solution:-
The volume of chrome stock solution was selected to give a weight of chrome equivalent to 9% of the hide weight, viz 4 gallons, 1½ pints.

Feed:- The chrome was added in three feeds:
1. Add 1/3, run 30 minutes.
2. Add 1/3, run 15 minutes.
3. Add 1/3, run 1 hr. 45 minutes.

The hides were removed and horsed up.

(Wednesday, March 17, 1954)

The sides were placed in one drum and the calf and sheep in a second drum.

Sides:-

Tanning continued for 1½ hour in liquor of previous evening.
1 lb. of Tanolin R in one gal. of water was added to the drum and run for two more hours.
Total time this day - 3½ hours.

Neutralization:-
4 ozs. of $NaHCO_3$ in 2 quarts of water were added in two feeds:
1. Add 1/2, run 30 mins.
2. Add 1/2, run 60 mins.
The hides stood a 4 minute boil test - removed and horsed up.

Calf and Sheep:-
A tanning liquor of 1 lb. of Tanolin T in 2 quarts of water was added and the skins run for 1½ hours.

Neutralization:-
1 ounce of $NaHCO_3$ in 2 quarts of water was added in two feeds:
1. Add 1/2, run 30 mins.
2. Add 1/2, run 60 mins.
The skins stood a 2 minute boil test.
The skins were removed and horsed up.

Drum #3 (1 degreased sheepskin - vegetable tanned) (evening class)

Float:- 2 quarts of water; 4 ozs. of NaCl.
Run 5 minutes to mix.
Add skin.

Tanning:- A solution of 3/4 of a lb. of liquid quebracho in 1 gal. of water was added in three feeds:
1. Add 1/4, run 20 mins.
2. Add 1/4, run 20 mins.
3. Add 1/2, run 60lmins.
Skins removed and horsed up.

(March 17, 1954)

Tanning:- 3/4 lb. liquid quebracho in 1 gal. water was added to the liquor used the previous evening and the skin was run 2 hours, then horsed up.

Drum #4 (2 sheepskins to be degreased) (evening class)

Degreasing Solution:
6 qts. Stoddard solvent
1½ ozs. Dupanol
Run 20 minutes - remove and wring skins.
Repeat with above amounts of fresh solution for 20 mins. & wring.

Wash:- 10 qts. Water
30 ozs. NaCl
½ oz. Dupanol
Run 10 minutes, drain and add fresh materials as above - run 10 mins., drain, remove skins and place in pickle.

(March 17, 1954)

Tanning:- (2 sheepskins, 1 calfskin) (11 lbs.)

Float:- 2 qts. pickle liquor

Tanning Solution:
1 lb. Tanolin R in 2 qts. of water added in three feeds.

Tanning:-
1. Add 1/3, run 30 minutes.
2. Add 1/3, run 30 minutes.
3. Add 1/3, run 2½ hours.

1 lb. Tanolin T dissolved in 1 qt. of water was added, run 60 minutes.
Total time - 4½ hours.

Neutralization:
1 oz. $NaHCO_3$ in 1 qt. of water was added in two feeds:
1. Add 1/2, run 30 mins.
2. Add 1/2, run 60 mins.
Drain and horsed up.

SCHEDULE

	March 16			March 17
Drum #1 2 calf	Aft. Tanned	Evening Neutralized		
Drum #2 2 sides 1 sheep 1 calf		Tanned	Separated	Sides tanned & neutralized Sheep tanned & neutralized & Calf
Drum #3 1 sheep		Vegetable tanned		Vegetable tanning (cont.)
Drum #4 2 sheep		Degreased		Tanned & neutralized

RETANNING

Third Year - Lecture #18
Experiment #3 March 23, 1954

Retan:- (1 side previously chrome tanned)
The side was set out and shaved.
Weight shaved 6 lbs.

Wash:- The side was washed for 10 minutes.

Float:- 4 gallon float used.

Tanning Solution:-
On the basis of 6 lbs. of hide the following were dissolved in 1 gallon of water:

1% Sumac	(20 grams)
7% Liquid Quebracho	(4.6 ozs.)
1% Tamol N	(20 grams)

Tanning:- The side was drummed for one hour and 30 minutes in above tanning solution. Penetration was not complete.
The float was extended to 6 gallons and the above quantity of tanning materials were added for a second feed and run for an additional 1½ hours.
Penetration was complete and the side was horsed up.

Retan:- (2 sheepskins, 2 calfskins previously chrome tanned)
The procedure and percentages were similar to those used on the side.
The skins were set out and shaved. Shaved weight 9 lbs.

Tanning Solution:-

Sumac	1.5 ozs.
Liquid Quebracho	10.5 "
Tamol N	1.2 "

The above dissolved in 1 gallon of water.

Tanning:- Penetration was complete in 1½ hours.
The above quantities were repeated in a second feed and the float extended to 6 gallons.
Run 1 hour, drain and horse up.

Bleach:- (Vegetable tanned sheepskin)
As this skin was too dark it was decided to bleach it.

Float:- One gallon of water at 110°F. to which was added 1 oz. Borax dissolved in 2 quarts of water at 110°F., run 15 minutes.

Wash:- The skin was washed 5 minutes at 110°F. and drained.

Neutralization:-

5 ml. of formic acid in 1 gallon of water at 110°F. was added and run for 5 minutes - drain.

Wash:- The skin was washed 10 minutes at 90°F.

Tanning:- (hide weight 2 lbs.)

5% Liquid Quebracho	1½ ozs.
½% Tamol N	5 grams

The above was added in 1 gallon of water at 70°F. and run for 1½ hours.

Then the skin was horsed up.

DYEING AND FATLIQUORING

Third Year -- Lecture #19
Experiment #4 March 30, 1954

SIDE LEATHER-CALFSKIN-SHEEPSKIN

One side, two calfskin, and two sheepskin were dyed and fatliquored during the laboratory period. The total shaved weight of 25 lbs. was used as a basis for all calculations. The skins were all processed together; all had been chrome tanned during a previous laboratory period.

Neutralization

The skins were neutralized prior to the laboratory period.

Wash:- The skins were washed 30 min. at 70°F.

Float:- 8 gal. of water were put in the drum at 70°F.

Feed:- 6 oz. of sodium bicarbonate were added through the gudgeon in one feed. The bicarbonate was dissolved in 2 qts. of water at 70°F. Skins were run 30 mins.

Bottom

Float:- 8 gal. of water were put in the drum at 90°F.

Bottom:- 3 lbs. 12 oz. Solid Quebracho
16 ozs. Leukanol R
1 oz. Sumac
The materials were dissolved in 4 gals. of boiling water which was cooled to 90°F. and added to the drum. Skins were run 20 min.

Wash:- Skins were washed 10 min. - the temperature was raised gradually to 120°F.

Dyeing

Float:- 14 gals. water at 120°F. were added to the drum.

Acid and Direct Dyes:- The following were dissolved in 4 gal. of boiling water, cooled to 120°F., and added slowly to the drum:

3.75 oz. Calcodur Orange ERL
.6 oz. Calcocid Brown Y
1.7 oz. Calcomine Catechu 2B Conc.
.15 oz. Calcomine Scarlet B

These dyes were run 20 min.

Set:- 18 cc Formic Acid in 2 qts. water was added through the gudgeon and run 10 min.

Basic Dyes:- The following dyes were added through the gudgeon in 2 gals. water at 130°F.

1.4 oz. Calcozine Phosphine 3R 50%
0.3 oz. Calcozine Supra Conc.
0.6 oz. Calcozine Phosphine PHM

The basic dyes were run 30 minutes.

Wash:- The skins were washed 15 min. at 120°F. and drained.

Fatliquor

Float:- 14 gals. water were added to the drum at 130°F.

Fatliquor:-

4 oz. Monopole Oil (sulfonated Castor)
12 oz. Sulphonated Neatsfoot A15
.2 oz. Mineral Neatsfoot

The oils were emulsified thoroughly in 2½ gal. water at 130°F. and added to the wheel.

The skins were run 30 min. and then horsed up overnight.

DYEING AND FATLIQUORING

Third Year - Lecture #20
Experiment #5

April 6, 1954

Dyeing of Retanned Skins

One side, two calfskins, and two sheepskins were dyed and fatliquored in a single lot. The skins had been retanned during a previous session. They had a shaved weight of 25 lbs.

Dyeing

Wash:- The skins were washed for 15 minutes, and the temperature was gradually raised to 120°F.

Float:- Two and one-half gals. of water were added to the drum at 120°F.

Dye:- One and one-quarter ounces of BBC (a combination of acid dyes) in 2½ gals. of water at 120°F. was added to the drum. The dye was run 30 minutes.

Fatliquor

Two and three-quarters pounds (11%) of 105A in 2½ gals. of water at 130°F. was added to the drum.
This fatliquor has an oil value of 37%.
The fatliquor was run for 30 mins.

The skins were horsed up overnight.

EXPERIMENT 5A

The side and two calfskins previously chrome tanned and colored were conditioned and staked in preparation for finishing.

LABORATORY DYEING TESTS - THE FORMULATION OF THREE BROWN COLORS

Third Year - Lecture #21
Experiment #6 April 27, 1954

The purpose of this experiment is twofold: to provide an acquaintance with the laboratory techniques involved in formulating colors and to provide a acquaintance with the mechanics of a color chart. The theoretical background for this work is to be found in Lecture #22 of the second year.

A brown may be produced by one or more dyes. Quite commonly two or three dyes are used in combination. It will be noted that the dyeing in Experiment #4 involved a combination of seven dyes to produce a brown. It must be understood that the selection of dyes will determine the levelness of the dye, the brightness (as opposed to sadness or blackness), and the hue (red browns, yellow browns, etc.). The lightness (as opposed to darkness or heaviness - i.e. strength) is a function of concentration.

The following illustrate combinations to produce a brown:

1. An orange and a black.
2. An orange and a blue.
3. A yellow and a maroon.
4. A yellow, a red, and a blue.
5. A violet, an orange, and a green.

Experimental

Samples: Twenty-gram samples of chrome-tanned side leather were used.

Stock Solutions: Stock solutions of 2 grams/500 cc of acid and direct dyes in water were made up. (1/500 solutions are usually used for basic dyes.) Dyes were dissolved in hot water and made up to volume in volumetric flasks.

Dyeing: The formulas for the dyes are worked out on the basis of using a weight of the dye representing a definite percentage of the weight of the sample (shaved wgt. of the leather). We used a volume of stock solution known to contain this weight of dye.

Example: Let us say that our formula calls for 1% Orange ERL.

a. 1% of 20 grams (sample) is .2 grams.

b.7 1 cc of stock solution contains:

$$\frac{2gr}{500\ cc} \text{ or } .004 \text{ grams}$$

c. .2 grams of dye are contained in

$$\frac{.2\ gr}{.004\ gr} \text{ or 50 cc of stock solution}$$

d. If, therefore, we use 50 cc of stock solution of Orange ERL in our formula, we have .2 grams of dye which is 1% of the weight of a 20 gram sample.

The formula volumes were measured carefully with pipettes. The formula was heated to 135°F. and placed in a 2 quart mason jar. The sample, previously neutralized to pH 5.5, was added. The samples were run on the shaker for 30 minutes.

Set: The dye solutions were exhausted by adding 5 cc of a stock solution of formic acid (50 grams in one liter), and tumbling for 20 min.

Fatliquor: Fifteen cc of a stock solution of 25 grams of CL2 oil in water were made up to 100 cc with water, heated to 140°F., added to the dye solution, and tumbled 20 minutes. The sample was set out and tacked on a board to dry.

Formulae:

Brown #1

27.5 cc (.55) Calcomine Fast Orange 2R
1.75 cc (.035%) Calcocid Violet 4BXN
.75 cc (.015%) Calcocid Milling Green 6B Conc.
.69 cc Water

Brown #2

46 cc (.92%) Polar Orange R Conc. (Geigy)
4 cc (.08%) Pontamine Black E Double
50 cc Water

Brown #3

23.75 cc (.475%) Calcocid Yellow 4BN
23.75 cc (.475%) Calcocid Fast Red A
2.5 cc (.05%) Calcocid Blue FFR Ex. Conc.
50 cc Water

In addition, 1% solutions (50 cc of stock solution and 50 cc of water) of each constituent dye were run.

FINISHING

Third Year - Lecture #22
Experiment #7 May 4, 1954

Finishes were applied to samples of buffed side leather in a general study, on a laboratory scale, of the finishing process.

I. A Water Finish Made at the Institute

A. Preparation of Pigments

The pigments used were ground in a vehicle made from the following stock solutions: (except for shellac)

1. Casein
   1 gal. Water
   1 lb. Casein
   4 oz. Borax

   The water was added at 180°F and continuous heat and stirring were applied until all of the casein was dissolved. A disinfectant was added.

2. Wax Solution
   1 lb. Carnauba Wax
   4 ozs. Oleate Soap
   1 gal. Water

   The solution was prepared in the same manner as the casein. A disinfectant was added.

3. Shellac Solution
   1 lb. Shellac
   4 oz. Borax
   1 oz. Ammonia (by volume)
   1 gal. Water

   The water was heated to 180°F.; the borax was dissolved; the shellac was added, then the ammonia. After the materials were dissolved, a disinfectant was added.

4. Moss Solution
   2.5 ozs. Dry Moss
   1 gal. Water

   The dry moss was added, with agitation, to the cold water. After the particles were fairly well broken up, the solution was heated to boiling, with agitation maintained. The heat was then reduced and the solution was allowed to simmer for an hour. A disinfectant was added.

After these stock solutions were prepared, they were combined into a vehicle into which the pigment could be ground.

Vehicle

32 ozs. Casein
32 ozs. Moss Solution
16 ozs. Wax Solution
8 ozs. Sulfonated Oil
40 ozs. Water

It will be noted that the shellac was not included in the vehicle. It figures importantly in the binder for the first spray coat and in the top finish.

Pigments

The following pigments were made up. Each was ground for six hours in a ball mill.

#1. 2 lbs. Red Oxide
1 gal. Vehicle

#2. 4 ozs. Carbon Black
1 gal. Vehicle

#3. 2 lbs. Chrome Yellow
1 gal. Vehicle

#4. 2 lbs. Red Toner
1 gal. Vehicle

So far, our work has netted us four pigment solutions and our shellac solution. It would seem proper to consider the significance of the materials used.

Moss is used to fill the open grain and give body to hold the pigments in suspension. The term moss is actually a misnomer. The material is Irish Moss, a bright green seaweed or kelp, which, incidentally, is found in profusion along the New England coast.

Carnauba Wax gives a bright surface and helps prevent the finish from sticking to the plate at higher temperature.

Casein is a good binder to carry the pigment. It makes a hard, bright, surface and is fairly flexible. Chemically, it is a protein.

Shellac makes a bright, hard film and is a good binder. Sulfonated oil is used to make the film flexible and to prevent cracking.

B. Stock Solutions for Finish Coats

Before spray coats can be made up, certain constituent stock solutions must be prepared. For purposes of identification, we have assigned code numbers to those which will be used here.

Finish Pigment #4957

Red Oxide in vehicle	7½ ozs.
Black in vehicle	3 "
Chrome Yellow in vehicle	1½ "
Red Toner in vheicle	1½ "
Binder #4	6 "
Water	6 "

This finish pigment was designed to finish the calfskin which we dyed on March 30 in Experiment #4. It was color matched to the dye.

Dye Solution #1

3.78 grams Sella Brown B 133%
2.27 grams Sella Brown G Supra
.53 grams Pontacyl Fast Red AS
.53 grams Buffalo Black NBR 126%
16 ozs. Water

This dye solution was also color matched to the dye in Experiment #4.

Binder #4

Casein Solution	4 ozs.
Moss "	4 "
Shellac "	4 "
Monopole Oil	1 oz.
Water	15 ozs.

This is the binder used in Finish Pigment #4957 above.

Binder #5

Casein Solution	40 cc
Moss "	40 cc
Shellac "	40 cc
Water	80 cc

Top Finish 4357

Shellac Solution	50 cc
Casein "	25 cc
Wax "	5 cc
Water	25 cc

C. The Finish Process

Three samples were given the same base coats:

#1 Received our Top Finish #4357
#2 Received Hydrolac PL (Rohm & Haas)
#3 Received Stahl Top Finish

1. First spray coat

Finish pigment 4957	100 cc
Dye #1	40 cc
Primal Finish B-52 (Rohm & Haas)	30 cc
Primal Finish B-41	14 cc
Ammonia	3 drops

Spray one coat and dry at 105°F.

Primal B-52 and B-41 are acrylic resin dispersions, which are flexible film forming materials.

2. Spray one coat of above and dry at 105°F.

3. Smooth plate 180°F. and 7½ tons.

4. Spray 1 coat:

Finish Pigment 4957	120 cc
Binder #5	10 cc
Dye #1	10 cc
Water	20 cc
Formaldehyde	4 drops

Dry at 105°F.

5. At this point a whole skin would be slaked lightly.

6. Top Finish

Spray 1 coat	1	2	3
Top Finish 4357	50 cc	-	-
Water	5 cc	-	-
Formaldehyde	2 drops	-	-
Hydrolac PL	-	60 cc	-
Water	-	70 cc	-
Stahl Top Finish 7014	-	-	40 cc
Water	-	-	60 cc

Dry at 105°F.

7. Spray 1 coat of above each.

Dry at 105°F.

8. Smooth plate at 180°F., 7½ tons.

Top coat #1 had slightly less luster than #2 and #3; daylight revealed, however, that #2 and #3 had made a marked change in the color.

II. A Stahl Finish

A commercial finish for smooth sides was applied to a sample for comparison. The color was slightly different so that the comparison could not be carried too far. The ingredients of this finish are not known to us.

Percentages are bsed on volume.

1. <u>First and Second Pigment Coats</u>
   Swab
   - 40% Permatex (a pigment lake dispersion)
   - 20% 984 Resin Emulsion
   - 40% Water
   - (Dry after each coat at 105°F.)

2. <u>Third Pigment Coat</u>
   Spray
   - 30% Permatex
   - 20% 4009 Binder
   - 5% 984 Resin
   - 45% Water

   Dry at 105°F

3. Plate at 180°F., 7½ tons.

4. <u>Top Coat</u>
   Spray
   - 40% Top 7014
   - 60% Water

   Add Pigment 4 oz./gal. and Formaldehyde 2 oz./gal.

5. After drying at 105°F., plate at 180°F. and 7½ tons.