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## LEATHER—AN IMPORTANT MATERIAL FOR DEFENCE

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Many articles made of leather are required by the Armed Forces, the most important being army boots and saddlery. The kinds of leather needed for making them are the heavy leathers, viz., sole and harness and medium substance leather for army footwear uppers.

These varieties of leather must be of the prescribed military specifications and of the best standards of quality. For this, the best available heavy buffalo and cow hides must be used, the former for making sole and harness and the latter for army footwear uppers. The techniques of manufacturing these leathers must also be of the highest possible order and the processes should be scientifically controlled.

The processes at present used in India for making the army leathers are described in this article. The scientific principles involved in the manufacture are also set forth. The disadvantages of the prevalent techniques of manufacture are shown and the methods of removing these disadvantages are suggested.

Many articles made of leather are essentially needed by the Armed Forces, Cavalry needs leather accoutrement for the horse such as saddles, reins and stirrup straps. Leather straps are required for the artillery. Many weapons have to be kept in leather cases. Military officers and soldiers alike must have army boots, belts, bandoliers etc., and cavalry men need also leather leggings; leather cases, leather water bags and leather jerkins are used by the army. While all these items are necessary army boots and harness and saddlery constitute the great bulk among army's leather stores.

The most important varieties of leather required in large quantities are therefore, the following :---

- (1) Sole leather for army boots.
- (2) Harness leather for saddlery, straps, waist belts, bandoliers, leggings, various kinds of leather cases etc.
- (3) Upper leather technically called ammunition leather for uppers of army boots.

All these leathers must be of the best possible quality and should conform to rigid military specifications because army's performance in the front and its safety depend to a considerable extent on the strength and durability of the leather. Meticulous care, is, therefore, taken in the selection of raw hides and carrying out of tanning and finishing of leathers from them.

Leather technology, which deals with tanning raw hides and skins and finishing the tanned leather to impart to it the specific properties which it should have to be suitable for making particular types of leather articles either for military or civilian use, although very old, is, still making progress. Its progress has been due to the application of various branches of science to it and research which is being carried out to explain the principles underlying the old craft of tanning, to throw light on the mechanism whereby the profound change viz., the conversion of putrescible raw hides and skins into imputrescible and permanent leather is brought about and to improve the old techniques of leather manufacture and to work out new techniques with the help of modern sciences and machinery.

The technology of the manufacture of army leather has followed the trend of general leather technology and has developed on scientific lines. This has been fortunate. The present global wars are very different from old local army conflicts. At present, army's activity is not confined to a limited area. It has to go forward far afield and fight on different terrains, in different climates and altitudes. A modern army is to be equipped with leather footwear and kit which will stand to the surroundings in which it will operate. An Army boot which is suitable for fighting in the tropics is utterly unsuitable for operations in very cold regions. Jungle warfare in rain sodden soil of the tropics requires different footwear from that needed in battles on open and dry land.

The leather industry of the West is endeavouring to meet the exacting demands of the army of today by research. For keeping India's army uptodate and its defence strong, similar leather research is essential in India. To make the scope and function of leather research for the army intelligible, it is necessary to describe briefly the technical methods of manufacturing at least the more important varieties of army leather.

#### Sole leather for army boots and harness leather for saddlery belts, straps, etc.

Raw Materials .-- For these leathers, slaughtered buffalo hides either in green or wet-salted condition weighing more than 45 lbs. in wet-salted state per hide are chosen. For light harness leather, wet-salted or green heavy cow hides may also be employed. The hides should be of good substance and free from grain and flesh defects. During the last war, which was before the partition of India, large quantities of suitable buffalo hides and a small quantity of heavy cow-hides for the purpose were obtained from the Western Punjab and North Western Frontier Provinces which are now in Pakistan. So, at present, this source of supply of suitable hides for military leather is lost to India. She has now to depend on hides available within her borders, a great bulk of which is not sufficiently heavy for military requirements. In addition to this, owing to the anti-cow slaughter movement, slaughtered buffalo and cow hides which are usually better in quality than hides of naturally dead animals are in short supply. This is a handicap to the manufacture of adequate quantities of military leather.

Process of tanning.—These leathers are technically classed as heavy leathers and, therefore, are usually manufactured by vegetable tanning carried out in pits and known as the pit tanning process. According to it, the limed and delimed hides are passed through a series of vegetable tanning liquors of increasing strengths, until the hides are tanned through, that is to say, fully penetrated by the tannin. The pits containing the liquors are normally divided nto sections called suspenders, handlers consisting of floaters and dusters and

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layers. The liquors of the suspenders are the weakest, those of the handlers (floaters and dusters) are stronger and those of the layers are the strongest. In tanning practice, the strength of the pit liquors is ascertained by their specific gravity which is measured by a special hydrometer called Barkometer. The liquors of each section are kept in a definite range of barkometer strength which increases from pit to pit within the range.

During the last war, the Government Harness and Saddlery Factory, Kanpur, used to prescribe pit tanning processes which tanneries supplying leather to the Government had to follow. The processes prescribed dispensed with suspenders, started with floaters and completed the tannage in the second layers. The prescription fixed the range of barkometer strength of floaters and the strengths of dusters, 1st layer and the 2nd layer and also the periods of time for which the hides had to be kept in the different liquor sections. In the first prescription, total periods of 3 months for medium and light buffalo hides and 4 months for heavy buffalo hides were recommended for complete tannage. But later on during the war, the periods of tanning had to be shortened to  $2\frac{1}{4}$  and 3months respectively and to ensure completion of tannage, it was recommended that the hides after being taken from the 2nd layer of 65° Barkometer should be drummed for 2 hours in a strong liquor of 80° Barkometer restoring the strength of the drum liquor to 80°BK. after 1st hour's drumming. This process is summarised below :-

Light & meduim buffalo hides

Heavy buffalo hides

•	Time in Months	Strength Barkometer		Pits	Time in Months	Strength Barkometer
	1	20-48°Bk		Floaters .	11/2	20-48°Bk
•	12	55°Bk		Dusters .	1	55°Bk
•	1	60°Bk		lst layer .	1/2	60°Bk
•	12	65°Bk		2nd layer .	1/2	65°Bk
•	$2\frac{1}{2}$ months			Total . Drumm	3 months aing 1 hour @ 8 1 ,, @	80° BK "
	•	$\begin{array}{c c} \hline Months \\ \hline \\ & 1 \\ & \frac{1}{2} \\ & \frac{1}{2} \\ & \frac{1}{2} \\ & 2\frac{1}{3} \end{array}$	Months         Barkometer           1         20-48°Bk           1/2         55°Bk           1/2         60°Bk           1/2         65°Bk           2/2         55°Bk	Months         Barkometer           1         20-48°Bk           1/2         55°Bk           1/2         60°Bk           1/2         65°Bk           21/2         55°Bk	Months     Barkometer       .     1       20-48°Bk     Floaters       .     ½       55°Bk     Dusters       .     ½       60°Bk     1st layer       .     ½       65°Bk     2nd layer       .     ½       .     ½	MonthsBarkometerMonths1 $20-48^{\circ}Bk$ Floaters $1\frac{1}{2}$ $\frac{1}{2}$ $55^{\circ}Bk$ Dusters $\frac{1}{2}$ $\frac{1}{2}$ $60^{\circ}Bk$ Ist layer $\frac{1}{2}$ $\frac{1}{2}$ $60^{\circ}Bk$ Ist layer $\frac{1}{2}$ $\frac{1}{2}$ $65^{\circ}Bk$ 2nd layer $\frac{1}{2}$ $\frac{21}{2}$ monthsDrumming 1 hour @ 6

The leather tanned according to the prescribed processes by tanneries which had orders for army leather were inspected by an Inspector of Leather Control and sent to the Harness and Saddlery Factory in Kanpur in crust condition. Finishing into sole and harness leather was effected in the Harness and Saddlery factory.

The tanning was carried out with liquors obtained by extracting such vegetable tanning materials as barks of wattle and be bul and myrobalans blended in suitable proportions. The extraction was done in batteries of large pits intercommunicated with one another called leach pits following the counter current principle of extraction. The strength of the liquor obtained from leaching in this way using a battery of 8 leaches was about 70 to 80°Bk and was sufficient for use in floaters and dusters. For layers, if required, the leached liquor was permitted to be strengthened by 10°Bk. by a mixture of Mimosa and Myrobalam extracts blended in the proportion 3 to 1. The drum liquor had also to • be similarly strengthened.

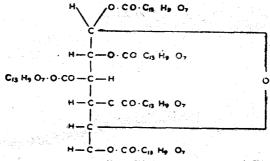
#### Scientific Principles underlying vegetable terring processes.

Scientific principles underlie vegetable tanning processes of which pit tanning process is the most practised type as yet in India. The basic technique involved in vegetable tanning is that pelts prepared for tanning by liming and deliming are first treated with an old and mellow liquor. From it the pelt absorbs little tannin whereby its grain and flesh layers are evenly coloured and very mildly tanned. This mild tannage prevents the shrinkage of grain and flesh surfaces and keeps the hair pores and capillary channels of the pelt open allowing the tan liquor to penetrate into the internal layers giving them a chance to come in contact with the liquor and become tanned by absorbing tannins from it and fixing the tannins to the fibres. The tan liquor penetrates the pelt by diffusion but the force of diffusion decreases as the tannin concentration of the liquor is reduced due to the absorption of the tannins from it by the pelt. The absorption of tannins by the pelt from the liquor in which it is steeped also depends upon the tannin concentration of the liquor. So, to ensure the progress of the tannage, the objective is to gradually increase the penetration of the tan liquor into the internal layers, of the pelt and to cause gradually increased fixation of tannins on the fibres and fibrils of the pelt. Hence to make the tannage progressive and eventually complete, the cardinal principle of vegetable tanning is to treat the pelt with tan liquors of increasing tannin strength. In olden times, the tanning was commenced and completed in one pit by gradually increasing the tannin concentration of the liquor by adding to it fresh tanning bark and discarding from it the old and spent tan bark. But, now the tan bark is leached and the leached liquor is used for tanning and instead of one pit, a series of pits containing tan liquors of gradually increasing tannin strength and freshness are used. The prepared pelts are gradually shifted forward from weaker and older to stronger and fresher tan liquors whereby a uniform and thorough tannage throughout the thickness of the pelt is effected.

Tan liquor is an aqueous solution of tannins and non-tannins but some insoluble substances are also present in it. Tannins are its most important constituent which actually effect the tannage. Tannins are organic compounds but are not single substances. It is now thought that every vegetable tanstuff owes its tanning action to a number of compounds which are extracted from it by water to prepare a tan liquor. These compounds are phenolic bodies of high molecular weights and present in the tan liquor as particles of different sizes and different degrees of dispersion. Those of higher molecular weights. and lower degrees of dispersion are liable to be absorbed by the pelt under tannage more quickly than those which are of lower molecular weights and higher degrees of dispersion. In early mellow liquors of the tanning process, the former are not present because they have already been absorbed by the pelts which have passed through the stronger and fresher liquors of the later stages of tanning. In the mellow liquors, tannins of lower molecular weights and higher degrees of dispersion occur which diffuse through the pelt easily without being much absorbed by the surface layers thus avoiding case hardening.

Tannins are now classified into two categories according to their chemical behaviours, viz., (i) hydrolisable tannins and (ii) condensed tannins or in
common tanning parlance, into pyrogallol and catechol tannins. The former on digestion with dilute sulphuric acid produce gallic acid, ellagic acid, sugars

etc., and the latter amorphous red coloured precipitates known as phlobaphenes. When treated with an iron salt like ferric chloride, a solution of pyrogallol tannins produces a blue colour and that of catechol tannins a green colour. The chemical constitution of one tannin is uptill now known with some degree of accuracy, *viz.*, that of gallotannin which is present in Chinese nut gall. Emil Fischer and his co-workers established this tannin as penta-digalloyl glucose having the following constitutional formula.

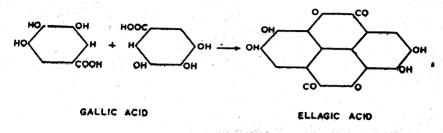


Among the vegetable tanstuffs which are commercially used, valonia, myrobalans, divi-divi, algarobilla and sumach are pyrogallo! tannins, and the others belong to the catechol group. Of the tanstuffs mostly used by the Indian tanning industry, myrobalans are a pyrogallol tannin while barks of wattle, babul, avaram, konnam, mangrove etc. are catechol tannins. Both categories of tanstuffs tan and make leather but the characteristics of leather made by each class are different. Usually in commercial tanning, mixtures of both classes are used to produce desirable effects. In India, wattle bark, its extract known as mimosa extract, babul bark and myrobalans are employed in tanning sole leather for the army as well as civilian footwear.

Besides tannins, a tan liquor also contains non-tannins which have no tanning effect but have a great bearing on the tanning process and properties of final leather. Some of these non-tannins are soluble and they consist mostly of organic acids like lactic, acetic, gallic etc., phenols like pyrogallol, carbohydrates like sugar and starch, organic salts, inorganic salts like chlorides and sulphates of calcium, sodium, magnesium and potassium and also vegetable colouring The colouring matter determines the colour of the leather which is matter. The acids very important as lighter the colour the more valuable is the leather. swell the pelt and thereby constrict its capillaries whereby the diffusion of the tan-liquor into the internal layers of the pelt is retarded. The salts exert an opposite effect. They reduce the acid swelling of the pelt and accelerate the diffusion of the tan liquor into it. The ratio of the tannins to soluble nontannins of the tan-liquor determines its astringency or the avidity of the tannins to combine with the collagen of the pelt. The higher this ratio the greater the astringency. In some vegetable tanstuffs, the ratio of tannins to soluble nontannins is high and in some low. The former are astringent tanstuffs and the Similar is the case with an old tan liquor through which latter are mellow ones. several lots of pelts have passed and to which it has imparted its tanning causing non-tannins which are not all absorbed by the pelts to remain in the liquor. The ratios of tans and soluble non-tans of old tan liquors are thus low and hence they are less astringent i.e., mellow. That is why they are used for treat- . ing fresh pelts to avoid case hardening of the pelt surfaces.

#### LEATHER AN IMPORTANT MATERIAL FOR DEFENCE

Besides soluble non-tans, tan liquors also contain insoluble non-tans, which are formed in the tan liquors then elves. The insoluble non-tans of pyrogallol tannins are called bloom and those of catechol tannins are called reds or phlobaphenes. The bloom is ellagic acid which is considered to be produced from 2 molecules of gallic acid by oxidation and dehydration in the following way :--



The insolubles of catechol tannins are phlobaphenes formed by the condensation of tannin molecules.

These insoluble non-tans are deposited on and between the fibres and fibre bundles of the leather and add to its weight and solidity. This deposition is very important for sole leather for which re son bloom producing, tanstaffs like valonia and myrobalans are much used in sole leather tannage. In Europe valonia is used for dusting sole leather in layers and in India, myrobalans serve a similar purpose.

During tannage, pelts for sole leather should be kept in swollen condition so that a thick leather may be produced. Optimum swelling depends upon the acid and salt contents of the liquor. Head liquors of modern sole leather tannages should have acid and salt contents of 200 mg. equivalent per litre. Formerly it was believed that acids were produced in tan liquors by the fermentation of sugar present in them. But that theory has been now abandoned. It is now held that tan-liquor acidity is due to the organic acids present in the liquors of and also the acidity of tannins. The effective acidity of tan liquors which is responsible for the swelling of the pelt and making the angle of weave in the fibre structure high is measured by their pH values The pH range of tanliquors of sole leather tannage is usually between 4.5 and 3. The early liquors should have a pH of about 4.5 and the liquors of head handlers should have a pH of about 3. pH measurement and the determination of the acid and salt contents and of Barkometer strengths of tan liquors are much used now-a-days for controlling sole leather tannage. Efficient pH metres are available. The acid and salt contents are determined by the resin exchange methods and the tannin strength of the liquor by a barkometer. In England, instead of relying upon the barkometer reading for the tannin strength of the process liquors, their actual tannins are estimated in several tanneries.

Rapid tannage of sole leather.—The pit tanning process, although it produces a satisfactory sole leather, is slow. Even the quickest pit process cannot complete the tannage of light and medium weight buffalo hides in less than  $2\frac{1}{2}$ months. Rapid tanning process is practised in the continent of Europe. According to it, surface delimed pelts for sole leather are given a preliminary tanrage in 12 suspender liquors in pits for 12 days the strengths of which range

from 15° Bk to 70° Bk. The hides are struck through in the suspenders, They are then completely tanned in revolving drums with strong tan liquors made from tanning extracts. The hides are put into the drum in a liquor of 100°Bk. In this the hides are drummed for 48 hours increasing the strength The drum revolves at the rate of 4 revolutions per minute. One to 110°Bk. tannery in India has been using this rapid drum tanning process for several years and has been turning out sole leather of a satisfactory quality. The adoption of the rapid tannage process for manufacturing army sole leather deserves consideration as during war, the large demand for it can be more easily met by the rapid drum tanning process than by the rather slow pit tanning one. Investigations on rapid sole leather tanning processes is being carried out at the Central Leather Research Institute, Madras, and results obtained are Three processes have already been worked out, which very encouraging. complete the tannages from raw hides to finished leather in 3 to 4 weeks.

Finishing of sole leather.—By whatever process, the sole leather is tanned, it has to be finished to make it suitable for use in making military boots. In finishing the thoroughly tanned hides are scoured by hand or machine, then bleached either by treatment with myrobalan liquor or special bleaching extracts, sammed, oiled up, further dried to condition for setting, set out by hand or machine, further dried to some extent so as to retain moisture in the internal layers, brushed on the grain with a little water, rolled on by a sole leather rolling machine with light pressure, completely dried and then rolled off again by a sole leather rolling machine using heavy pressure.

The sole leather thus produced should have a light colour, firm feel, good water and abrasive resistance. Water resistance of army sole leather is specially important. It can be increased by impregnation with rubber and similar materials. Researches on the impregnation processes of sole leather are being carried out at the Central Leather Research Institute.

The leather should have a fibre structure consistent with good quality.

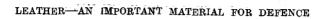
Microscopic control of sole leather manufacture.—Research has shown that a good sole leather should have the following fibre structure as indicated by the microscopic examination of a thin section cut from it by a microtome and by the photomicrograph taken of that section.

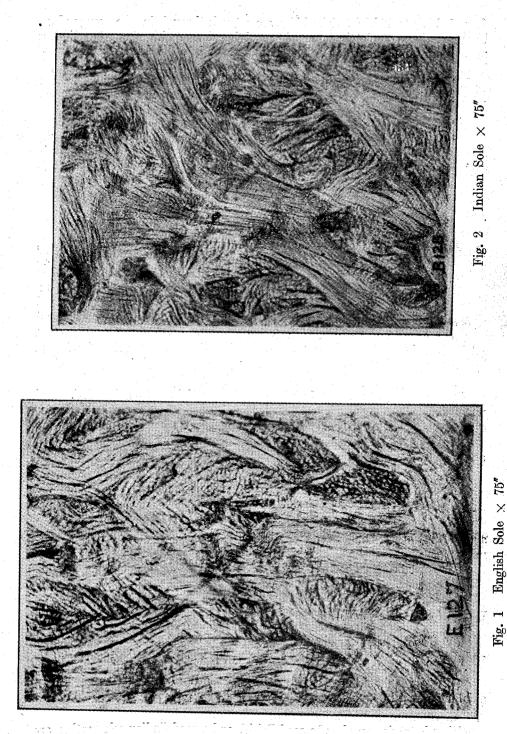
(i) Bold fibre structure with a compact and well-ordered, high angle or vertical weave of full and straight fibres.

(ii) The fibre bundles should be well-opened up into its component fibres and fibrils without any separation of fibres and fibrils.

(iii) Fibres should have clearly defined outline and any fuzziness indicates a falling away in quality.

The photomicrographs of a good British and a good Indian sole leather are shown in pictures (1) and (2).





It will be observed that fibre bundles in (1) are bold, compact, well-defined and vertically woven. The fibre bundles are opened into fibres but the fibres are not separated from one another.

In (2) the fibre bundles are less compact and of medium angle of weave and show more splitting and disclose separate fibrils. The weave is also not so well-ordered as that of (1).

Sample (1) is a better sole leather than sample (2).

This fibre structure depends upon the pre-tanning and tanning processes and the desirable structure can be obtained by suitable adjustment of the pH values of lime liquor and pH, acid and salt contents of tan liquors. The entire process of tanning should be regulated by examination under a microscope at various stages. Leather microscopy, therefore, occupies an important place in modern leather technology.

#### **II.** Harness and Saddlery Leather

Although the modern mechanisation of war has reduced the use of cavalry to a large extent, harness and saddlery are still required by military transport corps. For these, large quantities of harness leather are required. For making heavier types of harness leather, buffalo hides of good quality are used and for harness leather of lighter types, heavy cow hides may be utilized. Harness leather is produced like sole leather exclusively by vegetable tannage. tanned leather, however, is finished in a way different from the finishing of sole leather. After tanning, the harness leather is scoured, well-washed and bleached, if necessary. Then it is treated with grease. This treatment with grease and the operations connected with it are known as currying. Harness leather is, therefore, an example of curried leather. Treatment with grease is necessary to impart to the harness leather the required pliability, water resistance and tensile strength. The greasing may either be done by the hand process or by revolving the leather in a heated drum with molten fatty matters. The former is called hand and the latter drum-stuffing. The fatty matters used in hand greasing are usually a mixture of tallow and fish oil which is known as dubbing. In drum stuffing, harder fatty matters are used such as stearine, paraffin wax etc. along with tallow. After greasing, the hides are well set-out and carefully dried to make a light coloured and pliable leather of the required thickness.

#### **III.** Ammunition upper leather

The upper leather for army boots may be manufactured by vegetable, chrome or chrome-retan process of tanning. The vegetable tanning process is the oldest. Well curried vegetable tanned leather is quite suitable for the purpose and possesses some advantages over chrome leather. The vegetable tanned leather is fuller, less stretchy and when properly curried, is more water resistant than chrome leather. As vegetable tanning fills up the leather to a greater extent than chrome tanning, it is possible to make leather of the required army specification for thickness even from thinner hides by it whereas chrome-tanning will not produce from similar hides a leather of the specified thickness. This aspect deserves consideration in India at present due to the inadequate supply as referred to already of sufficiently heavy hides in the Indian Union. The vegetable tanning of cow hides for army upper leather can be carried out substantially according to the process described for sole leather but using weaker liquors and tanning for a shorter time. While the maximum tanning concentration for sole leather is about 100°Bk, for army upper leather, a liquor strength up to 40° to 50° Bk is sufficient. The duration of tanning need not exceed two months. Excellent materials for making army upper leather are the E. I. tanned kips of Madras. During the first world war of 1914-18, the Army Headquarters prescribed the use of vegetable tanned leather for making army boots and all the army boots manufactured in India during that war for the Indian and Allied Armies were produced from East India tanned kips tanned in Madras and retanned and curried principally at Kanpur and other centres. Large quantities of East India tanned kips of suitable weight were required for supplying the war needs and to tan them, large amounts of the tanning bark avaram (Cassia auriculata) were found necessary. Supply of the bark fell short and its price soared up. The Government of India set up a Tanning Research Institute at Maihar (Central India) to find out suitable substitutes for avaram bark from various forest products. Interesting data were collected from the researches carried out there. During the second world war of 1939–45, the Indian Army Headquarters, most probably on account of difficulties experienced during the first world war in obtaining adequate supplies of vegetable tanning materials, specified the use of full chrome leather for army uppers and most of the ankle boots produced in India during the second world var for the Indian and Allied Armies were made with full chrome upper 'eathers.

Chrome Process of tanning Army upper leather.—Flawless heavy wet-salted slaughtered cow hides are chosen as raw material. They are put through the pretanning processes of soaking, liming, bating and pickling adjusting them so that the desired properties in the final leather may be obtained as these pretanning processes have considerable effect on leather quality.

The pelts prepared by the pretanning processes are then tanned by the single bath chrome tannage in drums. Tanning is done with chrome liquor which may be prepared in various ways. The effective substance in this liquor which actually does the tanning is the basic chromic sulphate. Now-a-days, chrome liquor is prepared in India by reducing a solution of sodium bichromate acidified with such quantity of sulphuric acid as will produce a  $33 \cdot 1/3$  per cent basic chrome sulphate when the acidified bichromate solution is reduced with a reducing agent. The formation of this basic salt may be represented by the following general equation :--

 $Na_2Cr_2O_7 + 3H_2SO_4 + X \ge Na_2SO_4 + 2Cr(OH)SO_4 + XO_3 + 2H_2O$ 

In the equation X is the reducing agent which may be either inorganic or organic.

 $Cr(OH)SO_4$  is the 33·1/3 per cent basic salt as one-third of the acid radical  $SO_4$  of the normal chromic sulphate  $Cr_2(SO_4)_3$  has been neutralized. Chief inorganic reducing agents employed are hypo and sulphur di-oxide and many organic reducing agents like sugar, molasses, starch, saw-dust, spent tan bark, leather shavings etc. are used.

Except in the case of sulphur-di-oxide, the chemical reaction with all reducing agents takes place according to the equation given above. When sulphur di-oxide is used for reduction, no sulphuric acid need be added to the bichromate solution. The reduction takes place without acid according to the following equation.

 $\operatorname{Na_2Cr_2O_7} + 3\operatorname{SO_2} + \operatorname{H_2O} \ge 2\operatorname{Cr}(\operatorname{OH})\operatorname{SO_4} + \operatorname{Na_2SO_4}.$ 

A chrome liquor which contains only basic chromic salt and some sodium sulphate is obtained from sulphur-di-oxide reduction. When hypo is used, the reaction can be more or less accurately represented by the following equation :

 $3Na_2 Cr_2O_7 + 4 Na_2 S_2O_3 + 8H_2O \ge 6 Cr (OH) SO_4 + 6Na_2 SO_4 + Na_2 S_4O_6 + 5H_2O.$ 

But when organic substances like sugar, molasses etc. are used for reduction. a humber of organic acids are produced in the liquor which considerably affect the tanning action of the basic chromic sulphate and the leather quality. The effects of these organic compounds on the quality of the leather are on the whole beneficial but as their production in the liquor cannot be controlled and kept uniform, different batches of liquor produce leather of different quality and thus interfere with the uniformity of the leather. The compounds which are known to be produced in the liquor when organic substances are used for reduction are usually formic, acetic and oxalic acids and formaldehyde. These acids are known to be masking agents. Many other masking agents which are either organic acids or their salts have now been discovered. The masking agents when present in the chrome liquor resist the precipitation of chrome hydroxide from it on the addition of alkali. This is the reason why they are called masking salts as they mask the chrome salt by preventing its precipitation as hydroxide on the addition of an alkali. This resistance to precipitation of chromic hydroxide makes it possible to make the chrome liquor highly basic without precipitation. The highly basic salts induce more chrome fixation in the leather and conduce to its fullness. It may be noted here that the tanning action of the chrome salt is due to its basicity. The higher the basicity the more powerful is the chrome salt for tanning. By basicity is meant the degree of the neutralization of the acid radical of the normal salt in the preparation of the basic salt. Thus in  $Cr(OH) SO_4$  or  $Cr_2 (OH)_2 (SO_4)_2$  one third of the acid radical of the normal salt,  $Cr_2(SO_4)_3$  has been neutralized and replaced by hydroxyl groups. In  $\operatorname{Cr}_4(\operatorname{OH})_6$  (SO<sub>4</sub>)<sub>3</sub>, half of the acid radicals of the normal salt  $Cr_2(SO_4)_8$  or  $Cr_4(SO_4)_6$  has been neutralized and replaced by hydroxyl groups. Basic chrome sulphates within the range of basicities 28.5 per cent to 38.9 per cent have good tanning properties. Usually, if the basic sulphate is more than 58.3 per cent basic, it is precipitated. But this precipitation can be prevented by adding a masking agent to the liquor.

The composition of chrome salts is not so simple as to be represented by formulæ  $CrCl_3$  or  $Cr_2(SO_4)_3$ . The metal chromium forms complexes on account of its having 6 co-ordinate valencies in addition to its 3 primary or electrovalencies. By the 6 co-ordinate valencies, chromium in its salts may hold upto 6 molecules of water or anions forming complexes which may be cationic having 3 to 1 positive electric charges, neutral or anionic having 3 to 1 negative electric charges. Chromium forms 7 different types of complex salts, *e.g.* 

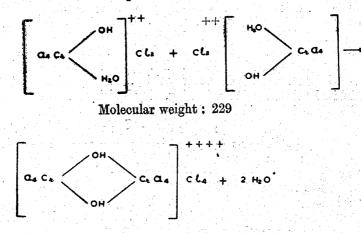
When a  $33 \cdot 1/3$  per cent basic chrome sulphate liquor is prepared for tan ning, the basic chromic sulphate may be present in the form of the following complexes

[a<sub>6</sub> Cr<sub>2</sub> (OH)<sub>2</sub> (SO<sub>4</sub>)<sub>2</sub>.]

or any other complexes of the seven types mentioned above according to the conditions of the reduction. The component of the salts within the large 'brackets is called complex. The masking organic acids formed in the chrome liquor by reduction with organic substances or purposely added to the liquor may enter into the chrome complex forcing water molecules out of it producing complexes in which organic anions are bound to the central chromium atom. Such chrome organic complex salts are milder in tanning action than entirely unmasked chrome sulphate.

It will thus be realized that the basic chromic salts in the chrome liquor may be several having different complex structures each exerting its own influence on the tannage and the quality of the final leather.

Another reaction has been recognised of basic chorme salts in chrome liquor which is called olation. This is usually represented as follows taking basic chromic chloride as example.



## Molecular Weight: 422

Thus 2 molecules of basic chromium chloride have combined or olated to form a bigger molecule of olated basic salt. This olation may go on involving more than 2 molecules and forming bigger molecules of chrome salt. The increase in the size of the molecules of basic chrome salts is not limited by their olation because they can grow to a still larger size by polymerisation. There is a difference between olation and polymerisation. In the former water is eliminated but in the latter, there is no water elimination but the molecules simply join up forming bigger molecules. The increase in the size of the molecules makes the basic chrome salts more and more colloidal and fixable to skin fibres.

Thus masking, olation and polymerisation go on in chrome liquors influending their tanning action and the properties of tanned leather markedly. In

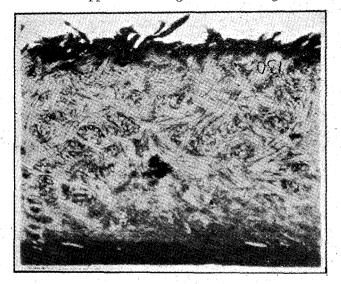
118

making army upper leather by chrome tanning, all these influences of chrome liquor are to be borne in mind and the making of the liquor and the tanning process are to be kept as far as possible uniform by chemical control to ensure uniformity of the final leather. If the properties of the final leather do not happen to be satisfactory by the use of a particular liquor or a tanning process, both may be changed under chemical control until a satisfactory leather is obtained. Usually the quantity of chrome liquor containing chromium equivalent to 5% bichromate on the pelt weight is used for full chrome tanning.

Chrome tanning makes the leather stand the temperature of boiling water for some time without shrinkage or hardening. This test is known as the boiling test which must be satisfied to ensure satisfactory completion of the tannage.

The tanned leather is then taken out of the tanning drum, horsed up to let the adhering liquor drip off, shaved to a thickness which will produce a finished leather of 2 mm. to 2.5 mm. in substance, then washed, neutralized, dyed black, and fat-liquored. A great deal of care is necessary in fat-liquoring. The composition of the fat liquor and the quantity of the fat-liquor used should be such as will not make the final leather too hard or too soft and raggy. Commercial fat-liquors are usually mixtures of sulphonated fish oil and mineral oil which readily emulsify with water. Fat liquors may also be made in the tannery from sulphonated and neutral oils. The black-dyed and fat liquored leather is set out, dried, wetted back, softened by mechanical staking, stretched on board, dried in the stretched condition, then seasoned, glazed and printed into shark grain by a leather press.

It is advisable to control chrome tanning process both chemically and microscopically to maintain uniformity of leather quality. A photomicrograph of a chrome tanned shoe upper leather is given below in figure 3.



Full chrome army upper leather Fig. 3

#### LEATHER-AN IMPORTANT MATERIAL FOR DEFENCE

Chrome retan process of tanning army upper leathers.-This process was developed in America after the first world war. It mainly consists in tanning cow-hides suitable for ammunition upper leather, first with one bath chrome tanning process and subsequently retaining it with vegetable tanning extracts. The pretanning processes are carried out as in the case of chrome-tanned army uppers. The chrome tanning is also done in the same way using basic chrome liquor equivalent to 5 per cent bichromate on the pelt weight. After chrome tanning, the stock is shaved to a substance which will give the thickness required for the final army upper leather and the shaved leather is then neutralized. For neutralization, the usual alkalis are not used but a special buffer mixture consisting of calcium formate and neutral syntan. This adjusts the pH of the leather to about 3.5. The leather is then retained with vegetable tanning extracts in the drum. In America, a blend of quebracho, mimosa and chestnut extracts is used. Sometimes, a syntan like Orotan TV is mixed with vegetable tanning extracts. 50 per cent of the mixed liquid extracts of 35 per cent tanning content is employed on the shaved leather weight. The leather is retanned in the drum for about 3 hours adding the tanning extract in three instalments at intervals of 45 minutes. The leather is then taken out, struck out and sammed for conditioning it for stuffing. The stuffing is carried out in a heated stuffing drum at about 190° to 200°F using a stuffing mixture composed of tallow, paraffin, Moellon Degras and wool grease mixed in suitable proportions. The stuffing lasts about half an hour during which time the grease is absorbed. The stock is then taken out of the drum, cooled, set out and paste-dried. The grain is corrected by snuffing. The leather is next coated on the grain with a solution of dye containing fillers like synthetic rubber etc. Then the leather is put through the burnishing machine which is like a buffing machine, the bolster of which is fitted with fine emery paper. This process of burnishing does not take off anything from the grain but simply presses the grain and makes it smooth and shining. The leather is finally shaved on the flesh side to get the correct substance and brushed on the grain. The grain is coated with pigment finish, two coats being applied by a machine. The leather is dried and a top coat of a casein and wax finish is sprayed on the grain. The leather is dried, rolled by a rolling machine and finally plated at a temperature of about 110° F. This completes the manufacture.

The most important effect of the chrome retan process is a marked increase of the thickness of the leather thus making it possible to make army leather of the required specification of thickness even from comparatively thin hides. As the supply of heavy cow-hides in the Indian Union, as already mentioned, is now inadequate, the introduction of the chrome retan process is very desirable to keep up the supply of ammunition boot upper leather to the required extent.

The process has not yet been introduced in the Indian tanning industry as its working details which may suit the available Indian hides and climatic conditions have to be worked out. This work has been started at the Central Leather Research Institute and a good deal of data have been collected. A photomicrograph of chrome retan leather produced at the Central Leather Research Institute, Madras is given in picture 4.

#### DEFENCE SCIENCE JOURNAL



# Chrome retan $\times$ 40

# Fig. 4

(The photomicrographs appearing in this paper were taken at the Central Leather Research Institute, Madras.)