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MR. W. F. REID IN THE CHAIR.

THE PRINCIPLES OF TANNING.

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Innumerable new methods have been proposed and patents have been taken out during the last century for the acceleration and improvement in tanning leather, mostly by those but remotely connected with the trade. In spite of this the general outline in process of tanning sole leather is much the same to-day as carried out a thousand years ago. In short the changes which have taken place between the tanning of sole leather even 1000 years ago and to-day consist not so much in principle as in a more intelligent method of carrying out the process.

The raw material for the British tanner is the hide of oxen and cows, and is drawn from practically all parts of the globe. From the Argentine, Uruguay, China, and Africa come hides which have been dried in the sun; from America, from all parts of Europe and the Colonies, come hides in what is known as the salted condition—the hides are piled, a sprinkling of salt between each, and gradually the salt draws out the water, becomes dissolved, and diffuses into the interior. After lying in pile for some time, the excess water is thrown off, and the hides are re-salted; in this condition they frequently contain as much as 30 per cent. of salt on the original weight of the hide. From the home market the hides are usually obtained "green" or "fresh." The first process, therefore, is the soaking and cleansing to soften the fibres, remove extraneous matters, salt, blood, dirt, etc., and to bring the hide back to its natural state. In bygone days this was done by suspending the hides in a running stream by the tanyard, but now the common custom is to soak the hides in pits containing water. The hides are usually given a change of one or two waters; salted hides receive a longer treatment and several changes of water until moderately free from salt; dried hides are, after a preliminary soaking, sometimes "stocked" or "milled," in a large machine which pummels the hide and gradually breaks up the fibres, after which the hides are returned to the water. Revolving drums and other similar appliances are also used. The softening of flint dried hides is by no means an easy operation and considerable care must be exercised in bringing the hide back to its natural condition without loss of pelt substance through putrefaction, the germs of which are present in the hide. With some hides it is difficult to soften in less than 6 to 8 days, and to aid the softening process sulphide of sodium, or caustic soda is often added to the soak water. These materials have a swelling effect which accelerates the penetration of the water, and the subsequent softening of the fibres, but at the same time they slightly increase the solubility of the hide. It has been shown that the higher the temperature at which hides are dried for preservation in foreign countries, the more difficult becomes the subsequent absorption of water, and consequent softening in the tan yard. It is very essential that hides should not only be thoroughly softened but they should be in a clean state before passing to the next process. The English tanner has a great fear of losing pelt substance by using too much water at this stage; but it is undoubtedly wrong to leave hides in a foul dirty water, and the more clean water they have the less is the loss of pelt substance. I was very much struck some three years ago when visiting the large tanneries in the United States, to note the efficient way in which their process of soaking was carried out, no hides being allowed to pass on to the next process without at least three changes of water, to which sometimes a half hour's running in a revolving drum was added. The pelt looked much healthier, there was no loss of pelt substance, and the hide gave a better leather, owing to the fibres being more open, and better prepared for the subsequent process.

The hides are placed in a saturated solution of lime containing lime in excess for the purpose of loosening the hair and swelling the hide. This process lasts from 7 to 10 days. The hides are laid flat one upon another in a pit containing the necessary amount of water to which slaked lime is added in the proportion of 8 lbs. per hide. Formerly it was believed that the lime swelled the fibres of the hide, dissolving the hair bulb or root and loosening the epidermis, thus rendering the removal of the hair easy; but the liming process is now known to be both chemical and physical, the loosening of the hair being largely due to the action of enzymes, and the products of bacteriological action. Hides cannot be unhaird by sterile lime, so that the process of Payne and Pullman, by which the hides were first soaked in caustic soda and afterwards in calcium chloride, so as to form lime within the fibres, was unworkable unless preceded by the soaking of the hides in a foul soak to obtain the necessary bacteriological action. By the action of lime on hides other products are formed, salts of amino acids and compound amines which play a vital part in the loosening of the hair and in their turn act upon the hide and influence the quality of the resultant pelt. The longer a lime pit is used, the more alkaline it becomes, the quicker the loosening of the hair, the greater the loss of good hide substance by solution, and the more flaccid the resulting product. Hides in the limes are frequently hauled, the lime pit thoroughly plunged up in order to keep it up to strength of saturation, the hides returned, and the process repeated until they are ready for unhairing.

The scientific control of the liming process deserves far more attention than it has hitherto obtained, for in this process, to use an old tanner's expression—"the leather is made or marred." At a well-known tannery some months ago I found that from one of the pits over 24 lb. of dissolved hide substance was going down the drain each time a "limo" was run off. Assuming that even only 50 per cent. of this loss could have been avoided, this would be equal to 12 lb. of dry hide substance (no unimportant matter with wet hides at 1½d. per lb.) which in the ordinary course of events would have produced 24 lb. of leather. If leather trades' chemists had given as much attention, time and thought, to this part of the process as they have to the vexed question of the method of analysis, it would have been more beneficial to our industry. Sodium and calcium sulphides are now becoming more largely used in conjunction with lime. These have an accelerating action on the process and are claimed to improve the results both in weight and firmness of texture. They have however, a destructive action on the hair, reduce the value of the flesh and require considerably more care and control, otherwise more serious losses may result than with lime alone.

After the hides have been properly limed the hair is removed; either by hand or by machines. The most satisfactory machines consist of a revolving spiral roller which travels over the hides as they rest upon a rubber bed, which yields to the pressure as it is increased and thus avoids damage. The reverse side of the hide is then freed from superfluous flesh, consisting of a thin network of coarse fibres heavily loaded with fat. This is removed on a similar shaped beam, the knife in this case being kept sharp. This by-product, together with the hide trimmings, including the nose, ears, shanks, tail, etc., form the raw material for the manufacture of glue and gelatine. The hide in this condition now becomes known as pelt, and on the pelt weight the tanner bases his calculations as to value and the probable yield in leather; he is also able to judge its quality, the fineness of the grain, etc. It is now customary to divide up the hide into "butt" or "back," shoulder and belly, a process known as "rounding." The back is the thickest and most valuable part, used altogether for the heavy soles of boots, belting and harness; the shoulder, being somewhat thinner, is used for light boots, and ladies' shoes; while the belly is of a porous nature and is used chiefly for stiffeners, heels, insoles, and sometimes even for the outer soles of the cheaper class of slippers and boots. This rounding process requires great skill and

judgment to determine what size to cut the different parts, which is regulated by the growth and character of the hide. As a general rule hides should yield 50 per cent. of their pelt weight in butt, 24 per cent. of shoulder and head and 26 per cent. of belly. Some well-grown hides from the best Scotch and Hereford cattle yield 51 to 52 per cent. of butt and from best Italian hides a higher percentage is sometimes obtained. The "pelt" or rounding table weights are important, for if the liming process has been regular the tanner can gauge at this stage whether his hides have been honestly weighed and well bought, which is difficult to judge in the salted or dry condition, and whether the grain is of good, smooth texture. From these weights the tanner calculates that he should obtain 72 per cent. of finished leather from the weight of butt pelt, 52 per cent. from that of the bellies and 54 per cent. from that of the shoulder, giving a total weight in leather from the green hide of some 56 to 60 per cent. These percentages vary with different classes of tannage.

The weighed and trimmed pelt is in a swollen condition; for the lime has not only swelled the hide and opened the fibres, but also made it firm and rubbery. As a general rule the pelt contains from $2\frac{1}{2}$ to 3 per cent. of lime. Before entering the tan yard proper a large proportion of the bulk of this lime must be removed and the swelling caused by the alkalinity of the lime must be reduced, otherwise a harsh, brittle, brown, blotchy coloured leather would result. Thirty years ago, or even less, tanners used to rely upon the acid early tan yard liquors to do the necessary deliming, but investigation has shown that if the liquors in the early process of tanning are too weak and contain an excess of acid, not only is the lime removed from the pelt, but pelt substance is dissolved in the form of soluble leather. It is now known to be not only safer and better, but also cheaper, to delime the pelt in a weak solution of boracic acid or other of the organic acids, lactic or formic being in most common use. The pelts are suspended on poles by means of strings in a pit containing water to which the requisite amount of acid has been added. They are handled frequently to insure regularity of action or kept in continual movement by mechanical means. The deliming is for sole leather never quite complete, a trace of lime is always left in the interior of the hide, and it is usually sufficient if the hides, on leaving the deliming pit, show no pink colour to phenolphthalein when a few drops are sprinkled on the surface. After a rinse through soft water, the butts, bellies and shoulders are ready for the tan yard.

Formerly the hides for sole leather were tanned whole without rounding, and, after colouring from six to twelve weeks in weak sour liquors made from oak bark and water, were frequently handled and moved forward from time to time into liquors of gradually increasing strength. After this colouring process, the bottom of a deep pit or vat was covered with a layer of ground oak bark, and the first hide was spread out on it, grain upwards, the head and flanks turned in. This in its turn was covered with a layer of bark, another hide on top and a further layer of bark and so on, hide and bark alternating until the pit was full. Water was then pumped in to saturate the bark, and the hides were left for about two months; after which the liquor was pumped off and used to supply the colouring pits. The hides were then raised, freed from the adhering bark, and then laid in a fresh pit for a longer period with more bark and this process repeated four or five times, each time increasing the quantity of bark between each hide and the length of time of laying away, and as the hides got older, bark liquor was pumped on the dry bark instead of water and frequently a little ground valonea was mixed with the oak bark in the last layer. The hides, after from 18 months to two years, being considered tanned, were removed, rinsed through liquor or brushed to remove adhering bark, allowed to drip for a couple of days, oiled on the grain, hung up in the lofts to dry and when nearly dry laid on a wooden, rounded beam or a hollowed stone bed and hammered to flatten out the leather and render it firm. Finally they were completely dried and were ready for the bootmaker who in those days bought the hide in its whole state. The strongest liquor in the tan yard probably never exceeded 1.030 specific gravity or 30° Bk.

containing perhaps at most 2 per cent. to 3 per cent. of tan. How different are present conditions, where the strongest liquor in a modern tan yard often contains from 14 to 16 per cent. of tannic acid, and has a density of from 130 to 150° Bk! Then an oxhide of 80 lb. weight yielded about 30 lb. of finished leather; to-day from a similar hide a yield of close upon 50 lb. weight is obtained, which even the severest critics must still call honestly tanned leather.

With the introduction of new materials, and the gradual substitution of machinery for hand labour, the old process above described has been gradually altered.

Among the newer materials which have come into use during the past century, valonea, the acorn cup of the Turkish oak, must be the first mentioned. Although introduced into this country at an earlier period, it is only in the early forties that it began to be used in other than experimental lots to blend with oak bark; its more extended use was chiefly due to the enterprise of some West of England tanners, who having allowed a shipper to store a large quantity of this material in their bark barns until it could be sold, had permission to use what they required in their process. Using a little at a time in more or less homeopathic doses they found that not only did its use do no harm to their leather, but it actually improved it and made it firmer and more solid. With further experience came more confidence so that a larger proportion of this material was blended with the oak bark, and still the leather appeared to improve, until the whole of the shipment of over 200 tons were used and they became regular buyers. Other tanners in the district followed suit, until in the seventies, Bristol or West of England leather, chiefly tanned with valonea, had achieved a reputation for solid hard wear, especially suitable for heavy walking boots and for repairs. It was not long before tanners all over England commenced to blend with this material.

Myrobalans (often miscalled myrabolams), the fruit of the "*Terminalia chebula*," one of the Indian forest trees, which had been used by the native tanners of India for many years, soon found favour when introduced because of its power of rapid penetration, the light colour which it imparted to the leather, and its somewhat rapid souring properties.

"Terra Japonica," or gambier, was early used for the purpose of modifying the sharpness or astringency of valonea, and in West of England tannage played an important role in the early tanning stages; its special characteristic was its swelling powers, thus keeping the texture of the hides open and nullifying the contracting action of the stronger tans.

Acacia bark (*mimosa*) from Australia and South Africa, dividivi from India, algarabilla from South America, all of them containing over three times as much tannin as does oak bark, had a considerable influence upon the changes that have taken place. Reference has been made above to the heavy layer of bark between each hide; this was afterwards burnt or thrown away half spent, but with stronger and better tanning materials in use, it became general to put this dusting material into large pits, called leaches, leeks and spenders, in which the tannin of the bark was extracted by means of water. These leaching pits were arranged in series and the liquor pumped from one pit to the other, until by passing through successive pits of partly spent material it gained sufficient strength for use in saturating the bark between the hides, producing liquors of much greater tanning strength.

The introduction of Tanning Extract in the early seventies, however, had more effect on the method of tanning than anything else. It was first introduced from France made from chestnut wood, and later from Hungary produced from oak wood. In the manufacture of this material, the wood is reduced to fine shreds by powerful machinery and the rasped wood is afterwards extracted in large wooden vats by the aid of hot water. The resulting liquor is decolorised by means of blood which is added to the cooled liquor; the temperature is then raised and the coagulated albumen separating out carries with it the darkened colouring matter of the bark together with some of the

tan. The clarified liquor is then concentrated in large copper vacuum pans at a comparatively low temperature, and shipped to this country in concentrated form in casks containing upwards of 30 per cent. of soluble tannin ready for immediate use, for blending in with the tanners' leach liquors.

The effect of these stronger liquors was that of hide which had hitherto been tanned in one piece, the thin part became too much tanned before the thick part had had sufficient tan, with the result that "rounding" became more general. This brought about a great change; and square pits sunk in the ground became general. These were half filled with liquor of the required strength, a butt thrown in and before it had time to sink in the liquor was sprinkled with a layer of bark, a second butt quickly following to be likewise sprinkled, and so on until the pit was full. By this means a greater volume of liquor was used than bark, and as the butts became older and more tanned they passed to stronger liquors and were dusted more heavily with valonea, myrobalans and mimosa bark, instead of oak. With the use of liquors of increasing strengths came an increased yield of leather as the fibres became saturated with stronger tan. Machines began to supersede hand labour, and machines for rolling the leather instead of hammering came into general use, followed by others for scouring, stretching, and polishing the leather. Boot manufacturers began to demand an article of better finish and appearance, smooth grained and flat. For the modern boot manufacturer, the leather must be prepared flat and smooth so that it will pass with ease through his sole cutting machinery and it must be of such a quality that it can be stitched direct by machine without soaking and without the aid of the cobblers' awl.

To return now to the delimed properly prepared pelt. The butts enter the suspender pits. These are a series of deep vats containing old weak liquor graduated in strength. In these the butts are hung on poles, being frequently handled to insure regular colouring and to accelerate the tannage, moved forward to stronger liquors once or twice daily, while in some yards it is customary to have these pits connected by a pipe from the top of the strongest pit to the bottom of the vat next lower in strength; by this means the liquor may be caused gradually to flow from the strongest to the weakest to replace the tan absorbed by the "hungry" hide. Mechanical means are also employed to rock the goods. In this process, which lasts from one to two weeks, the butts absorb tannin with great rapidity, some 50 per cent. to 60 per cent. of the total tannage taking place at this stage. The butts are then taken off the poles, and laid flat in pits containing liquor, which are called "handler pits," as the butts are here handled daily from one pit to another, into a liquor of greater strength; they remain in these for about four weeks. This early stage is almost the most important in the tanning process proper, as it is here that the colour, substance, and to a large degree also, the quality of the leather is made. The liquors in the handlers and suspenders must also not only be graduated so as to contain the requisite amount of tan to keep the pelt constantly feeding, but there must be the necessary amount of organic or mineral acid to swell and keep the pelt open, and so counteract the natural astringency of the tannic acid. If the pelt is not kept open at this stage and becomes contracted, it can never be recovered, and does not take up the normal amount of tannin, producing a thin, poor leather. The blending of the materials is also of great importance; at this stage considerable amounts of myrobalans, gambier and other light coloured plumping materials are used. When the butts leave the handler, they are usually "struck through," i.e., penetrated to the centre, and about 80 per cent. of the total tannage has been completed in the first six to seven weeks.

The butts are then taken to a series of pits known as "dusters" or "layers." These pits contain fresh, strong and more astringent liquors. The butts are laid flat in these pits and between each butt as it is thrown in is sprinkled a layer of tanning material, some

3 to 4 cwt. of the dry ground material being sprinkled in between say 100 butts, which generally forms a pack. The butts are allowed to lie in the first liquor for about a week, again lifted and placed in a still stronger liquor for a second week, once more lifted and the process repeated, each time increasing the strength of the liquor and increasing the time in the layer, with a corresponding increase of tanning material dusted between each butt. In the early dusters or layers, myrobalans and bark are used, but as the goods get older, ground valonea is substituted, until in the last layer the goods are left from 4 to 5 weeks. Thus they receive a total tannage of about six months, which is an average time for modern better class sole leather and strikes a happy medium between the 12 to 14 months still taken by the oak bark tanner and the three months or less required when a large proportion of tanning extract is used and no oak bark. In these layers the actual tanning which takes place is comparatively small when one takes the long time into consideration, but the goods gain greatly in firmness and solidity; in these pits the leather comes directly in contact with the fresh tanning material and from the fresh tanning liquors is deposited bloom or ellagic acid which is an almost insoluble product produced by the splitting up of the pyrogallol tannin; from the catechol tans, difficultly soluble anhydrides, which are of a gummy and more or less sticky nature, also deposit. This deposition occurs on and in the fibres and in the interstices of the leather and it is to the deposition of these difficultly soluble products that the resulting sole leather to a large extent owes its water resisting characteristics, and its firm and solid nature. Leather which has been largely tanned by suspension with continuous handling or even drumming never possesses this water-resisting, hard-wearing, characteristic, as no time is given in these quick tanning processes for the deposition of these more or less insoluble matters, nor for the subsequent complicated changes which normally occur in the interior of the butt.

The material which has been used for strewing between the butts in the layers is put on to the leaches to be thoroughly spent and plays a very important part in the production of the liquors. Many tanners, however, use this half-spent material to produce the liquors necessary for tanning bellies and shoulders, retaining the fresh material for making butt liquors, the butts being the most important part of the hide, having a value almost double that of the shoulders and bellies. The tannage of shoulders and bellies follow on in a similar manner to the butts, the only difference being that as this pelt is much thinner, and in the case of the bellies more porous and open, the time for tanning the shoulders seldom exceeds three to four months, and for bellies nine to twelve weeks. The strengths of the liquors are nearly as high as those given to the butts, but generally a blend of somewhat cheaper material is used; in other words, less valonea and a higher proportion of myrobalans and chestnut extract.

Among the points that specially require attention and chemical control is the ratio of tans to non-tans in the early liquors, i.e., the ratio in which the tannic acid exists in proportion to the natural acids formed partly by hydrolysis of tannins and partly by fermentation of the glucoses ever present in all tanning materials. If the early liquors are allowed to become too weak, stale or putrid, the pelt, instead of feeding and plumping, begins to fall, the grain becomes loose, and a pippy, flabby leather is produced; but if the liquor is allowed to become too astringent with tannic acid with an insufficiency of the natural organic acids (produced by ferments), the leather will become harsh and brittle, and when finished is liable to be hard, to crack on the grain, and to be generally of a bad colour. The speed of tannage should be controlled regularly by taking small samples of the half-tanned leather as it leaves the head suspender, and again on leaving the top handler, determining the nitrogen in it by Kjeldahl's method. In this way the progress of the tanning may be accurately checked. New blends of material can thus be tried, additions of special materials at this stage can be accurately tested without waiting six or seven months before the result can be ascertained.

on the finished goods. The nature of the layer liquors, which are subsequently used to make the handler and suspender liquors, must be examined, as also the leaching and extracting of the material. Whereas samples of the so-called spent tanning material from 22 of the larger tanneries in Great Britain, taken some 17 years ago, jointly with Professor Procter of Leeds, showed that over one-third of the available tannin in the material was being wasted and thrown away, recent analyses show that this waste has been reduced in many cases to below 5 per cent. It has been proved that the tannin contained in most tanning materials is not all readily soluble in cold water, and that each material appears to possess a special leaching temperature, at which the best yield of tannin is obtained. In most of the tanning materials this temperature is at least 80° C.; hence most tanners use hot water for the extraction of their tanning material.

The question of the water is of vital importance to a sole leather tanner. In a large sole leather tannery 5000 gallons of water in 24 hours is not by any means excessive. The average "hardness" of the water in the chief tanning districts of England is about 20 parts per hundred thousand. This means on 5000 gallons of water, that each day the tanner is adding 10 lb. of lime in the form of chalk to his liquors, which unites with tannin and forms useless tannate of lime, which is lost in the leaches and in the liquors. By forming insoluble products in the fibre of the tanning material it retards the extraction and diffusion of the tannic acid through the cell walls in which the tannin is contained; it also darkens the colour of the liquors and has a material effect upon the resulting leather, as it is well known that salts of tannic acid become oxidised and rapidly form dark compounds.

The drying and finishing of sole leather, as I have already indicated, was formerly simply a process of drying and hammering; to-day the shedwork of sole leather is almost a separate art, and there has grown up a body of journeymen finishers specially skilled in this process, which requires from three to six weeks, depending upon the period of the year. The butts are taken from the last layer, and after lying in pile for two to three days to drip (during this dripping process the strong tan tends to solidify, and the butts become firmer and more solid), they are scoured on the grain side by hand or machine with stone blades and brushes. The object of this scouring is to remove from this grain surface the insoluble "bloom," small particles of solid fibre, and other products which have settled on and in the grain. This process also removes a considerable quantity of the uncombined tan and presses out the strong tan liquor from the interior of the leather. It also softens and cleans the grain and renders it more supple. Up to a few years ago, the goods after scouring were simply rinsed through liquor, oiled and removed to the drying sheds, but to-day, in order to replace the weight that has been lost by scouring and if possible to add further weight, the butts are treated by a retanning process in pits containing a strong solution of some bright coloured tanning agent. For this purpose a comparatively new extract made from the wood of the quebracho tree, which grows in large quantities in the Argentine Republic, has been introduced. The wood of this tree contains over 20 per cent. of a red, very difficultly soluble tanning material. At first this material was little used, owing to the fact that it could not be made up into strong liquors. Lepetit, however, found some eight years ago that, by treating this material under pressure with sodium bisulphite, not only was it rendered easily soluble, but that the sulphite treatment bleached the objectionable red colouring matters and produced an extract which gave to the leather a warm yellow colour. This process also increased the penetrating powers of the tan, and has almost revolutionised the older methods of shedwork. This material is, therefore, largely used in the vatting of butts after scouring. The liquor in the vats is made up to great strength and then heated to a temperature of from 60° to 65° C. The butts are entered (sometimes suspended on poles, in other yards laid flat), and handled frequently; the process is continued for three to four days. This vatting or retanning not only replaces the tan which has been scoured out, but at the same time bleaches the

leather to a regular even colour, transforming the natural brown of the ordinary tannage to yellow fawn. The butts, on removal from these hot pits, are lightly rinsed through a weak sumac liquor to remove the extract from the surface, are allowed to drip for 48 hours and then go to the drying sheds. Here they are carefully wiped over on the grain with a damp cloth, and then well oiled with cod oil. The oiling process is extremely important. The oil used should be suitable; it should possess the necessary drying properties, it should be pure, and should not have too high an acid value. The object of the oiling is to soften the grain, and at the same time to prevent the leather drying through the grain side, the aim being as far as possible to make the leather dry from the flesh side so that the uncombined tan liquor be not drawn out upon the surface where it would become oxidised, darken, and make the leather "cracky." The leather is then hung up in dark sheds, and a cool draught of air allowed to pass through. The slower the drying at this stage the better is the product. If it is dried too rapidly the leather is dark, blotchy, brittle on the grain, and practically unsaleable. When the butts get to a rubbery condition, i.e., if the grain of the leather becomes slightly slimy so that one could write one's name with the finger on it, they are laid down in pile on one another to come to "proper condition." At this stage they are put through another machine similar to the scouring machine, but having steel or brass blades instead of stone, whereby the leather is stretched and the grain made beautifully smooth and level. The butts are again re-oiled, this time slightly, and further dried. In this condition they will stand a little more air until they begin to show signs of drying round the thinner parts, they are again laid in pile to come to "condition," and are rolled under a heavy roller to make them firm and solid; if rolled out of "condition" they "dry dark"; after the first rolling, known as "rolling on," the goods are redried. When they have taken their natural colour but are still damp in the interior, the butts are usually split down the centre into two parts, which are then known as bends. They are now re-rolled, the second rolling being called "rolling off." The bends are now taken to a heated drying room, and dried at a temperature of from 85° to 100° F. The leather thereby becomes very firm, and when perfectly dry it is brushed and polished on the grain and is ready for the warehouse, where it is sorted according to weight, colour, and quality.

This shedwork has been described in some detail, because this process in recent years has become one of the most important in connection with the manufacture of sole leather; needless to say, the time and trouble expended has also increased the manufacturing costs. Why should leather need take on an even yellow colour without irregularities, highly polished and smooth? The boot manufacturer cuts it up into soles and soaks them in water which is seldom clean. The damp sole is then stitched on to the boot, and as it passes through the various processes becomes stained with iron and grease; when firmly stitched on the boot and practically finished, it is put over an emery wheel, and the whole of the beautiful polish, colour, and finish, on which the tanner has spent so much time and money, is ground off. The boot manufacturer then paints the sole with a yellow or black varnish stain, which completely hides the colour and character of the leather, and finally polishes it. Even were it not for this custom of staining the leather, why should it be necessary to take all the care and trouble to produce leather of an even colour and regular shade only afterwards to be dirtied in the boot factory? And even if that were not the case, what difference does it make to the wearer of boots on a muddy day whether the colour of the soles be brown, black or green? This absurdity would not be so serious, were it not for the fact that, as is generally acknowledged by the trade, this vatting and bleaching seriously reduces the wearing properties and the water resisting character of the leather. The process of bleaching in hot liquors containing bisulphite of soda does to the insoluble products in the leather which have been deposited in the layers exactly what Lepetit found it did to the difficultly soluble quebracho tans; it renders soluble and removes from the leather those products which are so

valuable for the production of a sole leather which would not only wear well but would also resist water. This is surely a case of science misapplied, and this fad or fashion which demands that sole leather shall be of a light yellow colour is, in my opinion, having disastrous effects. The bleaching of sole leather is one of the most unnecessary processes that has ever been introduced, and must sooner or later destroy the reputation which British sole leather has long enjoyed all over the world, as a firm, hard wearing, water resisting material, and is certainly contrary to all the accepted principles of sole leather tanning.

The chemistry of the hide is not fully understood and the exact composition of many of the tannins is not yet established. Finally the newer science of colloidal chemistry urgently demands consideration and application.

DISCUSSION.

Mr. LUTWYCHE said as a Warden of the Leathersellers' Company in 1905, and, with the support of Sir John Pound, then the Master of the Company, Sir William Perkin, who was then a member of the Court, and others, he induced the Company to interest itself in technical education in connection with the leather trades. After doing useful work at the Herold's Institution, the Leathersellers' Company founded the magnificently equipped and well directed technical college of the Leathersellers' Company in Bermondsey.

Professor H. R. PROCTER said he wished to emphasize the statement as to the great waste in the cost of production of the leather and the great injury done to the leather by the bleaching process. The substances that gave firmness and waterproofness to the leather were soluble in the bisulphite solutions used and probably were actually dissolved in combination with the base of the bisulphite. In any case they knew this solvent action took place. Occasionally this sort of thing happened to a chemist in an analysis; they used generally a Berkefeld candle for filtering the tannin extract solution. These cost money, and they could not afford to use a new candle every time, so they washed them out; but if they had been using a candle for one of these extracts containing difficultly soluble matters and washed it as well as they could and then used it for an extract solubilised with bisulphite, they might find more than 100 per cent. of the solid bodies in the extract. The extract not only went through itself, but actually dissolved out some of the previously deposited matters in the candle which all the washing had failed to get out. When people complained that the leather of the present day was not equal to that of the good old times, there was a certain amount of truth in it, but a large part of it was due, not to the fault of the tanner, but to the desire to obtain a particular colour for which there was no real object, and to the use of bleaching extracts in order to get that colour.

Mr. HINTON agreed with the author's remarks on the colouring of leather to please the eye of the shoe manufacturer. Colour had no object whatever so far as wear was concerned. He held in his hand a piece of leather tanned in an English yard in 1874; it was tanned with oak bark and valonia and it took about 15 months to tan. It was intended for the soles of shooting boots, and had weather resisting properties and all the characteristics required for hard wear. The hide from which the butt was made was off a Highland bullock. Without being very handsome to look at, it was, to his mind, the ideal of what sole leather should be. The older race of men, who had no scientific knowledge, were able to turn out really good stuff. The manager of their yard used to walk round with the foreman and put his finger into the tan pits and taste the liquor; and he was thus able to tell whether it has deteriorated or not. He did not want to pose as a *laudator temporis acti*, but he did not think there was a tan yard in existence to-day worked on scientific principles which made better leather than, if as good as, the old people turned out. To-day, if a currier wanted reliable hides to make into trace or rein bucks, he sought from the few remaining bark yards.

Dr. S. RIDEAL said that the fate of the phlobaphens, at the time when he had a little to do with tanning many years ago, was not much considered; but it seemed to him they acted as a filling material; and, when they had got in, they ought to remain in, and not be taken out by any of the solvents, such as were used for the making of light leather. He was not prepared to admit that the addition of phlobaphens by filling up the pores of the leather between the fibres was really what produced the water resisting property; it seemed to him that perhaps there were other more suitable substances, e.g., rubber.

The CHAIRMAN said that in making an excavation in some old prehistoric Indian settlements in the Isla do Governador, a large island in the Bay of Rio Janeiro, occupied for many hundreds of years by Indian tribes before the discovery of America, he came across some skins which had been preserved in a very curious manner, namely, by vivianite or phosphate of iron; and they were blue. What the original preservative was, he did not know; but the form of the skin was very well preserved by the phosphate of iron. Again, in the bogs of Ireland, leather was very well preserved, as one would expect it to be in peat liquor. Coracles were still in use, but he had never seen one covered with leather. The fishermen in South Wales had given up the use of leather for this purpose. In the Guildhall Museum there were a number of Roman sandals which had been dug up in the City of London; they had been well preserved in the soil. The Pampas Indians prepared—he could hardly call it preserved—hides. The hides were dried in the sun, and the women would nibble a bit, and then nibble another bit, until the whole of the hide was softened. Those softened hides were a regular article of commerce with the Spaniards. Sometimes they were rubbed in grease afterwards, but the preparatory operation was chewing. With regard to the use of spent bark for fuel, at Heidelberg, the spent bark from the tanneries was often used as fuel; compressed into briquettes, it made a fuel which burnt out very quickly. In the district in the Argentine where quebracho was now prepared for tanning, he had often used it as building material. There were thousands of railway sleepers made from it, it being practically imperishable. No doubt that was due to the tannin it contained. The Cowey stakes driven into the Thames, near Weybridge, in the time of the Romans, if not before, still remained fairly sound. A wood in the River Plate, called nandubay, contained a good deal of tannin; it was of a dark colour, and probably that had prevented its use for tanning. Concretions of tannin might be found in the wood itself when it was cut open. Like quebracho, it sank in water. For many years he had worked on a substitute for leather, which was now being used in large quantities. The basis was felt, which was saturated with a material which had an advantage over tannin, in that it was waterproof. He thought tanners might very well, after they had tanned their leather and made it, what they called, bulky—which he would rather call spongy—waterproof it without any disadvantage to its sale, and certainly with very great advantage to those who had to use it, in our climate. He knew it had been tried, but it had not yet come into the market.

Dr. PARKER said, in reply, that he quite agreed that in the olden days all leather was good; to-day much of the leather was indifferent in quality. But at the Leathersellers' Technical College they were to-day making as good a leather as was ever made before, under scientific principles. He well remembered Dr. Rideal's articles in the Leather Trades' Review. He had mentioned these phlobaphens, which were deposited in the process of tanning and undoubtedly gave the leather certain valuable characteristics. There were plans for substituting other materials for phlobaphens; in fact, rubber was now put in under pressure; and he believed Mr. Evans knew something about "reinforced leather," in which the rubber was put under pressure into the pores in order to render it waterproof. The Chairman had made some very interesting remarks on the effect of phosphate of iron. It was well

known that both this material and the products of peat would produce leather; and there was a patent now being worked for leather making by what was known as peat tanning. That, however, was for the manufacture of light leather. The fact of women chewing leather to prepare it, was certainly new to him. He dare not speak of substitutes; he was too interested in leather. He should be the first to congratulate Mr. Reid upon any success made in his researches, but he liked the real thing. Much work had been done on waterproofing leather and no doubt more would be done.

Meeting held at Burlington House, on Monday, June 6th, 1910,

DR. J. LEWKOWITSCH IN THE CHAIR.

THE ACCURACY OBTAINABLE IN FUEL CALORIMETRY.

BY G. NEVILL HUNTLY, B.SC., F.I.C.

The economic importance of the determination of the calorific value of solid and liquid fuels is receiving increasing recognition among fuel users, and this is especially the case in the United States and on the Continent. The widely discrepant results obtained in the past in different laboratories for the same sample of coal led many engineers to regard laboratory tests as useless. These discrepancies have been traced to two causes, the imperfections of the calorimeters used and the errors of sampling. Comparisons of the various types of calorimeter (see Gray & Robertson, this J., 1904, p. 704, and Brame & Cowan, *loc. cit.*, 1902, p. 1230) have shewn that the bomb calorimeter gives more consistent results than any other form, and the Berthelot calorimeter is now by general agreement looked upon as the standard instrument. The operation of sampling is one over which the analyst has usually no control, but if carried out with due care the limits of error can be shewn to be of the same order as those of the calorimetric measurements. Consecutive determinations with a bomb calorimeter give such concordant results that there is a natural tendency to exaggerate the accuracy obtainable. Numerous bulletins of great value have been issued by the U.S. Geological Survey and by the University of Illinois embodying the results of a systematic study of various coal fields in the United States, and in all of these the calorific value is given to five significant figures (*e.g.*, 14,940 B.T.U. per lb.). These arithmetical exercises appear to be taken quite seriously by engineers, as for example in Bulletin No. 31, University of Illinois, where the corresponding boiler efficiencies are worked out to the second place of decimals, as 58.18 per cent. Similar examples could be easily quoted from our own engineering journals. It will be shewn in this paper, that apart from errors of sampling, an experimental error of 30 B.T.U. per lb. represents the limit of the most careful work, and for estimations carried out under commercial conditions errors of 150 B.T.U. per lb. may be regarded as probable.

The possible errors may be classified in three groups concerned with (1) the thermometer; (2) the correction for cooling; (3) the determination of the water equivalent.

The Thermometer.

There seems to be no work in English in which the difficulties of accurate thermometry are adequately dealt with. The only exhaustive book on the subject is that of Guillaume, "Traité pratique de la thermométrie de précision," Paris, 1889, which, although written 21 years ago, still remains the standard work on the subject.

The electrical resistance thermometer under favourable conditions undoubtedly gives a higher accuracy in temperature measurements than the mercury thermometer, but in practice, in spite of its defects, it is the latter which is generally used. Apart from the cost of equipment, the question of vibration militates seriously against

delicate electrical measurements especially in chemical laboratories in large towns or in a power station. With the mercury thermometer it seems to be generally assumed that the longer the degree and the larger the number of divisions into which it is divided, the more accurate will be the readings, and hence an instrument of the Beckmann type, with a range of about 6° C. divided into hundredths of a degree, and possessing a degree length of about 30 mm., is a favourite one. Apart from the disadvantages of the German type of thermometer (see *Méthodes de Calorimétrie*, W. Louguinine & A. Schukarew, p. 3) it was pointed out by Guillaume that no real advantage is gained by increasing the length of the degree above 10 mm., as the capillarity errors then become more important than the calibration errors, and this is especially the case in calorimetric thermometers, in which the capillarity effect is doubled if the thermometer is rising in the preliminary period and falling in the after period. The type of thermometer adopted by the International Bureau at Sèvres and constructed by Tonnelot, is made of hard French glass with a degree length of about 10 mm., and is divided on the stem into tenths of a degree. The stem is transparent so that the readings are not obscured by the thickness of the lines, an important advantage. From a thermal point of view (temporary depression of the zero) the French hard glass is only slightly inferior to Jena glass and it possesses the great advantage that fine sharp lines can be etched on it, down to 0.02 mm. wide. The author has not been able to get thermometers of Jena glass with divisions narrower than 0.06 mm., and these are somewhat ragged in outline when magnified in the telescope. When suitably illuminated and read through a telescope the division ($0^{\circ}.1$) can be read by estimation to one-hundredth, or $0^{\circ}.001$ (see Guillaume on this point). An eye-piece micrometer may be used for these readings, but it will be found that after some practice the micrometer may be dispensed with. A simple way of testing the accuracy of estimation is to prolong the observations of the cooling period after a combustion and plot the results on an open scale; the deviations of the readings from the straight line will shew the errors of estimation.

Since, in spite of its defects, the short range Beckmann thermometer is very generally used, it may be worth while to point out its most obvious faults and the means of eliminating them. Tubes with a flat elliptical bore should be rejected, as the capillarity errors are very irregular and the thread descends in jerks even though the stem be constantly tapped. The lines should be as fine as possible, as with, say, three lines to the millimetre, a line 0.1 mm. wide represents an error of $0^{\circ}.003$ when the thread is over the line.

Instruments by different makers vary very much in the thickness of the divisions. In some thermometers of English make divided into fiftieths, the lines are so coarse that readings closer than $0^{\circ}.01$ cannot be made. A more serious error, and one which sometimes appears to have been quite overlooked, is due to the fact that the value of the degree is variable, and depends on the temperature at which the instrument is used. A rough correction table is given in the Reichanstalt certificates, but this only applies when the thermometer is immersed to the zero line, a condition not generally possible. Moreover, it is obvious that the value of the degree must be determined by comparison with a standard, divided in tenths, and if, as seems to be commonly assumed, the latter can be read only to hundredths, the possible error of comparison over a 6° range is 1 in 300, and as a matter of fact it may be larger than this, owing to the impossibility of checking any zero change on the Beckmann thermometer. (For another method of dealing with this, see determination of the value of the degree.)

In the determination of a temperature the thermometer reading requires to be corrected for:—1. Calibration. 2. External pressure. 3. Internal pressure. 4. Zero. 5. Correction for the fundamental interval (value of the degree). 6. Exposure correction. 7. Reduction to the normal hydrogen scale.

Calibration.—The effect of this correction is to compensate for the inequalities of the bore of the tube, and to reduce the readings to those of a truly cylindrical tube