

THE PRESERVATION AND
STANDARDISATION OF
SOUTH AFRICAN
HIDES AND SKINS.

Being a thesis in fulfilment of the requirements
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Ph.D.
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Submitted by

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FOREWORD.

During the past fifty years the problems of the leather industry have been tackled from various aspects by scientific research workers all over the world, and "works control" today forms one of the important foundation stones of efficiently run tanneries and footwear factories. The raw materials of the tanning industry, hides and skins, constitute the largest proportion of the cost of production, and it is only natural that the improvement of these valuable raw materials should be given primary attention by any leather scientist.

Until only a few years ago, however, the South African hide and skin industry was at a serious disadvantage in that it had to base recommendations for improved production methods almost exclusively on overseas experience and practice. The importance of the differences existing between South Africa and European or American countries with regard to climate, slaughtering, hide and skin production in general, transport and sale, however, necessitates a different approach to our specific problems. The overseas hide and skin industry has had, since the beginning of this century, the support and particularly the guidance of scientific research; but it was not

until 1935, when, through the support of the Hide and Skin advisory Board, Prof. W. F. Barker founded the original Tanning, Hides and Skins Research Department at Rhodes University College, Grahamstown, that science actively entered the field of hide and skin production in this country. Much of the work done had of course to be based on the results obtained by overseas research institutions, and the adaptation of such results to suit our own problems for some time formed a considerable part of the investigations undertaken.

This thesis embodies the results of work undertaken by the writer since 1943 on specific problems of the South African hide and skin industry. Much of the work has already received publication through the Circulars and Journals of this Institute, but it is embodied here again in order to maintain the continuity. The attitude throughout has been to evolve methods of production suited to our own conditions, and the adoption of the recommendations contained in this thesis should lead to improvement in the quality of our hides and skins. Much still remains to be done, and it is the sincere hope of the writer that this work will stimulate and form the basis for subsequent investigations. For that reason more or less detailed descriptions are given of

all experiments conducted, and the theory of curing in its relation to tanning is briefly discussed. The literature in each of the four Parts has been attached at the end of that Part to facilitate reference work. At the same time, however, the writer kept in mind the requirements of the trade itself, therefore much of the work is discussed in popular terms. It is hoped that the correct balance between the two extremes has been arrived at.

During the investigations to be described herein the writer received information, help and advice from various sources and would like to express his acknowledgement and sincere appreciation to the following.

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Leather Industries Research Institute,
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P A R T I.

THE SOUTH AFRICAN HIDE AND SKIN INDUSTRY - GENERAL.

Chapter 1.

THE RELATIVE VALUE AND IMPORTANCE OF THE INDUSTRY.

The leather industry occupies a singular position among the other contemporary industries in that it is dependent for its all-important raw material on hides and skins, which constitute approximately 50% of the total cost of production of the finished leather. Hides and skins are basically only by-products of the livestock and meat industry and are consequently produced irrespective of demand. They have nevertheless become so important that it has been found necessary to apply to their production and marketing the same fundamental principles underlying all related industries, thus raising the organisation dealing with these products to the level of a separate industry, interdependent with that of livestock and meat production on the one hand and leather manufacture on the other.

Shuttleworth (1), in dealing with the problems of the South African leather and allied industries, has come to the conclusion that there is every likelihood of an increase in the production of hides and skins in the future, due to the growing world

population and a consequent increase in the demand for meat. On the other hand, improved means of communication will make it possible to meet the demand by the tanning industry for more hides and skins from a much wider source, with the result that only the best raw material will have a market. The increased marketing of artificial products also endangers the economic stability of the hide and skin industry, and it therefore would seem reasonable to conclude that it is essential for this industry to bring about such improvement in the quality of its products that it will be able to face such competition. During the past war the rapid expansion of the South African leather industry, especially in the production of the heavier types of leather, often outstripped the available amount of raw material, and the keen market for hides resulted in the acceptance of inferior quality goods. It can safely be assumed that the demand will not decrease rapidly, but sooner or later the difference between demand and supply will be smoothed out and there will be a demand only for quality standard products.

When discussing the problems of the South African hide and skin industry, the fact has always to be kept in mind that the country is vast and sparsely populated. This brings with it the production of hides and skins in small numbers, with

the result that it is very difficult to improve or to standardise such production. Slaughtering in municipal abattoirs contributes only about 60% of the total hide and skin output, and even at the larger centres the quantity is small if compared with the overseas meat packing concerns. The remainder of the hide and skin production originates from farms, both European and Native.

Despite intensive propaganda by the Hide and Skin Advisory Board, the Leather Industries Research Institute, the Anti-Waste Organisation and various other bodies, there is still a tendency among farmers, and even at abattoirs, to consider and treat hides and skins as offal - a necessary evil to obtain meat. In the case of European and Native farmers this is mostly due to the fact that their hides and skins are produced in very small numbers, except during periods of drought or disease. Therefore they do not feel the monetary necessity of improvement, not realising that any loss sustained by the industry as a whole must eventually be borne by themselves as primary producers. It has been shown by McLoughlin (2) that the hide of a compound or low grade ox in normal times represents between 10% and 20% of its total value, and that this amount is often the only profit obtained in producing such an animal.

During the years 1935 to 1939 hides and skins provided one of the main items of South Africa's agricultural export, the total annual value approximating the £2,500,000 mark. To this must be added a sum of about £500,000 representing the value of hides and skins handled by local tanneries. Hides and skins therefore rank with wool and fruit in importance as export products. This output does not

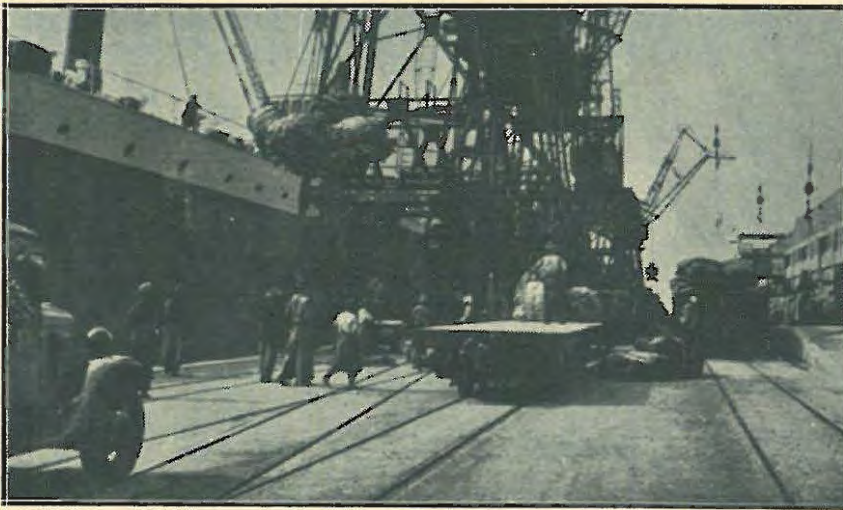


Fig. 1. Shipping Hides and Skins from a South African Port.
(Published by courtesy of Dr. S. G. Shuttleworth.)

receive any support in the form of a Government subsidy, and must be considered a valuable source of agricultural revenue. During the past war, however, the export of hides and skins suffered a severe decrease which was due to mainly two factors. The rapid expansion of the country's tanning capacity, caused by the necessity for increased war-time production of leather goods, resulted in a state of

affairs where nearly all hides and a much greater proportion of skins could be handled locally. The demand for hides led to the introduction of government control over wet-salted hides, which brought about some improvement and standardisation of these materials. On the other hand, serious difficulties were experienced with shipping facilities, so that large stocks, especially of skins, had to be kept in store at the coast for considerable lengths of time. Much damage was done to such stocks through the ravages of insect pests.

Table 1, taken from statistics published in 1936 by the Durban Wool Buyers' Association (3), represents the average figures of our pre-war export. How these figures will be affected during the next decade still remains to be seen. Britain, the United States and France were the main clients in the pre-war period, and it would appear that they will retain their positions on our market.

TABLE 1 : NUMBER OF HIDES AND SKINS
EXPORTED IN 1936.

| Destination | Hides | Goatskins | Merinos | Other Sheep |
|-------------|-----------|-----------|-----------|-------------|
| Britain | 648,756 | 504,968 | 1,051,028 | 1,671,140 |
| Italy | 157,183 | 3,530 | 38,019 | - |
| U.S.A. | 82,822 | 1,252,511 | 1,584,685 | 1,836,110 |
| France | 122,771 | 595,653 | 2,986,119 | 551,442 |
| Germany | 299,231 | 487,562 | 112,738 | 37,427 |
| Belgium | 95,869 | 7,296 | 41,957 | 1,675 |
| Holland | 66,459 | 23,385 | 384,181 | 5,113 |
| Japan | 81,621 | 1,336 | 10,697 | 400 |
| Canada | 100 | - | 9,500 | 2,700 |
| Other | 41,651 | 62,641 | 77,441 | 22,354 |
| Total | 1,596,463 | 2,938,882 | 6,296,365 | 4,128,341 |

Shuttleworth (1) investigated the organisation of the South African hide and skin industry, and concluded that its complexity militated against its efficiency. He represented the organisation graphically as shown in Fig. 2. The term primary producer denotes either the farmer or the butcher to whom the livestock is sold for slaughter.

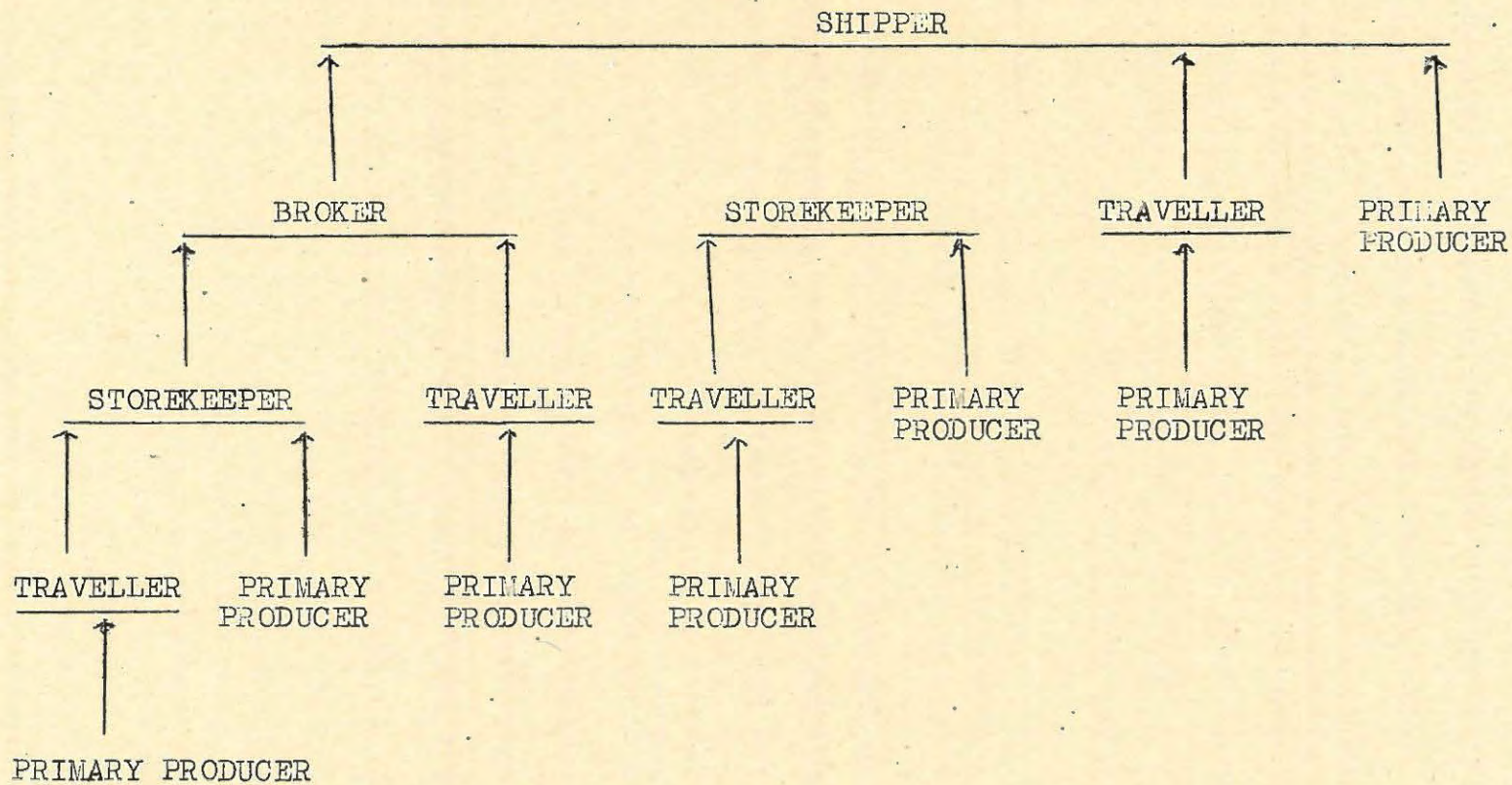


FIG. 2 : ORGANISATION OF THE SOUTH AFRICAN HIDE AND SKIN INDUSTRY.

Such a complex organisation necessarily results in much overlapping, waste of time and the accumulation of middle-men fees at the expense of the primary producer. Moreover, it makes it very difficult to bring about improvement and standardisation of hides and skins. However, since Shuttleworth has already adequately dealt with the economic aspects of the industry, the writer will refrain from discussing it again here.

SUMMARY.

The South African hide and skin industry brings into circulation annually about £3,500,000 and its export products rank high with other agricultural products. The quality of these hides and skins is, however, not of a sufficiently high standard to ensure a steady market in the face of increasing competition, but the complex organisation of the trade, together with the fact that hides and skins are produced in small numbers over a vast country, make the introduction of improved methods of treatment very difficult.

Chapter 2.

DEFECTS OF SOUTH AFRICAN HIDES AND SKINS.

(i) Introductory.

Before discussing those defects which are generally referred to when South African hides and skins are evaluated, it would perhaps be appropriate to mention here the inherent quality of our livestock. Only the broad outlines of the subject can be touched, but a more detailed account of certain aspects will be found in Shuttleworth's work (1).

According to Shuttleworth "the type of (American) slaughter stock described as inferior to common, would represent the best seen in most of the South African slaughtering pens, and a very much poorer type of animal is usually slaughtered." This state of affairs is due to a number of factors. The United States Department of Agriculture (4) has found that the best hide is derived from an animal bred purely for beef producing purposes, and this is very seldom encountered in South African cattle, the bulk of which is bred for the dual purpose of beef and milk production. Furthermore, a relatively large proportion of our cattle is native-owned and is generally of a very inferior type. Since the native regards his cattle as indicative of wealth, he usually refrains

from slaughtering animals which are still vigorous and in good condition. The inferior grade cattle of the natives have already shown ill-effects upon the quality of the stock owned by European farmers, and steps are now being taken by the Union Department of Agriculture to prevent cross-breeding of this type. European farmers are also averse to selling young animals, with the result that the larger proportion of stock offered for slaughter is of inferior grade. Animals of three to four years old not only yield the best beef, but the hides are sound and remove easily, thereby eliminating flay-cuts. It would therefore appear that we in South Africa are dealing with hides which are inherently of poor quality, making it even more necessary to improve as far as possible the methods of treatment during and after slaughtering and flaying, i.e. preservation. Furthermore, it is vitally important to eliminate the defects which are inflicted upon the hide or skin while still on the animal, as will be pointed out below.

The South African Merino, although an excellent woolsheep, does not yield a good pelt for leather manufacture (5). Owing to a former prevalent idea among wool farmers, the so-called wrinkled sheep was favoured for its wool-producing qualities and the pelt consequently suffered because of extreme ribbiness which made the grain more or less useless to the tan-

ner of light leather. Of late the tendency is again to breed smooth-bodied sheep because it is claimed that they yield more wool of better quality and are less prone to attack by the dangerous blowfly. Such sheep yield pelts of smoother grain, thus making them more valuable to the tanner of lining leathers. Furthermore, the merino skin has a marked layer of fat between the grain and the flesh, resulting in very loose leather. Merino skins are therefore usually tanned as grain and flesh splits, the former being used for cheap lining leather and the latter for chamois leather.

The Glover skin, as typified by the so-called Ronderib Afrikander, is undoubtedly one of the best skins on the world market for the production of gloving and clothing leather. Our chief competitor in this line is the South American Cabretta which is a smaller skin, requiring more handling per area unit of leather. Unfortunately it would seem that the true South African Glover is in danger of rapidly disappearing from the market, its place being taken by skins which do not possess the same leather making qualities. Over a period of some two decades the extent to which cross-breeding has been practised by farmers has had its effect upon the size of the stock of true Ronderib Afrikander and Namaqualand sheep, and the skins now offered as Glovers comprise many

types like the Blackhead Persian, so-called woolly Glovers, etc. These skins are generally smaller and, because of the longer hair (wool) do not possess the same leather producing qualities as the true Glover. The latter is now mostly confined to the hinterland of Cape Town and still rightfully enjoys its superior position on the market. A note of warning should therefore be sounded to farmers to be careful in cross-breeding, so as not to spoil the value of the pelts of their meat sheep.

Apart from the inherent quality of the hide or skin, three main criteria are used to evaluate a hide or skin from the point of view of leather manufacture. According to these the ideal hide or skin should be free from any defects on the grain, should have a smooth flesh side free from fat, meat and fly-marks, and should be in a perfect state of preservation, i.e. all forms of bacterial decay must have been prevented so that the material will resemble the fresh condition when put into the first tanning processes. Based on these standards it becomes apparent that the quality of South African hides and skins falls far short, and it is estimated that the industry loses 33%, about £1,250,000, of the total potential annual value of its products because of faulty, inefficient or negligent treatment. The loss incurred with

defective hides and skins is all the more magnified in the tannery and footwear factory by the amount of time, labour and expensive materials spent on preparing such a defective piece of leather. It is for example often the case that not one square inch of the grain of heavy leather has not been damaged in some way or other, consequently diverse means of overcoming such difficulties have to be devised by the tanner **who**, necessarily, must allow for extra expense when offering a price for his raw materials.

(ii) Defects on the Hide or Skin Whilst
Still on the Animal.

It has been estimated that damage of this type is responsible for an annual loss of £500,000 to the hide and skin industry, the greater part of the loss (about a quarter million pounds) being ascribed to indiscriminate branding alone, while barbed wire scratches, horn, whip, tick and thorn marks cause a further loss of approximately £100,000; the balance is put to the account of transport, slaughtering and flaying deficiencies. The bulk of this loss is borne directly by the **farmer** who is penalised by the lower prices offered for his slaughter stock.

(a) Barbed wire is unfortunately the recognised fencing material in this country, few farmers

realising the harm done thereby. In the Argentine (6) the losses due to barbed wire scratches are estimated at between 7% and 10%, and no doubt similar figures apply in this country.

(b) Horns and prime beef do not go together in cattle according to research done by the United States Department of Agriculture (4). It appears that dehorned cattle feed out much better, especially if the horns are removed when showing only as "buttons" on the calves. Truck-loads of horned cattle often result in bruised meat and damaged hides, and horn marks are quite frequent on South African hides.

(c) Tick marks, although apparently negligible on the hide or skin, show up very plainly on the finished leather and may cause the rejection of large areas in the clicking department of footwear factories. Especially Eastern Province and Natal cattle are prone to such damage, the so-called arsenic-resistant tick being in no small way responsible for this.

(d) The South African veld is, on the whole, very bushy in parts and thorn marks are frequently found on the grain. During some seasons considerable trouble is caused on sheepskins of all classes by steekgrass.

(e) Branding is perhaps one of the worst difficul-

ties in this country. The most valuable part of the hide is the butt which corresponds to the back and sides of the animal and which yields the best and stoutest leather. Any damage to this part of the hide is therefore relatively greater than it would have been had the same damage been inflicted on the

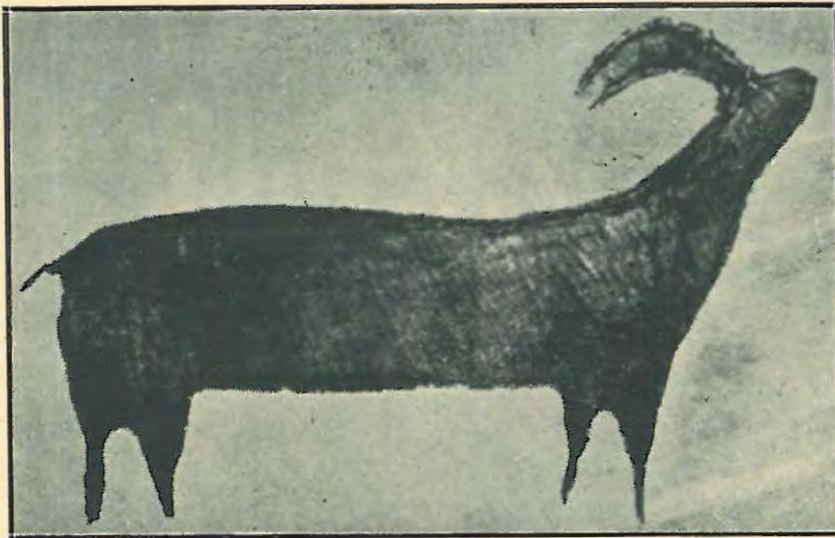


Fig 3. Brandmark Measuring Approximately 2 x 4 ft. on a South African Native Hide.

(Courtesy of Dr. Shuttleworth.)

neck or belly. In South Africa the accepted practice is to put the brand on the butt where it is claimed to be more easily visible. This brand is usually repeated with change of ownership, with the result that large areas are spoilt. Brands are often of outrageous size, especially on native hides, and in many cases the branding iron has been so hot or

so long applied that it is burnt through and can be seen on the flesh side of the finished leather.

(f) Bruises in transport arise from the fact that cattle pens at railway stations and cattle trucks for transport are constructed in a rather haphazard way with inferior material. The animals are often cut or bruised by wires, sharp edges and jutting angles. Too many animals are crammed into a small space, and horn marks and bruises are then frequent. Since this damage occurs when the animals are already on their way to the abattoir, the hide or skin does not get any chance of healing naturally and the marks and bruises show up very clearly on the finished leather.

(g) Faulty and/or inefficient slaughtering must be regarded in a very serious light. Shuttleworth (1) has given a detailed account of conditions prevailing in South African abattoirs, and his findings may perhaps be summarised as follows. Many of the larger abattoirs are equipped in a fairly modern fashion allowing of a certain degree of efficiency in the handling of stock, but there is still much scope for improvement. Most of the abattoirs lack suitability with regard to such matters as design, drainage, sanitation, hoisting facilities, cattle pens, runways, stunning pens, bleeding rails, sheep slaughtering equipment, tail extractors, flaying machines,

and hide and skin storing facilities. The labour employed, mostly non-European, is often of inferior types with little or no training. This is mostly due to the low wages offered. Each butcher usually has his own gang of slaughtermen, with the result that there is no efficient system of grading of men or of supervision. The outcome of all this is that

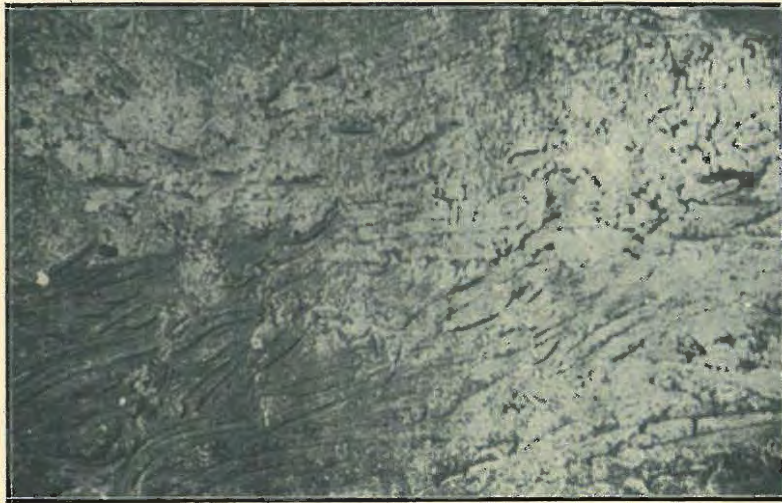


Fig. 4. Typical Flay-marks on a South-African Hide.

the hide or skin is bruised, becomes contaminated with blood and dirt, ripping and flaying are done on unscientific lines and much unnecessary damage is inflicted upon very valuable materials.

Slaughtering on farms has been investigated by Rose (7) who reported that "on most farms the slaughtering place is easily recognisable by the blood-stained ground, the manure that has been emptied from the intestines, and the buzz of many

flies. The slaughtering is done by a native whose clothes and body are filthy; consequently all the requisite conditions for rapid putrefaction are present." If it is true that slaughtering and flaying are bad in municipal abattoirs, it is even more so on the farms, and hide and skin dealers can without fail pick out the so-called country skins originating from farms. These hides and skins are



Fig. 5. The Effect of Correct and Incorrect Ripping Lines on the Resulting Sheepskin.

characterised by the lack of good pattern and by the many flay-cuts and scores present. Fat and bits of meat are quite often left on the skin, the material then being more prone to attack by the Dermestid hide and skin beetles.

One aspect of slaughtering needs special mention here. Animals are nearly always slaughtered on the ground or on the floor of the abattoir, and are then left lying there in pools of blood and dirt

while flaying is in progress. The hide or skin thus becomes contaminated with materials which not only may cause undesirable stains, but which form excellent media for the commencement of bacterial development. This is especially deleterious because of the fact that hides or skins are seldom washed prior to curing and are often left lying about for hours before being removed to the curing shed.

(iii) Defects on the Hide or Skin
after Flaying.

Damage of this type is perhaps the most serious in the industry, not only because it causes an annual loss of about £750,000, but because of the fact that in the past no suitable methods of treatment have been available for the prevention of putrefaction and of insect damage. The apparent apathy of those concerned, coupled with severe climatic conditions - conditions highly favourable to the propagation of bacteria and insects - have made it difficult to eliminate even part of this loss. In the following chapter will be described the past attempts at bringing about improvement, and in the next three Parts of this work will be given the latest methods evolved by the writer at the Leather Industries Research Institute.

The object of curing a hide or skin is to prevent or stop bacterial decay by such means as will not adversely affect the leather making qualities of the raw materials. This, in brief, is the theme of the work to be described in Parts III and IV of this thesis. It will therefore suffice to mention at this **stage** only the broader outlines of the various problems involved, so as to present the reader with a clear picture of the conditions generally ruling in the country.

(a) Washing.

South African climatic conditions are favourable in that the animals are not subject to long periods of stabling as is the case in European countries (8), therefore they are generally in a much cleaner condition prior to slaughtering. It is then not essential to wash the animal before it enters the abattoir. However, we in this country derive little if any benefit from this circumstance, since the relatively clean animals are subsequently subjected to filthy slaughtering conditions as pointed out above. We ourselves create the conditions which necessitate washing of the hide after flaying, but only in exceptional cases is this practised. Blood not only causes stains on the resulting leather, but by its presence prevents the curing salt from rapid penetration, thereby also facilitating decay.

Dirt on the hide also has the effect of preventing salt penetration and of stimulating bacterial development.(9,10).

(b) Curing Salt.

Commercial sodium chloride is the recognised curing salt in South Africa, but it will be shown in Part IV that the type of salt used by the industry is often of inferior quality. Moreover, it has been and to a certain extent still is the practice to re-use curing salt. Such salt gives rise to what has become known as true salt stains which are visible on the cured hide or skin and on the finished leather. A detailed account of this important subject will be given in Part IV.

(c) Curing of Hides.

Abattoir hides are usually sold to tanners in the wet-salted condition. The butcher either does the curing himself or has some arrangement with a hide and skin dealer who removes the hides from the abattoir to his curing shed. Often the hides are left too long at the abattoir, with the result that partial decay sets in and the blood congeals. During the war control over slaughtering and over the sale of wet-salted hides caused many hide and skin dealers to pool their resources of curing. This was benefi-

cial because a more uniform cure could be obtained at each centre, but there was more danger of serious delay in the handling of stock. The usual method of salting is to stack the hides flat in large square piles covering about 20 square yards of floor space, each hide receiving about 20% of salt on the tail weight. Another method of stacking also in vogue is that of putting the hides one on top of the other, flesh side up, in single piles or "batties". This method allows of better drainage than the former. The stacks are built to a height of three to four feet and then completely covered with salt. After ten to fourteen days the hides are pulled, i.e. the stacks are broken up, excess salt shaken off and the hides bundled for transport. Both methods of stacking are prone to adulteration, since in most cases the stack is hollow and the saline (usually bloody) solution cannot run clear. This approaches the method of pit-salting which was stopped a few years ago by the Government. Only in exceptional cases are the hide cellars cool enough and not subject to unnecessary draughts. Especially in summer the hides are attacked by red heat, the high temperatures in the stores stimulating the propagation of the halophilic (salt-loving) bacteria responsible for the development of this particular type of stain. Wet-salted hides quite frequently show true salt stains

due to dirt, blood and impure salt (9,10,11).

Farm hides arrive at the broker, shipper or tanner either in the dry-salted or sun-dried condition. The dry-salted hides are generally badly cured, due to mainly three factors. In the first place the amount of salt used is very seldom sufficient to saturate the hide. Secondly, the hide is put out to dry in the sun almost immediately after application of the salt, so that the latter does not penetrate the wet hide efficiently. Thirdly, the hide is generally put down flat, or worse still pegged out in the stretched condition, on the ground. The rapid surface drying results in hard crusts which prevent the moisture inside from evaporating. The temperature on the ground easily exceeds 37°C at which critical point the proteins commence to coagulate, thereby interfering with the tanning process. See Part IV. A most deplorable practice is that of pegging out the hide on the ground, since the tension on the fibres deprives the leather of much of its flexibility and tensile strength.

Native hides are nearly always offered on the market in the sun-dried condition, like some European farm hides, since the native can very seldom afford to pay for the salt required to produce good dry-salted material. As has been mentioned

above, the rapid surface drying traps the moisture inside the hide, consequently putrefaction can proceed unchecked. Sun-dried hides are usually flinty and hard as boards, and although outwardly in good condition, they are more often than not "green" and rotten inside. Many tanners find that such hides disintegrate in the soak pits, and this means serious loss to the industry since native hides form a large proportion of the total output.

Shade-drying is not yet generally practised, although it can yield much better results than sun-drying. The trouble with shade-dried hides is usually that they are allowed to putrefy due to too slow drying and the lack of antiseptic treatment. If drying proceeds fast enough to prevent such decay, the hide is usually in reasonably sound condition.

(d) Curing of Skins.

The above remarks on the conditions under which hides are produced at abattoirs also apply to sheep- and goatskins, except that these, because of the long wool or hair, are even more prone to contamination with blood and dirt which are seldom removed by washing prior to curing. Excess fat and pieces of meat are left on skins because of inefficient flaying. The tendency of hide and skin dealers to pool their curing resources also manifested itself in the case of skins. Recently some concerns intro-

duced hand-fleshing of fatty skins to remove excess fat. There is a wide variation in the curing methods in vogue at different centres, but no one method yields good results(12). A detailed account of the problem will be given in Chapter 15, therefore only a brief survey will suffice here.

A method referred to as the Cape Town cure consists of salting the skins with about four pounds of salt each, folding them double flesh to flesh along the backbone and stacking them in long piles about four feet high, one skin deep. After three or more days the salt is shaken off and the skins are stacked flesh to flesh in single piles or batties for a further period of three days to three weeks. Sometimes a second light salting is given prior to this battie-stacking. The skins are then dried over horizontal poles in the sun, the skins being hung with the necks and tails reaching downwards. This method allows of a reasonably good and light cure, but the bellies and legs are inclined to be papery and thin due to the continual loss of brine in the battie stacks. Another method is to stack the skins flesh to flesh in a square pile, about three feet high, for six or more days. In this case the seepage of the skins does not clear the stack as in the Cape Town cure, but drains into the skins lower down and contaminates them with blood and dirt, resulting

in a "heavy cure". This method is more prone to adulteration, but there is less danger of folds and grain cracks since the skins are stacked flat in the pile. In other cases the skins are put flat on the floor and salt shovelled over each layer. Such skins are excessively dirty and the wool or hair laden with salt. Some concerns fold the skins into square forms after salting and stack them to excessive heights. The result often is a distinct fold or crack on the grain. In all cases washing of the fresh skins is omitted, the salt is impure and too often re-used.

Farm skins are generally dry-salted, but the same deficiencies are found as in dry-salted farm hides. Too little salt is applied, the skins are dried flat on the ground in the sun and are dirty of appearance.

Native skins are, like hides, sun-dried and generally in a bad condition of preservation. Such skins lack the tensile strength and elasticity required of light leathers.

A general curing defect of South African skins is the excessive amount of adhering fat on the flesh side. Such a layer of fat prevents rapid and thorough penetration of the salt, renders drying a slow and inefficient procedure and results in greasy skins owing to melting of the fat in the sun (15).

(e) Marketing.

The marketing of abattoir produced skins and hides affords very little difficulty, but as has been pointed out in Chapter 1 the hides and skins from European and native farms reach the shipper only after having gone through the hands of a number of middle-men. During this period the material is prone to serious damage by hide and skin beetles and moths. Another difficulty is the way in which hides and skins are bundled for transport. Usually they are folded to make the parcel compact, with the result that grain cracks develop. The use of wire to fasten the bundles leads to iron stains on the leather.

(f) Storing.

The main difficulty in this respect is the damage caused by the Dermestid hide and skin beetles and the Tineid moths, damage which has been estimated at about half a million pounds sterling every year. The trouble is accentuated by the dirty conditions under which hides and skins are kept in many stores, the lack of ventilation, and the lack of insecticidal treatment.

SUMMARY.

The inherent quality of South African hides and skins is below that of the overseas products, necessitating even more care of the treatment during and after flaying. Defects inflicted on the hide or skin whilst still on the animal by such factors as barbed wire, thorns, steekgrass, whips, horns, branding, transport bruises and inefficient slaughtering render the hides and skins much less valuable to the tanner and result in an annual loss of about £500,000 to the industry. Faulty, negligent or inefficient treatment during and after curing is responsible for an even greater loss. On the whole the picture painted of conditions in the hide and skin industry is not re-assuring, and serious efforts will have to be made to bring about the necessary improvement.

Chapter 3.

PAST WORK ON THE IMPROVEMENT OF SOUTH
AFRICAN HIDES AND SKINS.

The inferior quality of South African hides and skins has caused concern for a considerable time. Shuttleworth (1) summarised the position up to 1929 in the following paragraphs.

(14)

"Schauder/mentions many historic references to hide and quality. He states that in 1904 the evidence given to a Government Select Committee showed 'that Colonial hides were inferior to those from overseas in that they were often in a damaged condition when placed on the market, being cut and scarred through unskilled flaying.'

"In 1911 some interesting evidence on South African hides and skins was given by tanners to the first Union Commission on Commerce and Industries (15). Mr. Coaton said that until the Government did something to improve the grain of the hides, he was afraid that the South African tanners could not do anything in the class of chrome leathers. He pointed out that Australia estimated its losses through branding on the butt as £300,000 per annum. He considered that, besides brand marks, considerable damage was done by barbed wire fences, thorn marks,

whip marks, tick marks and marks due to bad flaying. Mr. J. Neil Boss, giving evidence before the same Commission, pointed out that the hide export business had resolved itself into more or less of a gamble, or purely speculative business, as South African hides were frequently sold in the London markets much below South African prices, the exporters having contracted for every available skin many months ahead, thus limiting the supplies available for the local tanner. He recommended an export duty on hides and skins.

"In 1922 the Board of Trade and Industries (16) made the following remarks on the subject. 'We desire to refer to the serious allegations made by all tanners about the conditions of the skins and hides they receive locally. The damage done by branding all over the most valuable part of the hide, unskilled flaying and marks caused by tick bites, whip and barbed wire is described as enormous. The result is that according to information received by the Board our hides and skins fetch, when exported, some 4d per lb. less than those of other countries. Counting hides and skins used locally, this might easily mean a loss of £1,000,000 a year to the country. We do not feel called upon to make any particular recommendations to deal with this matter, but recommend that it be referred to the Agricultural authorities that,

where necessary, legislation be passed allowing for less wasteful branding and that a campaign be instituted to stop the waste now going on.'

"The South African Journal of Economics has, from time to time, called attention to the need for improvement. 'Even in present conditions of supply,' it said on one occasion, in an editorial (17),



Fig. 6. Flaying in Progress in a Municipal Abattoir. The Knife is used too frequently.

'much could be done to improve the quality of the hides available for conversion into leather. You may go into any South African tannery, and you will hear the same story of the damage done to the hides, whilst the animal is living and during flaying. Whip marks, scratches from barbed wire, tick bites and above all brands, contribute to lessen the value of the hide..... Bad flaying further lessens the value.'"

The first paper, with a scientific approach, on the improvement of farm skins was published by Rose (7) in 1929. Rose drew the attention of farmers to the monetary value of the skins and pointed out how large amounts of money were wasted annually because of improper methods of flaying, curing and marketing. He then proceeded to make recommendations for improvements along the following lines.

- 1) Slaughtering should be done on properly constructed platforms to avoid contamination of the skin with blood and dirt.
- 2) Flaying should be properly executed, resulting in a skin of good pattern, free from flay-cuts and scores.
- 3) The curing salt should be clean, of fine grain and relatively free from alum, calcium sulphate and lime, these materials being responsible for stains on the cured skin.
- 4) Since putrefaction sets in soon after death of the animal, salting of the skin must not be delayed too long.
- 5) It is recommended to fold the freshly salted skin for a period of thirty-six hours to ensure thorough penetration of the salt.

- 6) For fatty skins of the Blackhead Persian type a preliminary salting and rolling for 24 hours is recommended, followed by hand-fleshing to remove the fat, and a second salting applied.
- 7) Skins should never be exposed to direct rays of the sun, the surfaces baking hard and trapping moisture inside the skin. Pegging out of the skin should under no circumstances be practised. Drying is best done in the shade.
- 8) Skins should not be stored under conditions conducive to the development of Dermestid beetles and skin moths.
- 9) Methods for bundling and transporting of cured skins are described in detail.

In the same year a paper by McLoughlin (2) drew attention to the economic aspects of the hide and skin trade in South Africa. All these and other agitations resulted in the appointment of McLoughlin by the Union Government to investigate the local hide and skin industry, and as a direct outcome of his report the Hide and Skin Advisory Board was constituted by the Government, this new Board holding its first meeting in April, 1930.

The members of the Board were representative of all industries concerned with hides and skins,

i.e. from the primary producer to the tanner. A serious lack of scientific knowledge regarding the preservation of hides and skins urged the Board to send an officer overseas to investigate conditions. On the basis of his report (18) the Board could then put forward recommendations for improved production methods, and could pass regulations governing the export trade. Four hide and skin inspectors were appointed in 1935 at the four major ports.

It was, however, realised that conditions in South Africa called for specific methods in hide and skin production, and that much research would have to be done locally before any regulations in this respect could be enforced. Meanwhile, too, the onus was put too much on the shipper and exporter, while the producer could not be penalised for practising wrong methods. At the instigation of Prof. W.F. Barker of Rhodes University College, the Board made available a grant of £300 to that College in 1936 and of £400 in 1937 for the express purpose of financing research into the problems of the South African hide and skin industry. The Tanning, Hides and Skins Research Department thus formed could provide the Board with accurate data and information, and the grant of the Board has since been increased to £500 annually. The institution of the Leather Industries Research Institute, with improved facilities for research and

increased staff, has given this work a great push forward and the Board is now presented annually with detailed reports on the work carried out during the previous year. A summary of the reports which emanated from the old Research Department and from the new Institute will provide ample proof of the sound basis of the Board's decision to thus stimulate and support research.

A most valuable and important report was prepared by Shuttleworth (1) in 1937 on the subject of hide and skin production in this country. After an introductory discussion of the hide and skin trade in general, Shuttleworth proceeded to outline the deficiencies at the various stages of production. With regard to the low inherent quality of our slaughter stock he recommended the following:

- (i) "Continuation of the Government policy of stock improvement.
- (ii) Regulation of the infiltration of native scrub stock.
- (iii) Continuation of the Government policy of encouraging an export beef trade.
- (iv) Extension of the present (1937) system of meat grading to include the whole Union."

Shuttleworth drew attention to the defects inflicted upon South African hides and skin while still on the animal by such causes as skin diseases, ticks and mites, branding, horn marks, thorn and whip marks, "steekgras" and barbed wire. For the elimination of these obvious losses he recommended:

1. "Stricter enforcement of regular dipping.
2. Propaganda favouring increased cleanliness of stock.
3. Institution of branding regulations and propaganda.
4. Institution of dehorning by Government legislation and national propaganda.
5. Propaganda and legislation to reduce all types of scratches.
6. Reduction of damage sustained during trucking by legislation and propaganda."

A detailed investigation into the conditions obtaining in South African Municipal abattoirs led Shuttleworth to criticise this step in hide and skin production very severely. His recommendations in this respect are most valuable and are detailed here.

(i) "Improved design and equipment of abattoirs, with particular reference to such matters as arrangement, drainage, sanitation, hoisting facilities, cattle pens, runways, stunning pens, bleeding rails, sheep slaughtering equipment, tail extractors, flaying machines and hide and skin storage accomodation.

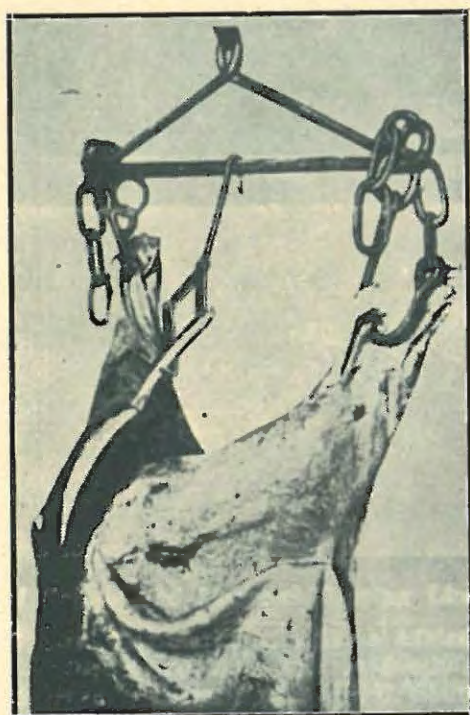


Fig. 7. Illustrating the Use of the Tail Extractor.

(ii) Formation of a central board to control and advise abattoir design and equipment.

(iii) The employment of a better type of labour for slaughtering.

(iv) The introduction of Municipal slaughtering.

If slaughtermen were Municipal employees, a smaller quantity of labour of a better and more permanent

type could be employed. The efficiency of this system has already been proved in South Africa, and its introduction is advocated by many superintendents of both large and small abattoirs.

(v) Stricter supervision of slaughtering.

(vi) A system of licensing head slaughtermen or perhaps all slaughtermen might be beneficial.

(vii) Grading of slaughtermen.

(viii) Education of slaughtermen.

(ix) Restriction of butchering licences to qualified experts.

(x) Improved trucks for transporting animals.

(xi) Regulations forbidding rough handling of animals.

(xii) Cattle pens, runways and floors to be of smooth construction.

(xiii) Enforced cleanliness in abattoirs.

(xiv) Propaganda and regulations to improve the take off of hides and skins.

(xv) The compulsory use of improved flaying apparatus such as the Pellex machine flayer and the Tasker flaying knife.

- (xvi) Educational propaganda to improve flaying.
- (xvii) Regulations to prohibit the slaughter of exhausted or excited animals.
- (xviii) Regulations to prohibit marking of sheep-skins with tar.
- (xix) Introduction of a system of regional abattoirs.
- (xx) Special registered marks for all abattoir hides and skins.
- (xxi) Elimination of delays prior to curing.
- (xxii) Enforced brokerage on the open market of all hides and skins. not supplied directly to tanners. This would direct more attention to quality.
- (xxiii) Research work on curing methods.
- (xxiv) Educational propaganda to introduce better methods of curing."

A summary of his recommendations regarding methods of improving the quality of European and native farm hides and skins would include the following points.

- (i) "Propaganda work to the farming community to emphasise the need for clean hygienic slaughter, proper equipment for flaying, rapid bleeding of animals and immediate flaying, correct methods of

take off, flay and trim, and immediate curing by the best methods.

(ii) Introduction of regional abattoirs.

(iii) Encouragement of sale of hides and skins on the open market through brokers.

(iv) Propaganda work amongst the storekeepers and traders.

(v) Education of the native to emphasise the need for early slaughter, rapid bleeding, early flaying and immediate cure in the shade or in such a manner as to avoid direct sunrays.

(vi) Education and regulations to improve native stock.

(vii) Enforced sale of hides and skins by traders and storekeepers on the open market in quality grades, to make it worth their while to assist in the improvement in quality."

After dealing comprehensively with deficiencies in the curing process caused by grease stains, salt sprout and allied defects, salt stains, general decay and hide substance loss, and damage caused during storing by the Dermestid beetles, Shuttleworth outlined his research into the evolution of improved production methods. His observations in this field

have formed the basis of most subsequent work by the Leather Industries Research Institute, providing a very useful guide in planning research, therefore a full summary of his work here is deemed necessary.

Shuttleworth summarised his experimental work on the curing of South African glover skins as follows.

"Many interesting conclusions can be deduced from these results. In the first place the yields for the sundried skins were considerably lower than those for the corresponding skins dried out in the shade. It would seem that the direct action of the sun withdraws more moisture from the fibres than indirect evaporation. At the same time the cured skins resulting from shade drying were just as well cured and permanent as those which had been sundried, indicating that the residual moisture in the shade-dried skins is not detrimental to the cure. Moreover the complete dehydration of the fibres due to fierce drying in the hot direct rays of the sun is a well known defect in skins, and tanners find that these skins do not soak back properly. It is interesting to note that the tannery report on these sundried skins criticised them as being "leathery". A further point is the length of time required for drying. The skins in series 1 - 4 were taken in at night, and consequently the drying period was limited to

about 8 hours per day. Under these circumstances drying was much slower than for the shade dried skins, which were protected from the weather, and dried out continually. Had the skins been left out they might well have been damaged by wet weather. Thus the evidence obtained in these experiments points to the conclusion that shade drying is not only preferable from the tanner's point of view, but also saves the hide and skin curer's time and labour, while producing yields of cured skins which may be anything from 5 to 10% higher, depending on the relative extents of drying. These higher yields will not necessarily be fictitious weight, as they may well be compensated by improved leather returns due to better fibre conditions of shade dried skins. A further point in favour of shade drying is the effect of the sun on the fatty tissue. It was very noticeable that the sun dried fatty skins were more oily than those which had been shade dried, and it seemed that the strong action of the sun had burst some of the fat cells, causing a movement of lipid particles into the skins.

"With regard to the fat on the skins, it is noticeable that throughout the 19 series this factor provided the greatest variations in quantity, and this was the chief cause of fluctuating yields. Superficial fatty tissue adhering to these gloving skins varied from 5 to 20% of the fresh weight,

which would imply a variation from 10 to 40% on the cured weight. In other words the gloving skin manufacturer would have to allow for the possibility that a parcel of skins might contain nearly half their weight of useless fat. He would **try to cover himself** against such losses, and consequently to pay less. Instead of buying skins on a definite basis of certain yield returns, his business is changed to one of pure speculation, with consequent loss of confidence. There can be no doubt that the removal of all fat from skins would enable the manufacturer to assess more accurately what leather returns he is likely to obtain from his raw materials, and a speculation would be changed into a sound business proposition. There would be a preference for a skin guaranteed free from adhering superficial fat, and improved prices would undoubtedly result. A further point in favour of a defatted skin is the fact that the fat adds useless weight to the skins, and that the freightage costs for this useless material have to be paid at the same rate as the skins. A calculation shows that approximately £3,000 per annum is wasted on shipping fatty tissue from South Africa. With regard to the difficulties of carrying out the cure, it is noteworthy that the defatted skins in every case took considerably less time to dry out, so that the time spent in scraping off the fat is greatly repaid by

the reduction of the subsequent work and the shortening of the curing period. The appearance of the skins which had been scraped free of fat was greatly superior to that of the fatty skins. This was particularly noticeable in the case of the sundried fatty skins, which were very greasy. The salt penetration of the fatty skins was poor, resulting in a patchy cure, so that there was a tendency to hair slip on the grain side below the fatty areas. Skin beetles showed a marked preference for these fatty skins, and they were usually attacked in preference to the defatted ones. With keeping the fat gradually changed colour, becoming a dark yellow, and putrefying to some extent. Hair slip became more apparent with time on the fatty skins, and skin beetle damage was marked. The defatted skins all remained in sound condition and there was no beetle damage on those which had been salted.

"It would seem safe to conclude that the South African Government would be well advised to prohibit the export of skins which contained adhering fatty tissue. The manufacturers would have to readjust their conceptions of weight returns but once they had gained confidence in the new type of skin, the South African hide and skin trade could not fail to benefit. There is, however, one note of warning, and that is the danger of scraping skins too

vigorously, thereby removing valuable portions of the corium of the skin. It is necessary to educate the producer in the correct method of removing the fat without damaging the skins.

"Washing the skins did not produce any marked or consistent variations in the yield returns, and the effect is probably a small one. The appearance of the washed skins was certainly superior to that of the unwashed skins, but, where salting and rolling had been carried ^{out} the differences were confined to the hair surfaces as the brine drained from the skins during rolling in salt seemed to remove blood etc. from the flesh surfaces. The washed skins definitely took a longer time to dry, and it was quite difficult to remove the last traces of moisture from the hair roots of shadedried skins. It was found that a day in the sun with the hair surface exposed was necessary to produce properly dried skins. The presence of moisture in the hair roots of washed skins made them more liable to bacterial and insect damage, so that the cure is improved in appearance only. It seems advisable to improve cleanliness by eliminating unclean slaughtering conditions, than by washing the skins, and therefore washing is not recommended.

"The percentage of salt produced marked changes in yield, and although the varying quantities

of fat and the differences in drying due to climatic variations, have masked these yield changes to some extent, it seems from the results that in considering salt contents ranging from 0 to 20%, roughly half the salt added contributes to the yield, the remainder being removed in the cure. Thus a 10% salting gives approximately 5% greater yields than unsalted skins, and a 20% salting approximately 5% greater yields than a 10% salting. These yield differences cannot be regarded as conclusive, and further experiments with defatted skins are being undertaken to enable more definite conclusions to be arrived at. Both the 20% and the 10% saltings produced well cured skins which kept well and were not greatly attacked by beetles. The 20% cures seemed somewhat more repellent to skin beetles than the skin which possessed the lower salt content. Superfluous salt was noticed on the skins cured with 20%, especially on the fatty skins, and for this reason the hide and skin experts preferred the 10% cures, as these would prove more acceptable to the overseas manufacturer. However there seems no reason why this superfluous salt should not be shaken or rubbed off prior to sale of the skins, and there can be no gainsaying the importance of salt from the point of view of skin beetle damage. The unsalted and brined skins were most subject to attack by skin beetles, and were more or less completely destroyed during storage. For this reason

neither brined skins nor unsalted skins can be recommended unless some satisfactory method of eliminating insect damage can be found. During curing the use of 20% salt caused much larger reduction in weight of the skins during rolling and stacking than the use of 10% salt, the average differences being approximately in the proportions of 3:2. This would imply a larger elimination of moisture during rolling, and a consequent reduction in drying time. It was found in practice that the 20% cures did seem to dry more quickly. At the present stage of research, it does not seem wise to recommend any particular percentage of salt, and further work on the subject seems desirable. At the same time it must be stressed that a good and thorough salting, applied evenly to the surface of the skin, seems to be an essential factor in the production of a well cured skin, resistant to damage by skin beetles.

"Rolling and stacking for varying periods did not seem to cause marked differences in cure or yield, and rolling alone appeared to produce the same results as both rolling and stacking. The latter seemed quite unnecessary. From the results it would seem safe to conclude that rolling overnight (16-18 hours) is quite adequate time to ensure complete action of the salt. If the skins are salted in the morning or early afternoon, and are left rolled up,

with flesh surfaces in contact with each other until the following day before being hung out to dry, a good even cure will result. Turning in the roll has also been suggested, but there were no signs of unevenness on any of the skins rolled and left in one position only, so that turning does not seem necessary. That rolling is necessary is shown by series 11-14, which produced unevenly cured skins with reduced yields. These experiments showed that rolling is essential to promote the penetration of the salt into the skin.

"Although a considerable amount of work still remains to be done, it seems safe to recommend the following:-

1. That all adhering fatty tissue should be removed from gloving skins.
2. That these skins should be given a thorough salting with clean salt well rubbed into all parts of the flesh surface of the skins.
3. That the skins should be rolled in such a manner that the flesh surfaces are in contact for 16-18 hours or longer.
4. That the skins should be dried in the shade with a sufficient circulation of air to ensure adequate drying."

The method for the curing of merino skins suggested by Shuttleworth was the following.

"After allowing time for the dissipation of body heat, remove any adhering blood or dirt from the skins with a damp cloth. Spread them out with flesh surfaces uppermost, and apply a thorough treatment of clean salt, well rubbed in, taking care not to contaminate the wool. Fold the skins flesh to flesh, and roll in such a manner as to avoid salt adhering to the wool. Leave overnight, and then hang in the shade to dry. When dry remove all adhering salt from both the flesh and wool surfaces."

Experiments with wet- and dry-salted hides gave results which were too inconclusive for definite recommendations to be made, but it appeared that washing of the fresh hide seemed desirable. At least 25% salt per hide weight was required to give satisfactory curing. Rolling of the hides, as with skins, seemed desirable.

Subsequent publications (19,20) from the Research Department emphasised the recommendations put forward by Shuttleworth.

Meanwhile the question of loss incurred through the activities of hide and skin insect pests was receiving attention. Smit (21) carried out some research on this problem, and recommended

for the prevention of damage by the hide and skin beetle (Dermestes vulpinus) that hides be poisoned with a 2 $\frac{1}{2}$ % solution of sodium arsenite. This method was not very satisfactory, and the matter was taken up by the Research Department. Cmer-Cooper (22) published a paper on the general aspects of the problem, and then directed the research subsequently undertaken by Miss Walker, who gave a detailed account (23) of that work. This research revealed that two species of Dermestid beetles were causing most of the damage done in the hide and skin industry. She was the first to describe Dermestes oblongus in this country. Experimental work on the control of these pests as carried out by Miss Walker will be described in Chapter 4. With Woodhead (24) she reported on the application of arsenite containing cattle dips in controlling insect trouble. See Chapter 5.

Harris (25,26) reported that two species of Tineid moths were causing damage to hides and particularly to Merino skins. He described these moths in detail and summarised past methods of control. Subsequent work by the writer (27-32) on these four insect pests revealed that sodium fluosilicate could be applied with very good results. This work is described in Chapters 6 and 7. Other scientific papers from the Insittute (5, 9-13, 33-36) will be dealt with in the appropriate places later on.

Shuttleworth's recommendations regarding propaganda for the farmers have also been followed up. A series of popular-scientific articles (37-53) from the Institute have dealt fully with all the aspects of hide and skin production in South Africa, and it is the intention to ensure by such means that the primary producer is always well acquainted with the most modern methods of treatment of these very valuable products.

SUMMARY.

The improvement of the quality of South African hides and skins has been the subject of a considerable amount of research work and re-organisation, but it was not until the Hide and Skin Advisory Board was formed by the Government that there was any co-ordination of those efforts. The subsequent institution of the Tanning, Hides and Skin Research Department (later the Leather Industries Research Institute) at Grahamstown provided the facilities for increased research into production problems of the industry with special reference to local conditions. The most important report in this connection was that submitted by Shuttleworth (1), a detailed account of his various recommendations being included in this summary of past work on the improvement of South African hides and skins.



SUMMARY OF PART I.

1. The South African hide and skin industry at present brings into circulation a sum of some £3,500,000 per annum, and constitutes a very valuable source of agricultural revenue.

2. The vastness of a sparsely populated country like South Africa brings with it the production of hides and skins in small numbers, this condition of affairs militating against an efficient organisation of the trade and consequently putting serious obstacles in the way of introducing improved methods of production.

3. Serious losses, amounting to about £1,250,000 annually, are borne by the industry because of careless or inefficient handling of livestock, hides and skins, much of the damage being inflicted on the hide or skin whilst still on the living animal by such factors as barbed wire, thorns, whips, horns, branding, bruises in transport and flaying. Inefficient curing and insect damage to stored hides and skins further depreciate the value of our hides and skins, which are already inherently of inferior quality.

4. Much has already been done to improve the quality of South African hides and skins, especially since the appointment of the Hide and Skin Advisory Board.

Research done in the past by the Tanning, Hides and

Skins Research Department (now the Leather Industries Research Institute) has made rapid strides in evolving new and improved production methods, but a large field is still to be investigated.

5. Aspects of hide and skin production which require further research in this country may be summarised as follows:

(i) Elimination of the enormous losses caused by the activities of the Dermestid beetles and Tineid moths in stored hides and skins.

(ii) Elimination of defects in cured hides and skins caused by red heat and other putrefactive bacteria, and salt stains.

(iii) Standardisation of the methods of curing hides and skins at Municipal abattoirs and on farms and in native territories. This would mean that the onus for improvement is made to rest with the primary producer and not, as has been the case in the past, with the shipper at the port.

These three themes form the basis of all the experimental work to be described in the next three Parts.

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P A R T II.

CONTROL OF THE DERMESTID BEETLES AND TINEID MOTHS
IN HIDES AND SKINS.

Chapter 4.

DESCRIPTIVE.

(i) Introduction.

As has been stated in Part I of this work, the activities of insect pests on stored hides and skins in South Africa are responsible for the relatively enormous loss of £500,000 annually to the industry. Few industries can face a capital depreciation of this magnitude without seriously considering means of its avoidance. The apparent unconcern of European and Native farmers, and in some cases also of hide and skin dealers at municipal abattoirs has, however, made it difficult to combat this trouble effectively. Moreover, as will be shown, easy methods of control have not been available.

The trouble is all the more serious since insect damage is so closely associated with the treatment of the raw material. Smit (1) states that badly flayed material is more liable to be attacked, especially if patches of fat and meat had been left on the

flesh side. Hides and skins showing putrefaction, because of faulty or insufficient curing attract insects more than well-preserved stock, and our warm climate encourages putrefaction and provides excellent conditions for propagation of insect pests. Rose (2) in 1932 estimated the annual loss due to bad flaying, improper curing and insect damage to sheepskins alone at £350,000 and this figure has no doubt increased with the increased output of sheepskins.

Four species of insects have been found to attack South African hides and skins. Two, Dermestes vulpinus F. and D. oblongus Sol., belong to the family Dermestidae of the Coleoptera. These beetles are usually known as "moth" or "worm" in the trade, and the writer has found that relatively few store managers are aware of the fact that the well-known black flying insects in stores are the adults of the hairy worms (larvae) so persistently found crawling on hides and skins. These larvae are extremely voracious and are responsible for the greater part of the damage of insect origin to stored stock. The other species concerned belong to the family Tineidae of the Lepidoptera. These true moths are usually referred to as "fly-moth" in the trade. They preferably attack merino sheepskins but have also been found in large numbers on hairy skins and on dried hides.

One species has been tentatively identified as Tinea homestia Meyr by Prof. A.J.T. Jantse of Pretoria; the other is apparently scarce.

Hides and skins are usually accumulated on the farm or at little country shops until a parcel can be made up for dispatch to the dealer, the broker or the shipper at the coast. Consequently the insects have ample opportunity to start and continue the damage, and often material arrives at the coast in a very badly infested condition. Here the insects multiply rapidly during the warm summer months and render many hides and skins practically useless. The filthy conditions under which such hides or skins are stored on the farms, in country shops and even in the big stores at the coast stimulate the activity of the pests, particularly if such stores are moreover dark and badly ventilated.

(ii) The Dermestid Beetles.

The insects belonging to the family Dermestidae (Coleoptera) are apparently world-wide in distribution and their ravages are very varied. The loss incurred to stored products through their activities has induced many workers to investigate and devise means of control. The figures given above speak for themselves as far as South Africa is concerned.

Howard (3) estimated in 1921 that D. vulpinus caused damage only to baled hides and skins in America to an extent of £200,000 annually, and no doubt similar figures apply to other countries. A bulky literature

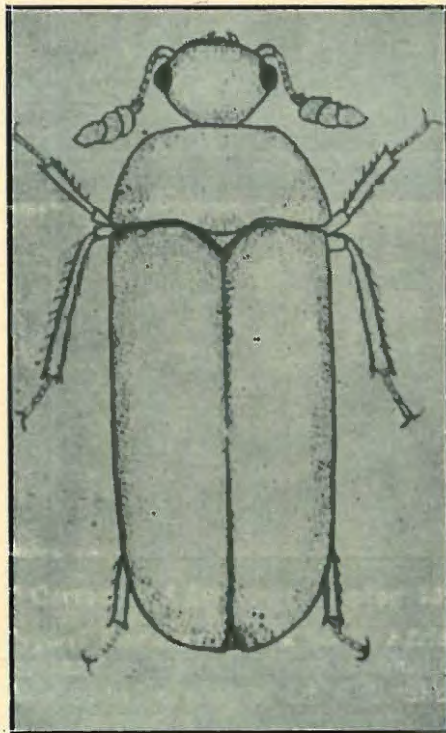


Fig. 8. Adult *Dermestes vulpinus* F. (x 9). - After Walker.

on the Dermestidae is available but only a number of papers having a bearing on the problem confronting the hide and skin industry in South Africa can be reviewed.

Apart from the damage to hides, skins and leather, Dermestid beetles have been reported to infest various other commodities such as tobacco (Runnar - 4, Deckert - 5, and Reh - 6), dried fish (Illingworth - 7,

and Kimura and Takakura - 8) and silkworm houses (Canzanelli - 9). Reh pointed out that the larvae only do this to obtain a safe place to pupate and not because they actually feed on these substances. Hayhurst, 1940, (10) also stressed that infestation is often **adventitious**, the goods usually having been

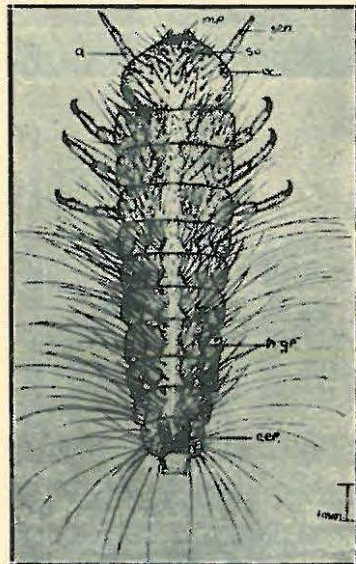


Fig. 9. Larva of *Dermestes vulpinus* F. (x 5). After Walker.

in close contact with infested hides or skins.

The methods of control applied in the past can perhaps best be summarised in the following form.

1. Temperature.

The effect of a sharp increase or decrease in temperature on the life of many insects has led a

number of workers to advocate this as a successful means of control in the case of the Dermestidae. Dean, 1913, (11) reported that he obtained good results in disinfecting books from D. vulpinus by increasing the temperature to 125°F without impairing the books. Zacher, 1925, (12) recommended cold storage of goods liable to be infested. In this he was supported by Clark (13). Robertson, 1933, (14) maintained that the pests could be killed within two hours by a temperature of 115° to 120°F but that they might stay alive for several days at a temperature as low as 5°F. Line (15) also advocated an increase in temperature as high as 125° to 140°F. Mansbridge, 1936, (16) found that D. vulpinus could not survive the cold English winter, but that D. lardarius stood up to such severe conditions. In New Zealand (17) cold storage at 40°F was recommended in cases where D. vulpinus had seriously attacked stored hides. Diakonoff and de Boer, 1938, (18) reported that all stages of this species could be killed by exposure to low temperatures.

The relatively warm South African climate favours the rapid multiplication of these beetles, but experience has taught that the activities and numbers of D. vulpinus are markedly decreased during winter. The difficulties presented, however, in controlling

beetle damage in hide and skin stores by means of an increase in temperature are too manifold to warrant the application of this method. In any case it is only temporary, since re-infestation is bound to take place once the temperatures are normal again. Hides and skins can be stored at low temperatures, although not lower than 32°F for fear of damaging the fibres, but high temperatures will bring about a very undesirable increase in putrefaction.

2. Naphthalene.

The value of this chemical for controlling insects in stored products has been known for a long time and only a few references need be quoted here. Clark (op. cit.) recommended its use in New Zealand for controlling D. vulpinus in stored opossum skins. Belavsky and Raschek, 1930, (19) also reported favourably on its use for hides and were supported by Stather, 1931, (20) and 1934, (21), Kemper (22) and Furlong, 1937, (23). O'Flaherty and Roddy, 1933, (24) on the other hand reported that naphthalene only acts as a repellent and not as an actual poison. In section (iii), paragraph 2 further references to the use and efficiency of this insecticide will be found. Notes on its application in South Africa are given in paragraph 6 below.

3. Fumigation.

Under this heading fall a large number of substances generally recommended by research workers on problems of applied entomology. Kimura and Takakura (8) reported good results with prussic acid gas (HCN) and carbon disulphide (CS₂) fumigation when combatting D. vulpinus and D. cadaverinus in dried cod. Zacher (12), Deckert (5) and Stather (21) maintained that the best results in exterminating insects of this type can be obtained with HCN. Clark (13) reported that infested opossum skins were cleaned by using CS₂. Robertson (14) advocated the use of HCN, CS₂, carbon tetrachloride and ethylene oxide, and was supported by O'Flaherty and Roddy, Kemper, and Line (op.cit.); the latter also found that sulphur dioxide could be applied with considerable success.

Fumigation with most of these substances will, if thoroughly conducted, undoubtedly kill all harmful insects in hide and skin stores, but in many cases it will be found practically impossible to treat such stores. Furthermore, re-infestation is liable to occur within a short time, especially during the South African summer. Smit (1) stated that D. vulpinus lives on the veld as a scavenger of dead animals, and the adults, being able fliers, can travel long distances; it is believed that the olfactory organs are well-developed. Hinton, 1943,

(25) also pointed out that members of the family Dermestidae find natural breeding places in the nests of bees, wasps, caterpillars, birds and rodents and that a natural reservoir is therefore always available.

4. Arsenication.

The toxicity of arsenical compounds presents these chemicals as possible means of control of insect damage to hides and skins. Robertson (14), and O'Flaherty and Roddy (24) recommended the use of arsenical powders for dusting purposes. Furlong (23) maintained that dipping of hides in or spraying with solutions of arsenical compounds gave excellent results, and that this method is used extensively in Madagascar, Nigeria, Tanganyika and other North African countries. In New Zealand (17) it was recommended that hides in store should be painted with a solution containing one pound of sodium arsenite in twelve gallons of water. The work done up to now in South Africa on the use of arsenicals is mentioned in paragraph 6 below.

5. Other Methods.

Para-dichlorobenzene has been recommended for controlling beetle damage to hides and skins. See Clark (13), Evreinova (26), O'Flaherty and Roddy (24), Line (15) and Kemper (22).

Belavsky and Raschek (19) and Stather (21) reported that hides and skins can be safe-guarded by spraying with a mixture of 20 parts petroleum, 3 parts crystalline phenol and 18 parts turpentine.

Rotenone has been recommended by many of the above authors.

Canzanelli (9) found that a bait containing 20% barium fluosilicate killed D. vulpinus, D. frischi, D. lardarius and D. surichalceus.

General recommendations include cleanliness in the stores, and constant moving and re-packing of material so as to remove the insects by means of sweeping etc. Where stock is badly infested it is recommended to put it into process immediately.

6. The Dermestidae in South Africa.

It has been stated above that the warm climate prevalent in this country stimulates rapid reproduction of insects, and especially during the summer months considerable difficulty is experienced in hide and skin stores.

Two methods are in vogue at present in warehouses to control beetle damage. Naphthalene is used extensively with comparatively good results, but it has often been found and proved that under store conditions it only acts as a deterrent. Shippers Poison, con-

-taining arsenical compounds, is used for spraying hides and skins prior to stacking or baling. Constant sorting, because of the extra labour involved, is seldom practised. In most cases however extensive damage is wrought before the hides or skins reach the coast, so that it seems that the remedies are wrongly based on curing instead of prevention.

Smit (27) was perhaps the first to draw attention to the specific damage by D. vulpinus. He found that insect damage is closely related to careless preparation of hides and skins: patches of fat and meat left on the flesh side are very attractive to the insects and proper flaying and curing are therefore recommended to eliminate part of the loss. In 1934 (1) he carried out a series of experiments on arsenication as a means of control. He concluded that "spraying sun-dried hides with a solution of arsenite of soda gave remarkable protection. The two-and-a-half per cent. solution gave better protection than the "Shippers poison". The spraying on the flesh did not altogether protect the grain of the leather although it did so to a very marked extent. Dipping, right off the animal, in a 2½ per cent. solution of the poison proved more effective than spraying. It protected the hides almost entirely from beetle attack".

A review of past work on the control of insects in hide and skin stores was given by Omer-Cooper (28) in 1939, together with valuable information regarding the life-history and activity of D. vulpinus.

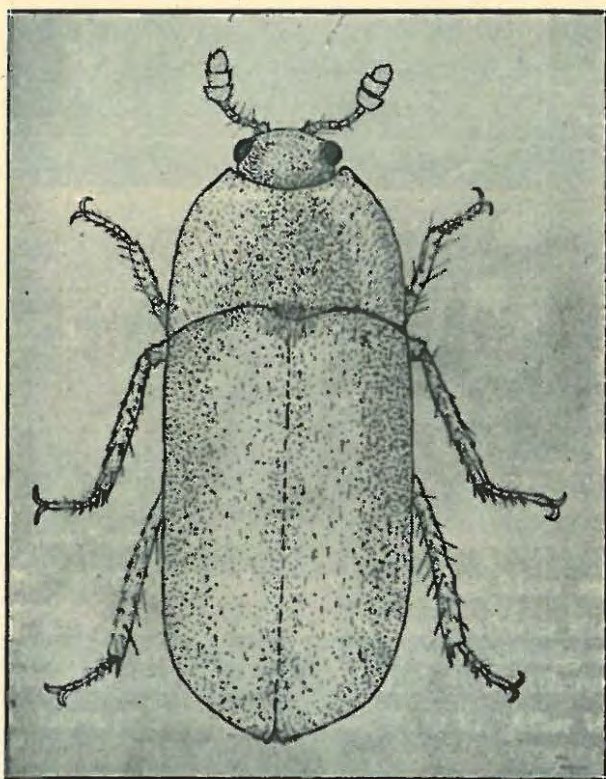


Fig. 10. Adult *Dermestes oblongus* Sol. (x 9). After Walker.

A most important piece of research on this problem was contributed by Walker (28a) in 1941. She was the first to describe the species Dermestes oblongus in South Africa, this species having been originally reported from Chile and later from America and Britain. Miss Walker gave the results

not only of a detailed anatomical and biological study of the species D. vulpinus and D. oblongus, but also of experiments on control measures. She found that borophenol gave excellent protection both as a repellent and as a poison. Sodium fluoride in solutions of 0.1, 0.5 and 1% for dipping of fresh material did not prove effective. Work on the enzyme, collagenase, possessed by these beetles, led Walker to believe that acid poisons would most probably be suitable since the enzyme could function only in alkaline or neutral media. With Woodhead (29) she reported favourably on the use of arsenite-containing cattle dips in which fresh material could be immersed for prevention of insect attack.

(iii) The Tineid Moths.

So far only two species of Tineid moths have been found to damage hides and skins in South Africa, according to Harris (30, 31). One species is described by Harris as follows: The head is ochreous yellow in colour and has a typical high vestiture. The forewings are uniformly pale yellow while the hindwings are light grey. The length of the body varies from 4 to 6 m.m. and the wings are from 8 to 13 m.m. Apparently the male is generally smaller than the female. This species has now been tentatively identified

by Prof. Jantse as Tinea homestia Meyr.

The second species has not yet been identified. It is apparently very scarce and the writer has never found any specimens. Harris described this species from one particular store and stated that he was not able to find it in any other store in Port Elizabeth. It resembles Tineola biselliella

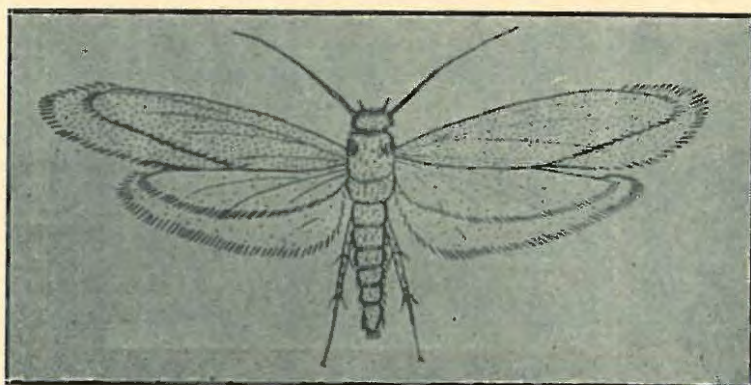


Fig. 11. Adult *Tinea homestia* Meyr. (x 9).

very closely. The forewings are darker than in Tinea homestia and have a characteristic white spot about halfway along the length of the wing.

A number of species of the family Tineidae have been recorded by Hayhurst (op. cit.) to damage wool and dried skins. These include Tinea lapella Hubn, T. pallescentella, T. pellionella L., T. flavescens, Tineola biselliella and Trichophaga tapetzella, all of which are generally referred to as

clothes moths.

In their investigations on the elimination of the damage wrought by these moths, workers have recommended a large number of methods, a few of which are discussed below.

1. Temperature.

As in the case of the Dermestid beetles, high or low temperatures affect the clothes moths adversely. Shafer (32) found that a temperature of 119°F killed the adults of Tineola biselliella. Marlatt (33) recommended cold storage of goods since the insects are rendered dormant at a temperature of 40°F. Keuchenius (34) stated that a temperature of 109°F killed the clothes moth in tobacco after five hours, but a temperature of 32°F (freezing point) only after 120 hours. This is in agreement with the work by Robertson (14) on the effect of low temperatures on the Dermestidae. Severin, 1920, (35) reported death of all stages of the moths within an hour at 140°F, in which he was confirmed by Line (15). Geigy and Zinkernagel, 1941, (36) found that the eggs of T. biselliella did not develop when exposed to a temperature below 50°F.

2. Naphthalene.

This chemical is used extensively in South Africa on sheepskins but the results are not always

satisfactory.

Pliginsky (37) recommended its use in biological collections to ward off T. pellionella. Benedict, 1917, (38) stated that the larvae of T. biselliella were actually killed in woollen goods by naphthalene, and he found support from Scott, Abbott and Dudley (39), Bruneteau (40), Herrick and Griswold, 1933, (41) and Kemper (22). The toxic action of naphthalene has been questioned by Bottimer, 1929, (42) who maintained that it was of little value as a repellent against clothes moth larvae. His opinion was shared by later workers like Evreinova (43), Billings, 1934, (44), Abbott and Billings, 1935, (45) and Frey, 1939, (46). Apparently naphthalene is effective only in enclosed spaces, but the continual draught in most hide and skin stores will render it less effective by removing the toxic vapours. It is often found that naphthalene treated stock is infested with moths and beetles on patches where little or no poison had been strewn, or where the highly volatile chemical had evaporated.

3. Fumigation.

This method has been widely applied for the control of clothes moths. Among the many fumigants recommended (see section ii) HCN seems to be predominant. References which may be consulted in this connection include Cooley (47), Pliginsky (37), Shafer (32),

Keuchenius (34), Andres, 1918, (48), Severin (35), Cotton and Roark (49), Hoyt (50), Bruneteau (40), Herrick and Griswold, 1932, (51), Line (15) and Kemper (22).

4. Para-dichlorobenzene.

The efficiency of this chemical has often been studied and its use has been recommended by Burgess and Poole (52), Herrick and Griswold (53), Line (15), Kemper (22), Evreinova (26, 43) and Frey (46). Bottimer (42), Billings (44) and Abbott and Billings (45), however, maintained that it has little or no value against clothes moths unless it is used in confined spaces.

5. Other Methods.

Scott, Abbott and Dudley (39) found that camphor and pyrethrum could be used with success against the Tineidae.

Rotenone has been recommended by Back, Cotton and Roark, 1930, (54), Line (15) and Kemper (22).

Colman, 1934, (55) obtained good results by spraying goods with hydrogenated naphthalene, while Shepard and Buzicky, 1939, (56) applied methyl bromide and claimed to have obtained excellent results.

(iv) Fluorine Compounds as Insecticides.

The value of fluorine compounds for controlling insect pests has been known for a considerable time, but it is only during the past twenty years that research has brought it to the fore in the ranks of insecticides of inorganic nature. As early as 1896 a British Patent was taken out by Higbee (57) under which were covered several fluorides and fluosilicates "for improved composition of materials for destroying insects". Since that time a bulky literature has been compiled on the subject as shown by Frear, 1943, (58). A few of these papers are briefly discussed below.

Shafer (32) stated that sodium fluoride acts mostly as a stomach poison to insects, but to a certain extent also as a contact poison, a small amount dissolving on the exudations of the body and taken up through the integuments. Work by Scott, Abbott and Dudley (39) proved that this chemical could be used successfully against various species of clothes moths and against the Dermestid beetle, Attagenus piceus. Fulton, 1923, (59) claimed that sodium fluoride has an equal or greater degree of toxicity than arsenious oxide and acts more rapidly than the latter when used as a stomach poison bait for the European earwig, Forficula auricularia L.

Marcovitch has been one of the principal advocates of fluorides and fluosilicates during the past twenty years. In 1924 (60) he reported that sodium silicofluoride (fluosilicate) acts both as a stomach and as a contact poison to various insects, and that it has the following advantages over arsenical compounds:

- (i) It is cheaper;
- (ii) It acts both as a stomach and as a contact poison;
- (iii) It kills more rapidly;
- (iv) It is not so toxic to humans;
- (v) It is toxic to a wide range of insects.

In subsequent papers, 1926 (61), 1926 (62) and 1928 (63) he brought forth more evidence to this effect and also came to the conclusion that sodium fluosilicate is a better poison than sodium fluoride. He recommended (61 and 1933, 64) that woollen goods be dipped in solutions of sodium fluosilicate for protection against Tineola biselliella and Tinea pellionella. His conclusions regarding the efficiency of this chemical as compared with that of arsenical compounds were confirmed by Osburn, 1926, (65). White, Fulton and Cranor, 1929, (66) and Minaeff and Wright, 1929, (67) also experimented on the use of the fluorine compounds to combat moth damage to textiles and

woollen goods. The two latter workers found that sodium fluoride was not as effective as sodium fluosilicate and recommended that materials be moth-proofed by dipping for 30 minutes in a solution containing 0.1% sodium fluosilicate, 0.01% oxalic acid and 0.3% potash alum, the two latter substances being added to increase the rate and degree of penetration of the actual poison.

In South Africa this insecticide has been recommended by Ripley and Hepburn, 1931, (68) and 1935, (69) and by Bishop, 1934, (70) for the control of the fruit flies. It is now used extensively by the Division of Entomology, Department of Agriculture.

Burgess, 1935, (71) claimed that wool can be protected effectively against the ravages of T. biselliella when dipped for 30 minutes in a solution containing 0.5% of sodium fluosilicate. Musser, 1936, (72) confirmed these results and stated that the larvae of the moths and of the beetles, Attagenus piceus and Anthrenus scropulariae, died either from poisoning or from starvation in cases where they refused to eat the treated material. He also noticed that the larvae of the beetles were more resistant to the poison than those of the moths. Hutzel, 1943, (73) successfully experimented with sodium fluoride crayons against the cockroach, Blatella germanica, and

came to the conclusion that the insects died of stomach poisoning when cleaning their tarsi from the powder left by the crayon marks. Parish, 1943, (74) used sodium fluosilicate as a substitute for sodium fluoride, which had become an essential material during the war, and found that poultry lice were effectively controlled either by dipping the fowls into a solution or by using a powder form of the poison. Griffiths and Tauber, 1943, (75) reported that sodium fluoride acted more as a contact than as a stomach poison when used against the roach, Periplaneta americana L. According to their work the cleaning by the mouth of appendages covered with dust is of negligible importance as a factor in the mortality, since death results from contact effects before the ingested poison has had a chance to become lethal.

Although an extensive search was made of all available literature, the writer has not yet (March, 1944) come across any reference to the use to which sodium fluosilicate has been put in the following work, viz. the control of the Dermestid hide and skin beetles.

SUMMARY.

A review of 75 references on the control of Dermestid beetles and Tineid moths has been given, with special attention to the conditions applicable in South African hide and skin stores. About the various recommendations for control measures the following may be concluded.

Temperature. Control by means of an increase or a decrease in temperature in the stores appears to be effective, but it is not practical under the conditions usually prevailing. Even should it be found practical in some cases, reinfestation will take place very soon owing to the fact that the Dermestid beetles live naturally in the veld and are capable fliers.

Naphthalene. This chemical appears to be only effective in confined spaces. Results obtained by South African hide and skin shippers show that it is not very effective. Impure naphthalene may cause stains on the leather.

Fumigation. This method is also unpractical because of the reasons given above with regard to temperature.

Arsenication. It would appear that this method can be used with success, but the objection

against its application in the past is that cured hides or skins are wetted back again. Furthermore, by the time the stock reaches the store for treatment, much of the damage has already been done. If the poison could be applied prior to curing it would be more effective.

Fluorine Compounds. Of the insecticides discussed in this chapter the fluorine compounds seem to be the most promising. Sodium fluosilicate can be obtained in South Africa and would provide a cheap means of preventing insect damage to hides and skins if it proved effective.

Generally speaking, it is suggested that the best method of controlling the insects in hides and skins will be that of prevention rather than cure, i.e. the poison must be put onto the hide or skin during the curing process to avoid damage in transit and during storage.

Chapter 5.

THE USE OF ARSENITE-CONTAINING CATTLE DIPS.

In most districts in South Africa the law enforces the dipping of cattle for the control of ticks, and arsenite-containing tanks are therefore within easy reach of all farmers, European and Native. The toxicity of arsenicals are well-known and in some countries hides are beetle-proofed with these chemicals before storing or shipping. Where the fresh hides are dipped into solutions of arsenicals, the treatment aims at prevention rather than cure, and it is thus all the more effective (23).

Preliminary Experiments.

The bactericidal value of sodium arsenite was tested by immersing pieces of fresh hide for fourteen days in solutions of varying concentrations and examining them macroscopically afterwards. The following strengths were used :

10, 8, 6, 5, 3, 1, 0.5 and 0.25%.

It was found that putrefaction could be prevented by the solutions of high concentration, i.e. above 0.25%, but below this the chemical was ineffective. This is of importance if cattle hides are to be dipped for long periods in such solutions.

Small squares were cut from the treated pieces

and subjected to beetle larvae attack in separate clean glass beakers at a temperature of 22°C. A control piece was kept in a separate beaker. After fourteen days the treated pieces were obviously still intact, but the control was badly damaged. The dead larvae were removed from the beakers and replaced by live ones each morning. The larvae seemed disinclined to eat the poisoned food, consequently the rate of mortality was rather lower than could reasonably be expected. Smit (1) found that hides could be fairly well protected against beetle attack by dipping them for one minute in a solution containing 2.5% sodium arsenite. These and otherwise treated hides were kept in the same store together with controls, so that the larvae could perhaps have shown a preference of food; this is possibly the reason why Smit did not find any dead larvae. The method of testing used above and described in detail below, obviates any such possibility and therefore gives more conclusive results.

In a report by Woodhead and Walker (29) it was concluded that arsenite-containing cattle dips could be used with success for beetle-proofing hides. They experimented on freshly prepared dips and soaked the fresh hides for 24 and 48 hours before subjecting them to larval attack. Fresh dips, however, do not

contain the large amount of foreign matter usually present in dipping tanks, and such materials might have an effect on the insecticidal value of the liquid. Furthermore, it has been stated above that concentrations of sodium arsenite lower than 0.25% could not prevent putrefaction. Dipping tanks usually contain less than this amount, especially in the case of the so-called three and seven day tanks. If a hide is left in such a solution for 24 or 48 hours, loss through putrefaction might result. The experiments of Woodhead and Walker were therefore repeated to test the efficiency of actual dipping liquids and to determine the minimum length of time required for dipping to render the hides beetle-proof.

Larval Tests.

A sample of dipping liquor was kindly provided by the local Grahamstown authorities, the sample having been taken directly after a number of cattle had been dipped so as to make sure that it was representative of the fluid in the tank on the whole. The liquid contained 0.16% sodium arsenite, a seven day strength being in use.

Eight pieces of fresh hide were soaked in a large quantity of this solution for 1, 2, 4, 8, 12,

16, 24 and 48 hours respectively. Mild putrefaction set in on the piece soaked for 24 hours, and in the case of the piece soaked for 48 hours a strong putrid smell was noticed. After drying the pieces in the shade, a small square of each was subjected to beetle larvae attack in separate 100 c.c. glass beakers. This method was adapted from the work by Minaeff and Wright (67) to suit the present problem. Onto each square were put ten mature or nearly mature larvae of Dermestes vulpinus and D. oblongus which had been starved for 48 hours beforehand to rid them of excreta. The beakers were kept in a semi-dark insectary at a constant temperature of 23°C, humidity being provided for by means of a large open dish of water inserted into the cabinet. Since the larvae were unable to climb up against the smooth glass sides, the beakers could conveniently be left open. The amount of loose hair and excreta was taken as an indication of the degree of damage done, especially in those cases where the actual damage was not easily visible. It was however found that after three or four days the larvae did not attack the food very seriously, but disclosed an inclination towards cannibalism: dead larvae were attacked and in extreme cases dying larvae and moults were eaten rather than feeding on the poisoned food. All the excreta present in a particular beaker did therefore not result from actual damage to the piece of

hide. The beakers were examined every morning for fourteen days, the dead larvae being replaced by others that had been starved beforehand. The mortality is represented in Table 2 (overleaf). Taking into account the optimum conditions and the relatively large number of larvae per square inch of hide, it will be agreed that the test is severe and should give a conclusive indication of the efficiency of the treatment.

TABLE 2: EFFICIENCY OF CATTLE DIP -
MORTALITY OF TEST LARVAE.

Hours Dipped.

| Days | 0 (Control) | 1 | 2 | 4 | 8 | 12 | 16 | 24 | 48 |
|-------|-------------|---|---|----|----|----|----|----|----|
| 1. | 0 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 4 |
| 2. | 0 | 1 | 2 | 2 | 3 | 4 | 4 | 3 | 4 |
| 3. | 0 | 0 | 1 | 2 | 2 | 4 | 3 | 4 | 5 |
| 4. | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 4 | 4 |
| 5. | 0 | 0 | 0 | 2 | 2 | 2 | 3 | 3 | 2 |
| 6. | 0 | 0 | 0 | 1 | 2 | 3 | 3 | 2 | 3 |
| 7. | 0 | 1 | 1 | 1 | 3 | 2 | 2 | 2 | 3 |
| 8. | 0 | 0 | 0 | 1 | 1 | 1 | 2 | 3 | 2 |
| 9. | 0 | 0 | 0 | 0 | 1 | 2 | 3 | 1 | 2 |
| 10. | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 2 | 1 |
| 11. | 0 | 1 | 1 | 2 | 0 | 2 | 2 | 2 | 2 |
| 12. | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 2 | 2 |
| 13. | 0 | 1 | 0 | 0 | 1 | 1 | 2 | 1 | 0 |
| 14. | 0 | 0 | 0 | 1 | 2 | 1 | 1 | 2 | 2 |
| TOTAL | 2 | 6 | 9 | 15 | 23 | 28 | 33 | 35 | 36 |

From the Table it will be seen that the mortality dropped lower after the first four days, due to the fact that the hide pieces were left more or less untouched by the larvae. An examination of the pieces

and of the beakers at the end of fourteen days conformed with the figures. The control had been severely damaged, and a considerable amount of damage had also been sustained by the pieces dipped for 1 and 2 hours. The fourth piece, dipped for 4 hours, was in a much better condition. In all the others no actual damage could be seen and the amount of excreta and loose hair present in the separate beakers was a minimum.

SUMMARY.

Experiments have shown that arsenite-containing cattle dips can be used for beetle-proofing hides on farms and in native territories where dipping tanks are available. Fresh hides should be dipped for 8 to 12 hours in such a tank. This time is sufficiently long enough for the hides to absorb an ample amount of the poison, and putrefaction will not set in. If they are left longer than 12 hours in the liquid, loss through decay might occur since the strength of a seven day tank is only 0.16% sodium arsenite, whereas a concentration of at least 0.25% is required to prevent bacterial decomposition of the collagen.

This treatment has the advantage of preventing the insects from attacking the hides at all, and is not based on "curing" of the problem after damage has already been done.

Chapter 6.

THE USE OF SODIUM SILICOFLUORIDE (FLUOSILICATE)
IN SOLUTION.

Minaeff and Wright (67), as a result of a large number of experiments on moth-proofing, recommended the use of sodium fluosilicate very strongly and gave the following directions for protecting wool-len and textile goods against the clothes moth :
Immerse the material for about 30 minutes in an aqueous solution containing 0.1% sodium fluosilicate, 0.01% acid (e.g. oxalic acid), and 0.3% potash alum. The two latter substances are added to increase the penetration of the poison.

The insecticidal properties of the fluorine compounds are well-known (Chapter 4) and experiments were therefore conducted to determine the value of sodium fluosilicate for the prevention of beetle and moth damage to hides and skins. This compound was chosen because it is more effective than sodium fluoride (vide supra) which is also an essential war material, and should it prove successful against the hide and skin pests, could easily be obtained in South Africa. It is at present manufactured by Messrs African Explosives and Industries Limited, Johannesburg.

(i) Preliminary Work.

Although, as was maintained by Minaeff and Wright, aluminium ions increase the rate and the degree of penetration of the poison into woollen and textile goods, it was discarded owing to its tanning properties.

Experiment 1.

The following solutions were prepared for use. Acetic acid was used in the place of oxalic acid.

- | | | | |
|----|-----------------------------------|----|------------------------------------|
| A. | 0.55% Na_2SiF_6 , | B. | 0.44% Na_2SiF_6 , |
| | 0.01% CH_3COOH . | | 0.008% CH_3COOH . |
| C. | 0.27% Na_2SiF_6 , | D. | 0.14% Na_2SiF_6 , |
| | 0.005% CH_3COOH . | | 0.002% CH_3COOH . |
| | E. | | 0.055% Na_2SiF_6 , |
| | | | 0.001% CH_3COOH . |

Four portions of each solution were taken, into which small squares of hide were to be dipped for 5, 10, 20 and 30 minutes respectively.

Twenty-one squares were taken from a wet-salted hide and all loose hairs removed; each piece was about one square inch. One of the squares was kept as a control and the others were dipped into solutions A - E

according to the periods given above. The twenty pieces were thus dipped for varying periods into solutions of different concentrations. They were put into separate 100 c.c. glass beakers and dried in the insectary at 25°C for 40 hours. The beakers were labelled A₁, A₂, A₃, A₄, B₁, etc. where A₁ represented the piece treated for five minutes in solutions A, A₂ for ten minutes, A₃ for twenty minutes, A₄ for thirty minutes, etc. The control was put into a separate beaker to avoid any preference of food possible to be shown by the larvae under test (vide supra). The method of testing the efficiency of the treatments was the same as described for the arsenic dips. In this case, however, fifteen larvae were used on each square and only Dermestes oblongus specimens were taken. This was done because it became apparent that this species is more active and vigorous in its destruction than D. vulpinus, and the larvae are more resistant to the action of poisons or to starvation. The dead larvae were replaced every morning by others which had been starved beforehand. Table 3 represents the rate of mortality over a period of 23 days, keeping the number of larvae at fifteen each day.

TABLE 3 : MORTALITY AMONG LARVAE OF D. VULPINUS WHEN FED ON
SODIUM FLUCOSILICATE TREATED HIDES.

| Days | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 11 | 12 | 13 | 14 | 15 | 16 | 18 | 19 | 20 | 21 | 22 | 23 | Total |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-------|
| Con. | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 4 |
| A.1 | 5 | 4 | 8 | 5 | 4 | 4 | 2 | 7 | 4 | 1 | 2 | 0 | 0 | 6 | 2 | 4 | 5 | 2 | 2 | 67 |
| A.2 | 9 | 4 | 10 | 5 | 4 | 7 | 3 | 3 | 3 | 2 | 5 | 3 | 1 | 7 | 3 | 3 | 2 | 2 | 3 | 79 |
| A.3 | 8 | 3 | 10 | 6 | 5 | 1 | 3 | 4 | 5 | 2 | 0 | 4 | 5 | 7 | 5 | 5 | 2 | 3 | 5 | 83 |
| A.4 | 4 | 4 | 6 | 3 | 3 | 1 | 4 | 6 | 6 | 4 | 3 | 3 | 3 | 5 | 5 | 6 | 4 | 4 | 4 | 78 |
| B.1 | 6 | 3 | 6 | 2 | 4 | 2 | 1 | 5 | 1 | 1 | 0 | 2 | 4 | 1 | 3 | 2 | 2 | 4 | 2 | 51 |
| B.2 | 7 | 5 | 8 | 5 | 5 | 4 | 3 | 3 | 3 | 0 | 3 | 3 | 3 | 8 | 5 | 4 | 3 | 1 | 3 | 76 |
| B.3 | 6 | 2 | 5 | 2 | 5 | 6 | 2 | 6 | 2 | 3 | 2 | 3 | 2 | 1 | 3 | 1 | 3 | 2 | 2 | 58 |
| B.4 | 10 | 4 | 9 | 5 | 3 | 2 | 3 | 3 | 2 | 4 | 4 | 3 | 2 | 5 | 4 | 1 | 4 | 3 | 4 | 75 |
| C.1 | 1 | 1 | 2 | 2 | 2 | 2 | 0 | 3 | 2 | 0 | 1 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 1 | 21 |
| C.2 | 6 | 2 | 1 | 3 | 2 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 2 | 2 | 0 | 2 | 2 | 2 | 1 | 29 |
| C.3 | 3 | 2 | 3 | 1 | 1 | 0 | 2 | 3 | 1 | 0 | 3 | 0 | 2 | 5 | 0 | 0 | 0 | 1 | 3 | 30 |
| C.4 | 4 | 2 | 4 | 4 | 3 | 0 | 2 | 6 | 0 | 0 | 2 | 2 | 0 | 1 | 2 | 2 | 2 | 3 | 2 | 41 |
| D.1 | 0 | 0 | 1 | 0 | 2 | 1 | 0 | 1 | 0 | 2 | 2 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 12 |
| D.2 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 6 | 0 | 1 | 2 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 14 |
| D.3 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 2 | 0 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 11 |
| D.4 | 0 | 3 | 0 | 0 | 2 | 0 | 2 | 2 | 1 | 0 | 2 | 0 | 1 | 3 | 1 | 2 | 1 | 0 | 1 | 21 |
| E.1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 1 | 1 | 2 | 0 | 0 | 1 | 0 | 0 | 1 | 12 |
| E.2 | 0 | 2 | 0 | 1 | 0 | 1 | 0 | 0 | 3 | 1 | 0 | 0 | 2 | 0 | 1 | 1 | 0 | 0 | 1 | 13 |
| E.3 | 0 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 2 | 1 | 2 | 2 | 0 | 3 | 1 | 1 | 1 | 1 | 1 | 20 |
| E.4 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 2 | 1 | 0 | 1 | 0 | 2 | 2 | 0 | 1 | 0 | 1 | 0 | 12 |
| TOTAL | 69 | 44 | 76 | 46 | 46 | 33 | 31 | 67 | 37 | 24 | 36 | 29 | 37 | 60 | 35 | 37 | 32 | 31 | 37 | 807 |

A few points of interest can be gleaned from this Table.

(i) It will be seen that the pieces of hide immersed in solutions A and B were more or less equally poisonous to the larvae, and that the length of the dipping time does not seem to have made much difference in the rate of mortality.

(ii) The pieces of hide treated with solutions D and E were obviously not very poisonous as compared with A and B, and here again the length of the dipping time did not make any appreciable difference. Apparently the solutions were too weak or otherwise too much of the poison had been precipitated by the sodium chloride from the hide. See under (ii) Kinetic Experiments.

(iii) Solution C seems to have been halfway between A and B on the one and D and E on the other hand.

(iv) In the control nearly all the larvae lived for the duration of the experiment.

(v) During the first day more larvae died than during any of the following days; a fairly constant number of 45 per day died from the second to the sixth day, then the number dropped to about 35.

An examination of the squares of hide and of the beakers conformed with the results (i) to (v) above. All the squares in series A and B were intact and did not show any damage; the amount of excreta and loose hair was nominal and more or less the same in all eight beakers. In series C the first three pieces had been attacked and the damage could easily be seen on both the grain and the flesh side; a comparatively large amount of loose hair and excreta was present. The fourth piece which had been immersed for 30 minutes was nearly as intact as those of series A and B. In series D and E all the squares were damaged nearly to the same extent as the control.

From the Table (see remark (v) above) it would appear that the poison slowly but gradually lost its potency. This impression is entirely false. It was noticed on the first day that the larvae ate unconcernedly for a few minutes and thereafter ignored the food. This was also noticed with the fresh starved larvae that were put in as replacements every morning, especially in series A and B. During the following days the survivors expressed an even greater dislike for the poisoned food and seemed to be trying to get away as far as possible from it. Dermestid larvae are accustomed to a semi-dark atmosphere and avoid light if possible. If, however, the

beaker was put in a beam of light with the poisoned piece of hide on the far (dark) side, the larvae would rather go towards the light. They seemed to prefer starving to eating the poisoned food, except of course in series D and E where they could keep on eating without suffering a severe death rate. This is in agreement with the findings of Musser (72). It could easily be distinguished between poisoned and starved dead larvae, since the former showed black patches on the ventral side of the thorax and of the abdomen. As before, cannibalism was noticed, but poisoned larvae were left untouched whereas those that had died from starvation were usually attacked from the ventral side. It would therefore appear that sodium fluosilicate can be recognised as poison by the larvae.

Experiment 2.

Since the larvae seemed to prefer starving rather than being poisoned, it was thought necessary to investigate their resistance to starvation under otherwise optimum conditions. For this purpose twelve nearly mature larvae were put into separate clean glass beakers (to avoid cannibalism) and kept under the conditions of the former experiment. The results were as follows:

| | | | | | | | |
|-------------------|---|---|---|----|----|----|-----|
| Day of Starvation | 6 | 7 | 9 | 10 | 17 | 18 | 20 |
| Total number dead | 0 | 1 | 5 | 7 | 8 | 10 | 12. |

Table 3 proves that sodium fluosilicate affords protection to the hide for at least a longer period than three weeks, and it would therefore be quite efficient as a beetle-proofing agent. Work to be described later in this chapter proved that the poison stays potent for at least six months, and some treated skins have been kept in store for eighteen months without being attacked by insects.

Larvae of the first and second stages, i.e. immature, were also subjected to starvation, and all died between the fourth and the seventh day.

Experiment 3.

To determine how soon the poison will kill off the larvae, the following experiment was put up.

Squares of hide were treated as in Experiment 1 with solutions A and B and were kept for eight days before exposing them to larval attack. Ten mature or nearly mature larvae were used on each square and, as in Experiment 1, the beakers were left open in the insectary at 24.5°C and 100% relative humidity. The results are given in Table 4. The notations A₁,

A₂, etc. correspond to those used before.

TABLE 4: TOXICITY OF SODIUM FLUOSILICATE TO MATURE AND NEARLY MATURE LARVAE OF D. OBLONGUS.

| Days: | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 9 | 10 | 11 | 13 |
|-------|---|---|---|---|---|---|---|---|----|----|----|
| A.1. | 5 | 1 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | - |
| A.2. | 3 | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 5 | 2 | - |
| A.3. | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | - |
| A.4. | 4 | 0 | 3 | 0 | 0 | 2 | 1 | - | - | - | - |
| B.1. | 3 | 0 | 1 | 2 | 2 | 0 | 1 | 0 | 1 | - | - |
| B.2. | 4 | 0 | 1 | 0 | 0 | 2 | 1 | 0 | 1 | 1 | - |
| B.3. | 5 | 0 | 1 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 1 |
| B.4. | 2 | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 2 | 0 | 2 |

As was noticed in Experiment 1 with series A and B, the degree of damage done to the hides was negligible.

A similar experiment with solutions A, B and C was conducted on larvae of the first and second (immature) stages. Again ten larvae were used in each case, and the results are given in Table 5.

TABLE 5: TOXICITY OF SODIUM FLUOSILICATE TO
IMMATURE LARVAE OF D. OBLONGUS.

| Days: | 1 | 2 | 3 | 4 | 5 | 6 |
|-------|---|---|---|---|---|---|
| A.1. | 6 | 3 | 1 | - | - | - |
| A.2. | 6 | 1 | 2 | 1 | - | - |
| A.3. | 4 | 4 | 1 | 1 | - | - |
| A.4. | 7 | 3 | - | - | - | - |
| B.1. | 5 | 1 | 2 | 1 | 1 | - |
| B.2. | 4 | 2 | 0 | 2 | 1 | 1 |
| B.3. | 6 | 2 | 1 | 1 | - | - |
| B.4. | 7 | 0 | 2 | 1 | - | - |
| C.1. | 1 | 3 | 2 | 2 | 1 | 1 |
| C.2. | 5 | 0 | 1 | 2 | 2 | - |
| C.3. | 4 | 2 | 3 | 1 | - | - |
| C.4. | 5 | 1 | 2 | 0 | 1 | 1 |

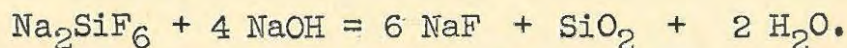
From the last Table it will be clear that sodium fluosilicate is highly toxic to the younger larvae and that the concentrations used will prevent any larvae from maturing. It will also be noticed that the younger larvae are not very resistant to starvation, should they prefer to leave the poisoned food untouched. The length of the dipping period in this case also did not make much difference.

These three preliminary experiments proved that a wet-salted hide could be effectively protected against the ravages of the Dermestid beetles if dipped for 10 to 15 minutes in a solution containing about 0.5% sodium fluosilicate plus about 0.1% acetic acid. To make up such a solution is rather cumbersome and unpractical, and experiments were therefore conducted to determine whether the acid could not be omitted.

The method used above infers that the stock must be already cured before it can be treated. When poisoning of the hide or skin is delayed until it reaches the store at the coast, most of the damage has already been done and the activity of the pests is stopped when it is too late. It would seem that the treatment should be given prior to or during curing, thus aiming at prevention of the damage by insects. Therefore the poison was used in the work described below on the fresh hide.

(ii) Kinetic Experiments.

Sodium fluosilicate will react with sodium hydroxide according to the equation:



A simple titration of the solution with 0.1N NaOH to

phenolphthalein as indicator can therefore be carried out, and the amount of sodium fluosilicate calculated according to the equation above. This method was used by Minaeff and Wright (67), who occasionally checked the results by the ferric chloride method and the rather tedious calcium fluoride gravimetric determination.

Effect of Time on Penetration.

A filtered solution of approximately 0.5% sodium fluosilicate was prepared; 20 ml. of this solution used 21.0 ml. 0.1N NaOH when titrated to phenolphthalein. Four portions of exactly 100 grams of fresh hide were shaken up in separate flasks, each with 100 ml. of Na_2SiF_6 solution for 5, 10, 20 and 30 minutes respectively. 20 ml. from each flask was then titrated with sodium hydroxide and the percentage loss calculated.

| <u>Minutes immersion.</u> | <u>ml. 0.1N NaOH used.</u> | <u>%Loss.</u> |
|---------------------------|----------------------------|---------------|
| 0 | 21.0 | 0 |
| 5 | 15.3 | 27.1 |
| 10 | 14.7 | 30.0 |
| 20 | 14.0 | 33.3 |
| 30 | 13.5 | 35.7 |

These figures on the penetration of the poison compare

favourably with those found by Minaeff and Wright who used wool. The duration of immersion does not influence the rate of penetration very markedly according to the above, and dipping for 15 to 20 minutes can therefore be regarded as adequate. It should be borne in mind, however, that the pieces used in this work were shaken up well with the solution and this would undoubtedly have an effect upon the rate of penetration.

It was then tried to determine the penetration of sodium fluosilicate in a wet-salted hide such as was used in the preliminary work described above. This was however found impossible owing to the fact that on addition of sodium chloride to a solution of 0.5% (i.e. nearly saturated) sodium fluosilicate, the latter will precipitate out.

Effect of Acetic Acid on Penetration.

Different volumes of glacial acetic acid were added to portions of the sodium fluosilicate solution used above and a number of pieces of fresh hide, each weighing exactly 100 grams, were shaken up for 20 minutes with 100 ml. of these acid-containing solutions. 20 ml. from each flask was then titrated with 0.1N NaOH to phenolphthalein. The amount of alkali neutralised by the acid was taken into account

and the results corrected correspondingly. The following Table gives the percentage loss in sodium fluosilicate in the solutions after dipping the pieces of hide.

| % Acetic acid. | ml. 0. 1N NaOH used (corrected) | %Loss. |
|----------------|------------------------------------|--------|
| 0 | 14 | 33.3 |
| .0025 | 14.7 | 30.0 |
| .005 | 15.8 | 24.8 |
| .01 | 16.0 | 23.8 |
| .05 | 16.3 | 22.4 |
| .1 | 16.4 | 21.9 |

It follows that acetic acid inhibits penetration of the poison, even when the acid is very dilute. The addition of 0.1% acetic acid inhibits about 33% of the penetration of pure sodium fluosilicate. It is possible that other chemicals may accelerate the penetration, but it has been found (in experiments to be described below) that a 0.5% solution of the poison affords efficient protection to all types of hides and the addition of such possible chemicals will therefore only incur unnecessary complications.

(iii) Larval Tests with Treated Hides.

The first series of experiments on the control

of the hides and skins beetles by means of a solution of Na_2SiF_6 as described in section (i) of this chapter were carried out on wet-salted hides. Since sodium chloride precipitates out the sodium fluosilicate, as stated above, it is possible that the amount of poison present in the pieces of hide used for those experiments was far less than it would have been in fresh hides. The cost of beetle-proofing a hide with such a solution is very low, and it is unnecessary to consider weaker solutions. Moreover, this may prove ineffective if large numbers of hides have to be put through the same dip. In all the following experiments a solution of 0.5% was used, i.e. nearly saturated.

A. Dipping Fresh Hides.

Four pieces of fresh hide, each weighing 2 Kg., were separately soaked for 15 minutes in two litres of 0.5% solution of Na_2SiF_6 and then cured as follows:

1. Shade-dried after soaking.
2. Sun-dried after soaking.
3. Salted with 33% NaCl after soaking and stacked with other wet-salted hides for a week.
4. Salted and stacked as No. 3 for three days, then sun-dried.

In each case a piece of fresh untreated hide was cured in the same way to act as control. About one square inch was taken from each of these eight pieces and separately subjected to larval attack as described before. Ten larvae of the mature or nearly mature stages were used in each beaker. The results are given in Table 6.

(Table 6 overleaf).

TABLE 6 : MORTALITY AMONG LARVAE OF D. OBLONGUS
WHEN FED ON HIDES TREATED WITH SODIUM
FLUOSILICATE BEFORE CURING.

| Days | Shade-dried. | Con-trol | Sun-dried | Con-trol | Wet-sal-ted. | Con-trol | Dry-sal-ted | Con-trol |
|-------|--------------|----------|-----------|----------|--------------|----------|-------------|----------|
| 1 | 6 | 0 | 7 | 0 | 6 | 0 | 8 | 0 |
| 2 | 5 | 0 | 4 | 1 | 8 | 0 | 6 | 1 |
| 3 | 7 | 1 | 6 | 0 | 5 | 0 | 3 | 0 |
| 4 | 4 | 0 | 4 | 0 | 4 | 1 | 4 | 0 |
| 5 | 4 | 0 | 5 | 0 | 6 | 0 | 3 | 1 |
| 6 | 3 | 0 | 2 | 0 | 3 | 0 | 2 | 0 |
| 7 | 2 | 0 | 3 | 0 | 1 | 1 | 1 | 0 |
| 8 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 9 | 3 | 0 | 0 | 1 | 2 | 0 | 4 | 0 |
| 10 | 1 | 0 | 4 | 0 | 3 | 0 | 3 | 0 |
| 11 | 4 | 0 | 3 | 0 | 1 | 0 | 5 | 0 |
| 12 | 2 | 0 | 2 | 1 | 3 | 0 | 2 | 1 |
| 13 | 3 | 0 | 1 | 0 | 4 | 0 | 1 | 0 |
| 14 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 0 |
| TOTAL | 47 | 2 | 44 | 3 | 48 | 2 | 44 | 3 |

The figures presented above indicate that the poison does not lose any of its efficiency, irrespective of the method of curing adopted after dipping. The untreated controls on the other hand seemed to

provide excellent food for the larvae. At the end of fourteen days the beakers were inspected and the results conformed with those in the Table. All the controls had been badly damaged as was indicated not only by the excreta and loose hair, but also by the tunnels eaten into the hide proper. The dry-salted piece seemed to have been damaged to a worse degree than any of the other. All the poisoned pieces were intact and a minimum of loose hair and excreta was present.

From these experiments it can therefore be concluded that fresh hides will be beetle-proofed if dipped for 15 minutes in a 0.5% solution of sodium fluosilicate, irrespective of the curing they receive afterwards.

B. Dipping Cured Hides.

As was described in section (i) of this chapter, a wet-salted hide can be safeguarded against beetle attack by dipping it in the sodium fluosilicate solution recommended. A large percentage of hides in the stores are however dry-salted, sun-dried or shade-dried and these types are especially prone to damage by insects. It was therefore considered necessary to determine the efficiency of Na_2SiF_6 solution on such hides. For this purpose three pieces of fresh hide

were shade-dried, sun-dried and dry-salted respectively. After thorough curing, one kilogram of each was separately dipped for 15 minutes in one litre of a 0.5% solution of the poison; a small square of each was then dried and subjected to beetle attack under the conditions described before. In each case a control was used. Ten larvae were put onto each piece, the dead replaced every morning as before and the mortality recorded - Table 7.

(Table 7 overleaf).

TABLE 7 : MORTALITY AMONG DERMESTID LARVAE FED ON
HIDES CURED PRIOR TO TREATING WITH
SODIUM FLUOSILICATE.

| Days | Shade-dried | Con-trol | Sun-dried | Con-trol | Dry-salted | Con-trol |
|-------|-------------|----------|-----------|----------|------------|----------|
| 1 | 6 | 0 | 6 | 0 | 5 | 0 |
| 2 | 5 | 0 | 5 | 0 | 4 | 0 |
| 3 | 4 | 0 | 6 | 1 | 7 | 0 |
| 4 | 7 | 0 | 4 | 0 | 4 | 0 |
| 5 | 4 | 0 | 3 | 0 | 3 | 1 |
| 6 | 2 | 1 | 2 | 0 | 5 | 0 |
| 7 | 3 | 0 | 3 | 0 | 2 | 0 |
| 8 | 1 | 0 | 1 | 0 | 0 | 0 |
| 9 | 0 | 0 | 3 | 0 | 3 | 0 |
| 10 | 3 | 0 | 2 | 1 | 1 | 0 |
| 11 | 2 | 1 | 0 | 0 | 2 | 0 |
| 12 | 1 | 0 | 2 | 0 | 1 | 1 |
| 13 | 4 | 0 | 1 | 0 | 3 | 0 |
| 14 | 2 | 0 | 2 | 1 | 2 | 0 |
| TOTAL | 44 | 2 | 40 | 3 | 42 | 2 |

In both Table 6 and Table 7 it will be noticed that the mortality was higher during the first few days. This has been explained above. When the pieces were examined, those that had been treated with the poison were still in excellent condition, whereas the controls had suffered badly again.

Permanence of Treatment.

After three months some of the pieces of hide used in the experiments described were again subjected to larval attack and it was found that the poison had lost none of its efficiency. After eighteen months treated skins which were kept in store were still immune to beetle damage, and it can therefore be assumed that the treatment recommended is "permanently" effective, since it seldom is necessary to store hides or skins for more than two years.

(iv) Large Scale Experiments.

Although it has been proved by the work described above that all cured hides, when dipped for fifteen to twenty minutes in a cold, nearly saturated solution of sodium fluosilicate, can be regarded as permanently beetle-proofed, some objections against the practical application of such a method can be raised. It is detrimental to soak dried material, since it creates an opportunity for putrefactive bacteria to resume their activities. Furthermore, even if dipping is contemplated, a large area would be required to dry the hides again. This dipping method, as tried out experimentally on hides (section iii), was therefore adapted for use only with fresh (green)

hides and skins, and another method was developed for treating unpoisoned stock in the store. See Chapter 7.

A. Wet-salted Hides.

Smit (1) found that "salt thoroughly applied, gave excellent protection against beetle attack". These hides to which he referred had been heavily brined and then salted. Hides which had only been salted were attacked by the larvae, especially on the grain and the edges. It is the experience of the writer that, if other material is not available, the beetles will attack any hide, however heavily it might have been salted.

In the present work five stacks of wet-salted hides were prepared, each stack containing twenty fresh butcher hides. Two to three hours after flaying, the hides were thoroughly washed in cold running water for an hour to remove blood and dirt. 33% clean new salt on the tail weight was then evenly applied and the hides folded and rolled for 48 hours before stacking hair to flesh. The bellies were folded over towards the median line, flesh to flesh, then the hide was folded down the backbone and rolled into a tight bundle.

- Stack 1. Control, treated as above.
- Stack 2. 1% sodium fluosilicate was thoroughly mixed with the curing salt beforehand.
- Stack 3. 2% Na_2SiF_6 mixed with the curing salt.
- Stack 4. 5% Na_2SiF_6 mixed with the curing salt.
- Stack 5. After washing, the hides were dipped for 15 minutes in a saturated solution (1%) of sodium fluosilicate in a wooden tank. The solution was strengthened up after each batch of hides treated, by stirring in 6 ounces of dry powdered Na_2SiF_6 for every 100 lbs. of hide dipped. After this treatment the hides were salted as for stack 1.

The stacks were left undisturbed for the period July/August to January in a store infested with Dermestid beetles. Adult beetles and larvae were obtained from Port Elizabeth at intervals and let loose on the stacks of hides.

Examination of Stacks.

On the 25th of January the stacks were opened and examined for beetle damage.

Stack 1. Most of these hides, although heavily salted, had been attacked on the grain and on the flesh

sides, particularly along the edges which were somewhat dry in appearance. The four top hides of the "battie" or stack had been severely damaged, and a fatty portion on hide No. 2 was riddled with tunnels and holes.

Stack 2. Three of these hides, numbers 1, 2 and 4 from the top of the battie, had sustained damage in isolated spots on the grain. A large number of dead larvae and adults were found with blackened bellies, indicating that they had been poisoned. Vide supra.

Stack 3. Only the two top hides had been slightly attacked on the grain along the edges. As in Stack 2, dead beetles and larvae were found.

Stack 4. One small spot of damage could be found on hide No. 2, where the hair had been eaten away, very near to the edge. The rest of this hide and all the others were intact.

Stack 5. A thorough examination disclosed that no damage had been done either to the grain or to the flesh to any of these hides. Dead larvae and adults were found but no other sign of their activities was discernable, the poison having obviously taken effect very soon.

From these five experiments it became evident

that the best results can only be obtained by dipping the hides in a saturated solution of the poison. If the poison is used as an admixture to the curing salt, a relatively high efficiency can be reached, but the hides are still prone to damage although only to a limited degree. In a wet-salted stack the lower hides receive the dripping brine from the upper, and this liquid, containing as it does a weak solution of sodium fluosilicate, spreads the poison evenly over the lower hides and prevents them from being attacked by the beetles. Where the grain of one hide is in close contact with the "poisoned" flesh of the one just underneath it, the beetles are warded off but the outsticking edges are still vulnerable. It is impossible to mix the poison and the salt very evenly, and patches of the hide might therefore not receive any preventative treatment. Furthermore, as will be shown in Part III of this book, the dipping method is much superior to the mixed-salt method for the prevention of the development of red heat and consequently of other putrefactive bacteria on wet-salted stock.

B. Dried Hides.

Shade-dried, sun-dried and dry-salted hides and skins are more susceptible to insect damage than

wet-salted stock, and most of the loss suffered by the hide and skin industry through insect activities results from the damage to such dry stock in stores. The laboratory experiments described above were therefore repeated on works scale to test the efficiency of the dipping method under normal store conditions.

Experiment 1. Twenty green butcher hides were washed for an hour in cold running water and then dried in the shade, suspended by ropes. These hides acted as control.

Experiment 2. As Expt. 1, but dipped for 15 minutes in a cold saturated solution of sodium fluosilicate before drying.

Experiment 3. Ten green hides were washed, salted with 33% NaCl on the tail weight as previously described, rolled for 48 hours and then dried in the shade. Control for Expt. 4.

Experiment 4. As Expt. 3, but dipped before salting.

Experiment 5. Five green hides were washed and then dried in the sun. Control for Expt. 6.

Experiment 6. As Expt. 5, but dipped before drying.

The hides were put in separate stacks in a store infested with Dermestid beetles.

Examination of Packs.

Between September and January the hides were not disturbed and occasionally more adults and larvae were procured to provide infestation of the packs. They were opened and examined at the end of January.

Experiment 1. On all these hides large numbers of adult beetles, larvae and Tineid moths were found and some hides were seriously damaged in patches. This was especially noticed on hides which had been badly flayed and had fatty patches on the flesh sides.

Experiment 2. Although a number of dead insects were found in this pack as well as a few live larvae crawling about, no damage whatsoever could be seen. All the hides were in excellent condition.

Experiment 3. The beetles had shown a marked preference for these dry-salted hides and extensive damage had been sustained in one case, the hide being riddled with tunnels and holes near the left shoulder where a patch of fat had been left in flaying.

Experiment 4. No damage could be found here, as in Expt. 2.

Experiment 5. These hides could be compared with

those in Expt. 1 as far as damage was concerned. Large numbers of Tineid moths were present and their larvae and pupae were found in the characteristic silken tunnels.

Experiment 6. No damage was done to any hide. Only dead larvae and adults of Dermestes vulpinus and D. oblongus were found. No Tineid moths were seen.

The condition of the treated and the untreated control hides in these six experiments provided ample proof that the method of dipping the fresh hides before curing can give excellent protection to stock against the ravages of the Dermestid beetles and Tineid moths.

C. Sheepskins.

The larger part of the insect damage to sheepskins is due to the activities of the two Tineid moths described in Chapter 4, Section (iii). Minaeff and Wright (67) found that dipping woollen and textile goods in a 0.1% solution of sodium silicofluoride proved effective against the clothes moth, and it was consequently considered reasonable to expect that the treatment given to hides against the beetles would

also be effective against the moths if applied to sheepskins. Musser (72) found that the larvae of the clothes moth were not as resistant to this poison than the larvae of the carpet beetle. On the other hand, the Dermestid beetles also attack sheepskins in store, and the treatment therefore must be effective against these pests in the first place.

It is very difficult to dry wool-sheepskins after washing and/or dipping, and a method had to be developed to deal with this type of skin. The following experiments were put up.

The treatment of the skins was as follows (hairy Capes were used): Wash thoroughly, then apply 10% salt of fine to medium grain evenly to the flesh, well rubbed in, and roll as for hides. Leave for 24 hours, re-salt with 10% salt on the skin weight, roll for 24 hours and dry. Drying was done on frames, the skins being loosely fastened to prevent tension on shrinkage. The frames were put at an angle of 45°, the flesh side up, facing due South so that the rays of the sun struck the surface at an angle all day and overheating could be prevented. Drying took one to two days in this way.

Experiment 1. Twelve Capes treated as above. Control.

Experiment 2. Twelve Capes dipped in the recommended solution directly after washing, then treated as above.

Experiment 3. Twelve Capes treated as for Expt. 1, but with 2% Na_2SiF_6 mixed with the curing salt beforehand.

Examination.

These skins were stored in a beetle and moth infested room for the period August to February. At intervals beetles and moths were collected and let loose on the skins to increase the infestation.

Experiment 1. Adult beetles and larvae and adult moths were found in large numbers on these skins. On closer examination moth larvae and pupae could be seen. In most cases the hair had come loose in patches and the grain had been damaged.

Experiment 2. Dead insects were found in this pack, but no damage was seen. A few adult beetles and moths crawled over some of the skins, but no live larvae could be found.

Experiment 3. The skins in this pack compared very favourably with those of Expt. 2. The flesh and grain sides were undamaged by beetles, but a few live

moth larvae were found in the hair of one skin.

All the skins used in these experiments had been very well cured, were free from fat and dirt, and consequently the infestation was not as heavy as is usually the case in stores.

SUMMARY.

Experiments on the control of the Dermestid hide and skin beetles have shown that sodium fluosilicate used in solution form is a powerful beetle-proofing agent. Wet-salted hides dipped for 20 minutes in a solution containing 0.55% Na_2SiF_6 plus .01% acetic acid were rendered immune from attack by these beetles under controlled conditions as described.

Kinetic experiments revealed that acetic acid inhibits penetration of the poison into fresh hide and should therefore not be used. The effect of time on penetration was also studied and it could be safely concluded that dipping of fresh hides for 15 minutes into a saturated solution of the fluosilicate would ensure adequate penetration.

Pieces of fresh hide dipped beforehand for 15 minutes into a solution containing 0.5% sodium fluo-

silicate were cured in different ways and, when subjected to beetle larval attack under controlled conditions, proved to be effectively protected.

The same treatment to cured hides gave excellent protection against the beetles.

Large scale experiments on dipping of fresh hides and skins prior to curing (wet-salted, dry-salted, shade-dried or sun-dried) for 15 to 20 minutes in a saturated solution of sodium fluosilicate confirmed the results obtained in the laboratory. The Tineid skin moths are also effectively controlled by this method.

The alternative method of mixing the curing salt and the solid poison for wet-salted hides or for dry-salted skins will help considerably to avoid insect damage, but the treatment does not give very good results and is not recommended.

It was proved that the method of dipping the material prior to curing renders all hides and skins permanently insect-proof. Skins have been kept for eighteen months without showing any signs of insect activity.

Chapter 7.

THE USE OF DRY POWDERED SODIUM FLUOSILICATE
FOR DUSTING.

Since the method of dipping cured hides or skins in a solution of sodium fluosilicate for the prevention of insect damage is effective but impracticable and detrimental to the stock as shown in the previous chapter, it was decided to experiment on the use of the poison in dry form as a dust. This method of using Na_2SiF_6 has been tested by various workers against different insect pests, and should it prove effective would be of great value to the hide and skin stores at the coast where material often has to be kept for considerable periods before shipping.

(i) Laboratory Experiments.

The first experiment aimed at determining the weight of pure sodium fluosilicate necessary per hide. Four pieces of wet-salted hide, each weighing 4 Kilograms, were sprinkled on the flesh side with different amounts of the chemical to give the following percentages solid poison by weight on the pieces : 0.5%, 1%, 2% and 3%. After treatment, the hide pieces were stacked with other wet-salted hides in the battie and

left for seven days. A small piece of about one square inch was then taken from each and dried at 25°C. These squares and a control piece of untreated wet-salted hide were subjected to attack by mature and/or nearly mature larvae of both Der-
mestes vulpinus and D. oblongus by the method described before. Ten larvae were put into each beaker and this number was kept constant by replacing the dead ones every morning. All the larvae were starved beforehand to rid them of excreta. The mortality in the five beakers over a period of fourteen days is given in Table 8.

(Table 8 overleaf).

TABLE 8 : MORTALITY AMONG DERMESTID LARVAE
 FED ON WET-SALTED HIDES DUSTED WITH SOLID
SODIUM FLUOSILICATE.

| Days | Control | 0.5% | 1% | 2% | 3% |
|-------|---------|------|----|----|----|
| 1 | 0 | 3 | 5 | 6 | 8 |
| 2 | 0 | 2 | 4 | 4 | 6 |
| 3 | 0 | 2 | 6 | 6 | 5 |
| 4 | 0 | 1 | 4 | 4 | 6 |
| 5 | 0 | 0 | 2 | 5 | 3 |
| 6 | 1 | 2 | 3 | 3 | 4 |
| 7 | 0 | 1 | 4 | 2 | 2 |
| 8 | 0 | 3 | 1 | 3 | 4 |
| 9 | 0 | 2 | 2 | 4 | 5 |
| 10 | 1 | 0 | 1 | 2 | 3 |
| 11 | 0 | 0 | 3 | 1 | 3 |
| 12 | 0 | 2 | 2 | 3 | 2 |
| 13 | 0 | 1 | 2 | 4 | 4 |
| 14 | 0 | 2 | 1 | 2 | 3 |
| TOTAL | 2 | 21 | 40 | 49 | 58 |

A careful examination of the test pieces of hide and their respective beakers revealed that in all the treated pieces the amount of damage done was either very slight or was entirely negligible. The

0.5% treatment gave good results, but damage was visible on the piece of hide, apart from the loose hair and excreta present in the beaker. In all the other treated pieces the amount of loose hair and excreta was a minimum. The control had been severely damaged. From this experiment it may be concluded that 1% sodium fluosilicate dusted over the flesh side of a wet-salted hide will afford excellent protection under the conditions of the experiment. It must be remembered however that the test pieces were stacked in a wet stack with other hides, therefore the poison had a chance to spread evenly over the surface of the hide. Even so, it is difficult to dust the hide evenly, hence the fact that damage on the piece treated with 0.5% poison showed up only in patches.

Wet-salted hides are, however, very seldom stored and they would not require such treatment. Dry hides on the other hand are always prone to insect attack, consequently the efficiency of the poison in dust form had to be tested on such hides.

For this purpose pieces of shade-dry, sun-dry and dry-salted hides were dusted on the flesh side alone with 1% sodium fluosilicate per weight of hide and small squares of each subjected to beetle attack

under the same conditions as before. A control was used in each case and ten larvae were put into each beaker. The mortality is recorded in Table 9.

TABLE 9 : MORTALITY AMONG DERMESTID LARVAE FED ON
CURED HIDES DUSTED WITH SODIUM FLUOSILICATE.

| Days | Shade-dried | Control | Sun-dried | Control | Dry-salted | Control |
|-------|-------------|---------|-----------|---------|------------|---------|
| 1 | 6 | 0 | 5 | 0 | 6 | 0 |
| 2 | 5 | 0 | 5 | 0 | 6 | 1 |
| 3 | 6 | 0 | 4 | 0 | 4 | 0 |
| 4 | 4 | 0 | 4 | 1 | 5 | 0 |
| 5 | 5 | 0 | 5 | 0 | 3 | 0 |
| 6 | 3 | 1 | 3 | 0 | 4 | 0 |
| 7 | 4 | 0 | 2 | 0 | 3 | 0 |
| 8 | 2 | 0 | 3 | 0 | 1 | 0 |
| 9 | 1 | 0 | 2 | 0 | 2 | 1 |
| 10 | 3 | 0 | 0 | 0 | 2 | 0 |
| 11 | 2 | 1 | 1 | 1 | 2 | 0 |
| 12 | 3 | 0 | 3 | 0 | 1 | 0 |
| 13 | 1 | 0 | 2 | 0 | 2 | 1 |
| 14 | 2 | 0 | 1 | 0 | 3 | 0 |
| TOTAL | 47 | 2 | 40 | 2 | 44 | 3 |

A careful examination of the pieces of hide in the separate beakers showed that no damage had been

done to any of the treated pieces, whereas the controls had been attacked both on the grain and on the flesh. The dry-salted control had lost nearly all its hair.

Adult beetles.

Some of the pieces of hide used in the experiments described above were subjected to attack by the adults of Dermestes oblongus and D. vulpinus. In all cases the poison was lethal and in some instances killed off all the beetles in the particular beaker within sixty hours. This will prove a considerable help in the control of the pests, since the adults will be prevented from reproducing, should they perhaps survive the larval stages or enter the stores from the veld. Whether the beetles and larvae are killed by contacting the poison or by ingestion, is not yet certain. See Griffiths and Tauber (75). From the above experiments it would appear that death is due to both factors. Hide pieces dusted only on one side were not attacked on the unpoisoned side and the mortality was high among the larvae although the places where they had eaten could not always be discerned.

Note: From Table 8 it was concluded that more than 0.5% solid sodium fluosilicate per weight of hide was

required to prevent damage. This is possibly another reason why those hides salted with a mixture of sodium chloride and the poison had been attacked to a certain extent as described in chapter 6.

(ii) Large Scale Experiments with Commercial
Solid Sodium Fluosilicate.

The sodium fluosilicate as supplied by Messrs. African Explosives and Chemical Industries contained 15% moisture and was rather too lumpy for dusting purposes. It was therefore dried and sifted before use, the moisture content thereby being decreased to 2%.

Two series of experiments were put up, one with hides and the other with sheepskins.

A. Hides.

Hides in store can, according to preliminary experiments as described above, be beetle-proofed by dusting with dry powdered sodium fluosilicate. One method of protection in vogue at hide and skin stores is that of spraying the hides with Shippers Poison which contains arsenical compounds. Both these methods were therefore tried out in a store, using Na_2SiF_6 .

Thirty sun- and shade-dried hides were selected in a store and all eaten patches carefully painted red to avoid confusion with possible fresh damage. These hides were selected because the beetles had shown a preference for them. All of them had been folded double along the backbone, hair to hair. Three sets of ten each were used.

Experiment 1. These ten hides were bundled and tied without any treatment to act as control.

Experiment 2. The hides were opened slightly to dust them both on the grain and on the flesh with dry powdered sodium fluosilicate prior to bundling. Six to eight ounces of powder were used per hide.

Experiment 3. A 1.5% "solution" of sodium fluosilicate was sprayed lightly over the flesh side alone of the hides before bundling, in the same way as Shippers Poison is applied. The solution had to be stirred continuously to keep the poison in suspension.

Examination of Hides.

The three bundles were stored together in a semi-dark corner of the store from November to March to subject them to the concerted attacks of the

beetles during the summer months.

Experiment 1. These hides were heavily damaged on both sides by Dermestid beetles and Tineid moths. In two cases the grain was covered by the silken tunnels spun by the moth larvae and the hides were in a very bad condition.

Experiment 2. A number of dead beetles and moths, both adults and larvae, were found on these hides but no fresh damage could be discovered. A few live moths and adult beetles crawled over some of the hides; they were apparently only "visitors" from the control bundle. With regard to insect damage these hides seemed to be in excellent condition apart from the effects of attacks before the treatment.

Experiment 3. As in the case of experiment 2 many dead insects were found on the hides, but in this case the grain had been attacked in small spots. The hides had also developed mould growth despite the fact that they had been dried for 24 hours after spraying.

B. Sheepskins.

The difficulties presented in insect-proofing this type of material have already been mentioned earlier when it was pointed out that dipping was imprac-

licable in some cases and spraying detrimental.

750 dry-salted glover skins of the Cape Persian type were selected in a store and divided into five lots of 150 skins each for the following experiments.

Experiment 1. The skins were baled immediately without any treatment to act as control.

Experiment 2. Naphthalene was strewn over the flesh side of each skin while the bundle was being made up, in the manner practised by shippers and brokers.

Experiment 3. These skins were sprayed on the flesh side with Shippers Poison and dried in the store for 24 hours as usual before baling.

Experiment 4. About one quarter of an ounce of solid sodium fluosilicate was dusted over the flesh side of each skin as it was being put into the bale. The skins were stacked hair to flesh.

Experiment 5. These skins were dusted on the flesh as for Expt. 4, and then the sides of the bale lightly dusted with about six ounces to each side.

Experiment 6. In this experiment 110 Short Wool Merino skins were baled without treatment, the bale

weighing 500 lbs. After baling, each side was dusted with eight ounces of powdered sodium fluosilicate.

Examination.

The six bales were stored together in a semi-dark store heavily infested with Dermestid beetles and Tineid moths, and left undisturbed for the period November to March. An examination of the bales revealed the following.

Experiment 1. Live beetles and moths, both adult and immature, were abundant in this bale and extensive damage had been wrought, not only to the flesh but also to the grain and hair. The moth larvae were especially responsible for the latter type of damage. The edges of the skins in the bale had been particularly attacked. Pupae of the beetles and of the moths were found, indicating that the larvae had been in the bale for a long time.

Experiment 2. These skins were in a much better condition than the former, but limited damage had been sustained along the edges where the naphthalene had either fallen off or had evaporated. Live insects were found inside the bale, apparently not deterred by the smell.

Experiment 3. The skins in this bale could be compared with those in the former bale. Moths were present in considerable numbers and some skins had been attacked by both moth and beetle larvae. The skins were wet and mouldy, despite the drying they had received after spraying. Apparently longer drying in the store, or drying in the sun would be necessary to remove all the moisture applied during spraying so as to prevent mould growth. This would, however, incur extra labour and would require a large space to handle a large number of skins.

Experiment 4. This bale was in a better condition than the three former with regard to insect damage. A large number of dead beetles were found. Only along the edges a few live moth larvae were seen in their silken tunnels, but the skins had sustained practically no damage.

Experiment 5. No insect damage of any form was done to the skins in this bale, although dead adult and immature beetles and moths were abundant. A few live adult moths and beetles were found on the edges of the bales, these having probably come there while the bales were being moved for inspection.

Experiment 6. The merino skins of this bale were excellently protected and no damage could be discovered. The powder had not affected the wool and stayed on

remarkably well despite handling of the bale.

From these results it can be concluded that sodium fluosilicate powder is more effective than either naphthalene or Shippers Poison and can be used without danger to the skins. The best method of application would be to dust one side of every skin lightly while making up the bale or pile, using about one pound of dry powder for every fifty skins. After baling, the sides of the bale are also dusted, eight ounces per side being applied. The efficiency of the powder when applied only to the flesh side depends upon the fact that the wool or hair of the next skin comes into direct contact with the poison and is therefore protected against insects.

It should be pointed out that sodium fluosilicate is poisonous to human beings, although nine times less so than lead arsenate, and no unnecessary risks should therefore be taken by workmen handling the powder.

SUMMARY.

Laboratory experiments showed that all types of cured hides could be effectively protected against damage by Dermestid beetle larvae by dusting one side

only with about 1% of dry powdered sodium fluosilicate per weight of hide. This treatment also proved lethal to adult beetles.

Large scale trials, using 6 to 8 ounces of powdered sodium fluosilicate dusted onto both the flesh and the grain sides of dried hides, proved the efficiency of such a treatment against the Dermestid beetles and Tineid moths.

Large scale experiments with cured (dry-salted and sun-dried) sheepskins revealed that sodium fluosilicate is more effective than either naphthalene or shippers poison in preventing insect damage. The most efficient treatment was that of dusting each skin (one pound of powdered sodium fluosilicate for every fifty skins), followed, after baling, by a light dusting (6 to 8 ounces per side) of the bale sides.

SUMMARY OF PART II.

1. A review has been given of past work on the control of the Dermestid beetles and Tineid moths attacking stored hides, skins and woollen materials, with special reference to the two species of Dermestes occurring in South Africa: D. vulpinus F. and D. oblongus Sol.

2. Experiments proved that arsenite-containing cattle dips, such as are found in nearly every district in South Africa, can be utilised in controlling insect damage to hides and skins. Fresh hides dipped for 8 to 10 hours in such a tank prior to curing will be afforded excellent protection, but there is danger of loss through putrefaction.

3. Investigations on the use of sodium fluosilicate as an insecticide in the hide and skin industry led the writer to recommend the following.

A. Fresh hides and hairy skins should be dipped for 15 to 20 minutes in a saturated solution of sodium fluosilicate. After such treatment any recognised method of curing can be applied.

B. Where it is not possible to dip the fresh material, 2 to 3% of the solid poison should be well mixed with the curing salt. This method is recommended for sheepskins which dry with difficulty when wetted by washing or dipping.

C. Hides in store should be dusted on both sides with dry powdered sodium fluosilicate, 6 to 8 ounces being applied per hide.

D. Sheepskins in store are best protected by

lightly dusting each individual skin on the flesh side while making up a pile or bale, one pound of powder being used for every fifty skins. After piling or baling, the sides of such a pile or bale are dusted with about one pound of powder per hundred square feet.

4. General recommendations, following from past work on this problem and from the writer's own experience, include the following.

(i). Better flaying, to remove fat, renders hides and skins less prone to attack by the Dermestid beetles. Handfleshed cured Glover skins can be kept quite long without any treatment.

(ii). Stores should be kept as clean as possible so as to deprive the insects of breeding places.

(iii). A light, well-ventilated store is less easily infested than a dark, damp store.

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APPENDIX A.

D. D. T. IN THE HIDE AND SKIN INDUSTRY.

The wide interest aroused by numerous reports upon the efficiency of D.D.T. (Dichlorodiphenyl-trichloroethane) as a new synthetic organic insecticide against a great variety of insect pests has been the cause of considerable speculation upon its value in controlling the insect pests attacking cured hides and skins in South Africa. Soon after details of its manufacture had become available, Mr. A.M. Stephen of the Institute staff prepared a sample of D.D.T. for laboratory scale experiments with larvae of the Dermestid hide and skin beetles. These experiments were commenced during December, 1944.

Since D.D.T. is insoluble in water, but readily soluble in cheap organic solvents like household paraffin (kerosene), the latter was chosen as solvent. It has the advantage of evaporating, thereby leaving a thin layer of poison over the hide surface without increasing the weight of the hide as easily happens in the case of Shipper's Poison.

According to many reports in overseas

entomological journals D.D.T. is so effective that concentrations of .025 milligrams per square centimetre prove lethal to various insects. In the preliminary work with the D.D.T. prepared at the Institute, concentrations ranging between .005 and 0.25 milligrams D.D.T. per square centimetre were used, being sprayed onto the pieces of hide with a small perfume spray. None of these were lethal to the Dermestid larvae, and only the concentrations above 0.1 mgm/sq. cm. succeeded in slightly repelling the larvae from damaging the test hide pieces. Tests with the same sample of D.D.T. against the housefly and fleas showed that it was toxic enough to these insects.

In order to ascertain the validity of the negative results obtained with the first sample against the Dermestid larvae, further experiments were conducted with two commercial samples of D.D.T. and a sample of thrice crystallised D.D.T. prepared by Mr. Stephen. Kerosene was again used as solvent, the mixture being sprayed onto both sides of the test hide pieces. The procedure was as follows:

Four pieces of dry-salted hide were sprayed on both sides to give concentrations of .01, .05,

0.1 and 0.25 milligrams D.D.T. per square centimetre of hide, and then left in the insectary at 24°C. for ten days to allow the kerosene to evaporate thoroughly. One such series was prepared with each of the two commercial samples (A and B) and the sample prepared at the Institute (C). A thirteenth piece of hide was kept as untreated control, while a fourteenth was sprayed with pure kerosene also as control. The fourteen pieces were put into separate clean glass beakers and left in a semi-dark insectary at 24°C., humidity being provided for by means of a large dish of water. Onto each piece were put ten starved larvae of Dermestes oblongus of the fourth stage. Each morning dead larvae were recorded and replaced by others which had likewise starved for 48 hours beforehand to rid them of excreta which might otherwise give erroneous indications of the efficiency of the treatment. In a few cases larvae pupated and were then replaced by fresh specimens. The mortality is recorded in Table 10 below. Up to the sixth day no larvae died.

TABLE 10. MORTALITY OF DERMESTID LARVAE FED ON
HIDES TREATED WITH D. D. T.

| Days | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | TOTAL. |
|---------------------|---|---|---|---|----|----|----|----|----|--------|
| A .01 | 0 | 1 | 1 | 0 | 0 | 0 | 2 | 0 | 0 | 4 |
| A .05 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 2 | 5 |
| A 0.1 | 0 | 2 | 2 | 0 | 0 | 3 | 1 | 0 | 1 | 9 |
| A 0.25 | 0 | 1 | 1 | 2 | 3 | 1 | 0 | 2 | 1 | 11 |
| B .01 | 0 | 0 | 1 | 2 | 0 | 0 | 1 | 0 | 0 | 4 |
| B .05 | 0 | 2 | 0 | 0 | 1 | 3 | 1 | 0 | 1 | 8 |
| B 0.1 | 0 | 1 | 1 | 2 | 2 | 0 | 1 | 0 | 2 | 9 |
| B 0.25 | 0 | 1 | 3 | 1 | 2 | 1 | 0 | 3 | 1 | 12 |
| C .01 | 0 | 0 | 1 | 2 | 0 | 0 | 1 | 0 | 0 | 4 |
| C .05 | 0 | 1 | 0 | 1 | 1 | 2 | 0 | 1 | 0 | 6 |
| C 0.1 | 0 | 2 | 1 | 1 | 2 | 1 | 3 | 0 | 1 | 11 |
| C 0.25 | 0 | 1 | 0 | 3 | 1 | 0 | 1 | 2 | 2 | 10 |
| Control | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 2 |
| Paraffin Control | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 3 |

Although only very slightly so, the pieces treated with D.D.T. were more toxic to the larvae than either of the two controls.

Examination of the pieces of hide and the beakers after the test period showed the following:-

- (1) Both the controls were severely damaged, the hair being nearly completely removed in both cases.
- (2) Visible damage had been sustained by all the pieces treated with .01 and .05 milligrams D.D.T. per square centimetre.
- (3) The damage done to the pieces treated with 0.1 and 0.25 mgm/sq. cm. could not be detected on the pieces themselves, but was indicated by a small amount of loose hair and excreta present in the beakers.

This second series of experiments therefore showed that the negative results obtained with the first sample of D.D.T. were valid. D.D.T. appears to have only a slight toxic effect upon the larvae of Dermestes oblongus as compared with its effect upon other insects. To a certain extent it will repel the larvae from damaging the hides.

Further investigations appear to be necessary before a completely negative report is accepted. Such investigations should determine the relative value of different solvents and/or emulsions of the poison.

APPENDIX B.

THE USE OF GAMMEXANE IN THE HIDE AND SKIN INDUSTRY.

In June, 1945, a new insecticide was released from the laboratories of Imperial Chemical Industries, and its apparent potency against many types of insects caused considerable comment, especially since it was claimed to be more powerful than the newly applied D.D.T. This new insecticide contains several isomers of chlorinated benzene and has been given the name of 666 or Benzene hexachloride (B.H.C.). One of the isomers, the gamma, is the most toxic, and is known as "Gammexane". Usually crude 666 or B.H.C. contains about 10% Gammexane. A sample of poison dust, containing 20% 666 mixed with gypsum as carrier, was obtained through the courtesy of the Senior Entomologist of African Explosives and Chemical Industries at Grahamstown, and was tested out on laboratory scale against the larvae of the Dermestid hide and skin beetles.

Since the amount of poison to be used was so small, it was decided to mix the dust with three parts its weight of pure acid washed Kaolin to act as carrier with the gypsum, in order to obtain more

even distribution.

Five pieces of dry-salted hide were dusted on both sides with this mixture, calculated to give concentrations of 0.25%, 0.5%, 1%, 1.5% and 2% of the original dust as supplied per weight of hide. The concentration per area, in milligrams per square centimetre, was approximately as follows: 0.6, 1.2, 3.4, 4.6, 6.0.

One piece of the hide was dusted with Kaolin (20 mgm per sq. cm.) to act as control. Another piece was kept as control. Another piece was kept as untreated control.

The experiment was then conducted along the same lines as used formerly with sodium fluo-silicate in dust form. The seven test pieces of hide were put into separate clean glass beakers which could conveniently be left open. Onto each piece were put ten larvae of Dermestes vulpinus of the fourth and fifth larval stages. All the larvae had been starved for 24 hours beforehand to rid them of excreta. The seven beakers were then inserted into a semi-dark insectary at 24°C; humidity was provided for by means of a dish of water. Each morning the dead larvae were removed and recorded. The mortality was as follows: (Table 11).

TABLE 11 : MORTALITY OF DERMESTID LARVAE FED ON
666 TREATED HIDES.

| Days | Control | Kaolin control | 0.25% | 0.5% | 1% | 1.5% | 2.0% |
|------|---------|----------------|-------|------|----|------|------|
| 1 | 0 | 0 | 2 | 4 | 4 | 5 | 6 |
| 2 | 0 | 0 | 1 | 2 | 3 | 4 | 3 |
| 3 | 0 | 1 | 3 | 2 | 2 | 1 | 1 |
| 4 | 1 | 0 | 1 | 1 | 1 | - | - |
| 5 | 0 | 0 | 2 | 1 | - | - | - |
| 6 | 0 | 0 | 0 | - | - | - | - |
| 7 | 0 | 0 | 1 | - | - | - | - |

From the Table it is apparent that Kaolin did not affect the validity of the 666 results. It would appear that 1% of the 20% dust supplied per hide weight is required to bring about mortality quickly enough.

Examination of the test pieces and the beakers showed that both the controls had been severely attacked, the damage being visible on both the flesh and grain sides. The piece treated with 0.25% dust also showed damage as was indicated by the amount of hair and excreta in the beaker. This applies to a more limited degree also to the piece

treated with 0.5%. In all three of the other beakers no loose hair or excreta could be seen.

From this laboratory experiment it would appear that 1% of the dust as supplied was required to prevent Dermestid beetle damage to hides. Since, however, the sample of dust as supplied contained only 20% crude 666, or in other words 2% of Gammexane, only .02% of Gammexane per hide weight (0.068 mgm per sq. cm.) is necessary. Gammexane is therefore much more potent than sodium fluosilicate when used in dust form. Further experiments with this new poison are being undertaken on large scale to ascertain its value under works conditions.

Information on the toxicity of 666 points to the fact that about 37 grams or 3 ounces of crude 666 or B.H.C. would constitute a lethal dose to a human being. Gammexane is more poisonous, and 13 grams or $\frac{1}{2}$ ounce would suffice to bring about death. The poison is therefore of low toxicity to mammals. Furthermore, it has no cumulative toxic effects, and it would appear that there is not much danger of contracting dermatitis when working with the poison as it is supplied in diluted dust form.

SUMMARY.

1. Experiments with the new insecticide 666 or Benzene hexachloride (respectively Gammexane) on laboratory scale have been described.
2. A concentration of 0.68 milligrams crude 666 (0.068 mgm Gammexane) per square centimetre proved effective in killing the Dermestid larvae within four days, thereby preventing all damage.

In practice this would mean that one pound of crude 666 per 700 square feet or one pound of Gammexane per 7000 square feet would be effective in safeguarding hides and skins against the Dermestid hide and skin beetles.

PART III.

SALT STAINS AND RED HEAT.

Chapter 8.

HISTORICAL REVIEW : 1910 - 1944.

Most farmers, hide and skin dealers, tanners and footwear manufacturers have no doubt encountered stains on cured hides and skins or on the finished leather. Until quite recently the presence of these was taken as an inevitable and irremediable occurrence in the industry, but during the past three decades extensive and intensive overseas research has aimed at disclosing the root of the trouble and at devising means and methods for its elimination. It appears that in South Africa very little attention has been paid to this aspect, despite the fact that our climatic conditions differ so markedly from those obtaining overseas, and it has been known for some time that climatic conditions influence the development of certain types of stains.

From an exhaustive study of available literature it became clear that there is still confusion over this problem, therefore, before discussing investigations undertaken by the writer in this connection, it

will be necessary to give a brief summary of some of the aspects of this vexed problem.

(i) Nature of the Stains.

Stains occurring on cured hides and skins vary widely in appearance, colour and colour intensity. This variance is often correlated with the treatment given to the hide or skin prior to curing, and with the method of curing practised. Three types can be distinguished, each type including various manifestations of the particular stain group involved.

1. True Salt Stains.

This type comprises small coloured spots, seldom larger than one square inch. The colour may vary from light yellow to reddish-brown, and in some cases may even be dark blue. The stains are scattered over both the flesh and the grain sides of the hide or the skin and each spot is usually distinctly demarcated; the margins may however overlap to form larger patches. On the finished leather these spots usually appear as dark stains which are particularly troublesome in light-coloured leathers. Such stains are collectively known as true salt stains, and they are more or less always present on salt-cured hides and skins, but may also be encountered on sun- or shade-dried material.

2. Red Heat.

The yellow to brick-red stains covering large areas of the flesh and sometimes of the grain of hides and skins which had been kept in the wet-salted condition for some length of time are perhaps better known because of their conspicuous nature. These stains are especially prevalent in summer. The entire flesh side of a wet-salted hide may be affected, but usually only the edges are attacked if the stack is left undisturbed. The affected areas are always slimy. This type of stain is commonly called red heat, because it has been associated with the development of heat in the salted stacks.

3. Other Discolourations.

Violet-blue to violet-red stains are occasionally encountered on wet-salted hides, sometimes by themselves, sometimes accompanied by red heat. Such stains usually cover only patches of several square inches, but the writer has examined a number of hides which had been discoloured over the entire area of both flesh and grain sides, while in the same hides red heat had been limited to the edges only.

(ii) Causes of Stains.

Many theories have been advanced to explain the cause of stains on salt-cured hides and skins. These

theories to some extent overlap, but in general they may be divided into two groups : those attributing the stains to chemical causes and those attributing them to bacteriological causes.

1. Chemical Salt Stains.

According to Hausam, 1938 (1), the law in most of the countries of Central Europe enforces the use of denatured salt for commercial purposes, i.e. salt made inedible by the addition of various substances. Such denatured sodium chloride led to the development on cured hides of quite a number of stains which had their origin in (i) the presence of coloured substances in the salt, or (ii) in the formation of coloured products by the reaction between the impurities in the salt with one another or with the biochemical compounds of the hide. Stains originating thus are usually small localised spots, belonging to the group of truesalt stains.

In the first type of true salt stains the trouble arises from the presence of impurities such as tar, oil, red chalk, chrome and copper salts, all of these substances being introduced as denaturants of the sodium chloride. Yocum, 1913 (2), B.L.M.R.A. Reports 1927 (3), Kaye 1930 (4), and Hausam 1938 (1) have drawn attention to the loss incurred by such denaturants.

The stains belonging to the second type of true salt stains can, it seems, be traced to the reaction between impurities in the salt and the iron present either in the blood or in the salt itself. Many articles have already appeared on this subject and the views of a few workers are given here. Abt, 1912(5), pointed out that the stains he examined contained more iron, calcium and phosphates than the unstained areas; he believed that the calcium sulphate naturally present in the curing salt reacts with the ammonium phosphate set free from the nucleic acids to form ammonium sulphate, the latter solubilising the iron compounds. In this view he is supported by Weber, 1913(6). Yocum, 1912 (7) and 1913 (2) as well as Kohnstein, 1913 (8) maintained that the iron contained in the blood pigment is the cause of stains. The blood pigment, oxyhaemoglobin, containing iron, is oxidised to haematin which slightly tans the hide and thus fixes the iron. Moeller, 1917(9) expressed similar views on the matter. Abt, 1914(10) maintained that the iron is liberated from the chromatin in the nuclei and from the blood, and in the presence of calcium sulphate stains are formed. The views of Vourloud, 1925 (II) are more or less in agreement with those of Abt; he

suggested that the iron is liberated by bacterial activity. Pericaud, 1925 (12) and 1923 (13) maintained that coagulated blood is the main cause of stains, resulting from the activity of proteolytic enzymes. Javenitz, 1926(14) was also of the opinion that stains are mostly due to the blood. Stather, 1928 (15) reverted to the theory of Abt(5), attributing the stains to the presence of iron, phosphorus, sulphur (in the form of sulphates) and calcium, these substances being found in larger amounts in the stained areas than in the unstained. Patwardhan and Sastry, 1932(16), supported by Chambard and Gastellu, 1939 (17), ascribed the stains examined by them to iron sulphide. Bacterial activity solubilises the iron salts present in the curing salt, and the iron is precipitated as iron sulphide by the hydrogen sulphide liberated in the decomposition of the proteins. Rigot, 1932(18) concluded that the ammoniacal fermentation of blood serum is the principal cause of salt stains. Ammonium carbonate forms carbonates with the calcium salts present in the curing salt and solubilises the iron compounds in the salt or in the hide. Although some of the views upheld by the various authors are contradictory to a certain extent, it will nevertheless be clear that the impurities in the curing salt and the presence of iron (or the

blood) are great assets for the formation of salt stains on cured hides and skins. Further discussions on this matter will be found in Chapters 9. and 14.

2. Bacteriological Stains.

It has been known for a considerable time that bacteria play an active part in the leather industry. Wood, 1910 (19) was one of the first investigators to realise that "salt stains" are of various origins, and that bacteria are to be held responsible for at least one type of these stains. He remarks on page 363: "There are some bacteria able to grow in the presence of salt, one species of which produces a colouring matter which it is impossible to remove from the skin, and which is one of the causes of the defect known as salt stains". Becker, 1912 (20) ascribed most, if not all of the stains to the action of aerobic bacteria which he was able to cultivate on culture media. Besson, 1912(21) favoured the same view. Abt, 1913 (22) was able to separate bacteria from the stains, capable of forming dark-coloured colonies on gelatin, and Moeller, 1917(9) claimed that these bacteria are able to utilise sulphur and iron, coloured substances being formed. Stather, 1928(15) isolated six species of chromogenic bacteria to which he ascribed the ability

to produce stains, and with Liebscher, 1929 (23) he isolated several more. These two workers, and also Bergmann, 1929(24) concluded that the red stains on salt-cured hides and skins are due to the activity of chromogenic aerobic bacteria which are able to live in high concentrations of sodium chloride. Jordan Lloyd, 1929 (25) was probably the first to use the term "red heat" in connection with the red stains occurring on the flesh of wet-salted hides. She ascribed such stains to the activity of halophylic, i.e. salt-loving, bacteria present in the marine salt, but Stather, 1930 (26) proved that these organisms are also to be found in mine salt. Utenkow, 1931(27) isolated a bacterium from red-stained Argentine hides, which was able to form pigment under aerobic conditions in the presence of calcium and magnesium sulphates. Hausam, 1931(28) isolated quite a number of chromogenic bacteria to which he attributed the ability of producing coloured stains on cured hides and skins. Experiments carried out by Robertsen, 1932 (29) revealed that the halophylic bacteria in marine salt are to be blamed only for certain stains on the hides, since the bacteria ordinarily present in the dust and hides also play a part in discolouring cured hides and skins. Stuart and Swenson, 1934 (30) agreed with Robertsen that the halophylic bacteria are responsible for red heat,

and they maintained that these chromogenic bacteria belong to the higher bacteria, possibly to the Myxobacteriales. Bergmann and Hausam, 1933 (31) showed that the pigment producing micro-organisms of salt stains are mostly micrococci forming orange, cream and ochre pigments; they were of the opinion that the stains are probably due to quite a number of bacteria, and succeeded in isolating several species of chromogenic forms. In this field of research, the work of Stuart, 1935(32) is of very great importance. He cultivated a series of bacteria from the single species isolated in 1934 (30) and was able to show that this species stayed constant in morphology and physiological activity when kept on the same culture medium. When the media were changed with regard to the salt concentration and especially the organic nutrient material, the morphology and activity of the species underwent very remarkable changes, and Stuart concluded that most of the forms enumerated by previous workers belong to one and the same species. The different forms are to be attributed to different media. This bacterium was tentatively identified as Myxococcus rubescens Thaxter. He was further able to show, 1941(33), that this halophylic bacterium flourished in high salt concentrations with a slightly alkaline reaction, and that it

prefers a relatively low oxygen tension for optimum growth. This explains why red heat is usually confined to the edges of wet-salted stacked hides.

The blue-violet to red-violet stains described by Stather, Schuck and Liebscher, 1930(34) differ from the red stains in that they are more localised. A number of bacteria were isolated from such stains by Stather and Liebscher, 1930(35) capable of producing pigments. With regard to blue-green to violet stains, Patwardhan and Sastry, 1932 (16) claimed that they are produced by iron sulphide, the insoluble iron compounds being solubilised by bacteria and then converted to iron sulphide by the hydrogen sulphide arising from the decomposing proteins, caused by chromogenic bacteria able to thrive in high concentrations of sodium chloride.

Damage by Stains.

The fact that true salt stains incur loss in the leather industry has been acknowledged as early as 1912 by Paessler (36) and later by Moeller, 1917 (9). Such loss is due to the fact that stained leather depreciates in value, especially in the case of light coloured leather.

Since red heat is more or less usually confined to the flesh side, the resulting stains are not to be regarded as a serious trouble, unless the bacteria

causing this discolouration actually attack the hide substance. Becker, 1912(20) and Abt, 1914(10) claimed that these bacteria do not disintegrate gelatin and are therefore not responsible for any loss. Stather, 1928(15) and Stather and Liebscher, 1929(23), however, showed that the fibres are changed histologically, often looking intact and "dissolved". Bogomolowa, 1933(37) maintained that red heat damages the hide substance, the hair becoming loose owing to a swelling of the hairbulbs. The report of Stuart, 1936(38) on the action of chitinivorous halophylic bacteria of the chromogenic group is also important, since it might be of interest in determining the actual damage caused by red heat bacteria.

(iii) Preventative Measures.

Most of the workers on the stains problem recommended precautions to be taken in accordance with the theory they propounded on this problem. It will, however, only be necessary to summarise these precautions in the light of our present knowledge of the subject, so as to avoid a lengthy discussion.

- (i) The slaughterhouse should be kept as cool and clean as possible since bacteria thrive well at higher temperatures, in dirt, dung and blood.

- (ii) Flayed hides should be washed thoroughly to remove all dirt, dung and blood which form optimum nuclei for bacterial activity. This is preferably done with water from a hose-pipe. The removal of the blood will, at the same time, limit the stains resulting from the iron in the haemoglobin.
- (iii) Salting should not be delayed for longer than three hours, since post mortem changes may easily set in and cause unnecessary damage.
- (iv) A preliminary brining before salting appears to give better results than salting alone.
- (v) Not less than 25% salt should be used since sodium chloride in weaker concentrations is inefficient. (At this Institute 33% salt per weight of hide is used).
- (vi) The salt should be as pure as possible and of medium grain. Impurities cause stains and coarse grain salt produces salt pits. Denaturants such as tar, oil, chrome and copper salts, should not be used in curing salt.
- (vii) Salt should not be re-used, since it is contaminated with blood, iron and

halophylic bacteria.

(viii) Quite a number of disinfectants have been recommended by various workers to inhibit the propagation of the bacteria causing decay in general, as well as that chromogenic group responsible for the development of red discolourations on cured hides. Since the application of disinfectants is of great importance, it will be necessary to discuss at length some of the substances recommended.

Generally speaking, bacteria prefer media which are neutral or even slightly alkaline in reaction. The obvious line of attack would therefore be either to increase or to decrease the pH to limits which are unfavourable to bacterial activity, but which will not harm the hide substance. It should be kept in mind that some bacteria are capable of thriving in media which are fairly alkaline or fairly acid in reaction, thus making it very difficult to inhibit all bacterial activity.

1. Sodium Carbonate: Jouve, 1912 (39), was one of the first investigators to point out that alkaline curing salt inhibited the formation of stains. Paessler, 1912 (36) recommended the use of 4% sodium carbonate on the curing salt. Hausam (1) summarised the previous work on the use of sodium carbonate in

curing salt and came to the conclusion that 2% Na_2CO_3 on the salt yielded excellent results, especially when 1% naphthalene was used with it. Sodium carbonate has been and still is widely used in Germany. Hasaum admits that sodium carbonate cannot prevent all red heat discolourations, since some of the chromogenic bacteria are capable of thriving at a pH of about 9. It has moreover been claimed by Robertson (29) and Lloyd (25) that the use of sodium carbonate resulted in weak leather, the fibres being loosened and disarranged. Further details are to be found in Chapter 10.

2. Zinc chloride is acid in reaction and is used in America for the preservation of cured hides and skins. Solutions of 0.01% are applied either as a dipping fluid or as a spray. Guthrie and Sastry, 1933 (40), have shown that, although zinc chloride can be used with reasonable success, stains still occur.

3. Sodium bisulphate and sodium bisulphite have been used owing to their acid reaction. Robertson (29) stated that sodium bisulphite inhibits bacterial activity, and she is supported in this by Grassmann and Hausam (41) who found that salt + 0.25% sodium bisulphate inhibited the development of red heat to a certain extent. Guthrie and Sastry (40) claimed that even .3% sodium bisulphite is not effective since

red heat developed during their experiments. They passed the same verdict on sodium bisulphate and maintained that this inefficiency was due to the fact that the initial pH of 5.0 gradually changed to 8.4 at which level bacteria thrive well. Babakina and Kutukowa (42) stated that sodium bisulphite undoubtedly damaged their hides and that the leather was of inferior quality.

4. Sodium trichlorphenate: Stuart and Frey, 1954 (43) investigated the red heat problem and found that 0.1% sodium trichlorphenate on the salt yielded excellent results. It is not certain whether this preservative is dangerous to the workmen handling it.

5. Sodium sulphate has been used in Italy for preservation, 10% of this chemical being applied per weight of hide. It has been shown by McLaughlin and Highberger, 1926 (44), that the bacteriostatic value of sodium sulphate is lower than that of sodium chloride.

6. Fluorides will be discussed in Chapter 11.

SUMMARY.

The stains usually encountered upon cured hides and skins can be of three different classes. The first comprises small coloured spots, varying

in colour from light yellow to reddish-brown. They are caused by impurities in the curing salt or by chemical reaction between such impurities and the biochemical compounds of the hide. Blood and iron appear to play an important part in the development of such stains. The second class includes the more or less localised violet-blue to violet-red stains, these being most probably caused by bacterial action. The third class comprises red heat stains, produced by the activities of halophylic bacteria of the chromogenic groups. These three classes of stains are responsible for troublesome defects in leathers, and may be responsible for loss of valuable hide substance.

Chapter 9.

IRON STAINS.

1. Theoretical.

It has been known for a long time that iron is responsible for the occurrence of some of the true salt stains on salt-cured hides and skins, but the explanations for this phenomenon appear to be in conflict with one another. Some authors put the onus for iron stain formation exclusively on the blood, whilst others maintain that the iron in the curing salt is to blame.

Abt (5,22) found that iron was always present in stained areas of the hide, together with calcium, sulphates, and phosphates. This iron is present as insoluble iron carbonate on the surface of the hide. With denaturation of the nucleic acids of the hide proteins ammonium phosphate is liberated which then reacts with calcium sulphate from the curing salt to form insoluble calcium phosphate and soluble ammonium sulphate. The latter easily diffuses through the hide, solubilises the iron compounds and thus distributes the latter through the hide. The iron compounds then again precipitate, giving rise to the well-known localised stains. It is also possible that bacteria play a part in this reaction, perhaps by forming

soluble iron bicarbonate as a result of fermentation. In a later paper (10) Abt maintained that the iron may be liberated from the chromatin of the nuclei and from blood, stains then being formed in the presence of calcium sulphate.

Yocum (2,7) and Kohnstein (8) expounded further on the theory that blood is the cause of stains. The blood pigment, oxyhaemoglobin, containing iron, is oxydised to haematin which slightly tans the hide, thus fixing the iron permanently. Moeller (9), Vourloud (11), Stather (15) and Jovanovits (14) were of the opinion that the iron is liberated from the blood by bacterial action. Iron hydroxide, formed by such activities, is a tanning agent and will fix itself permanently to the hide. The iron bacteria have the ability of concentrating very small quantities of iron and of depositing such iron as the hydroxide. Rigot (18) also favoured the theory that bacteria are responsible for ammoniacal fermentation of the blood serum. Liberation of ammonium carbonate results in the formation of calcium carbonate and solubilisation of the iron present in the salt. Pericaud (12,13) maintained that coagulated blood is the main cause of stains, proteolytic enzymes being responsible for the liberation of the iron contained in the blood.

The theory that the iron contained in the curing salt is largely responsible for true salt stains developing on hides and skins was first put forward by Turnbull (45). A report from the B.L.M.R.A. laboratories (3) also stressed the necessity for using pure salt with low iron content. Patwardhan and Sastry (16), supported by Chambard and Gastellu (17) ascribed the stains examined by them to the precipitation of blue-green to violet coloured iron sulphide. The iron in the salt is solubilised by the action of bacteria and then converted to the insoluble sulphide by hydrogen sulphide which results from the decomposition of the hide proteins.

All these theories may be summarised as follows. It is now known that stains may result from the iron present in the blood pigment, haemoglobin, as well as from iron present as an impurity of the curing salt. In all cases it would appear that the action of bacteria is responsible for liberating and concentrating the iron in localised spots where such iron is then permanently fixed to the hide through partial iron tannage, the stains removing with difficulty during the tanning process.

Although so many papers have been published on this vexed problem, no definite figures are available as to the critical iron content of the salt. Stather (15) merely stated that "traces" of iron are suffi-

cient to allow the iron bacteria to concentrate it in localised spots. Phillips (46) found that most salts examined by him contained less than 10 parts of iron per million of salt, which (p. 100) "appears to be the iron content of a good curing salt." In a stained portion of a hide he found .024% Fe as compared with .009% in an unstained portion. Bergmann and his co-workers (47) reported that salt which had caused stains on French calfskins contained 0.17% Fe_2O_3 (915 parts Fe per million), and that the stained portions contained more iron than stain-free areas. Lokschin and Luxemburg (48) suggested that curing salt should contain less than 100 parts Fe per million of salt.

Experiments conducted by the writer revealed that fresh hide washed for fifteen minutes with water from a hose contained between 50 and 150 parts Fe per million (on a moisture-free basis) over different parts of the hide, all of this iron being in the insoluble form. Unwashed fresh hide contained between 50 and 600 parts of Fe per million (on a moisture-free basis) over different areas. Such a high iron content in South African (unwashed) hides is due to the conditions under which the hides are produced at the abattoirs. Attention has been drawn in Part I to the undesirability of contaminating

the hides with dirt and blood at the abattoir, since these only cause stains and act as nuclei for the commencement of bacterial putrefaction. The iron in the blood is chiefly responsible for the development of stains, and until slaughtering and flaying are carried out more carefully and with more clean-

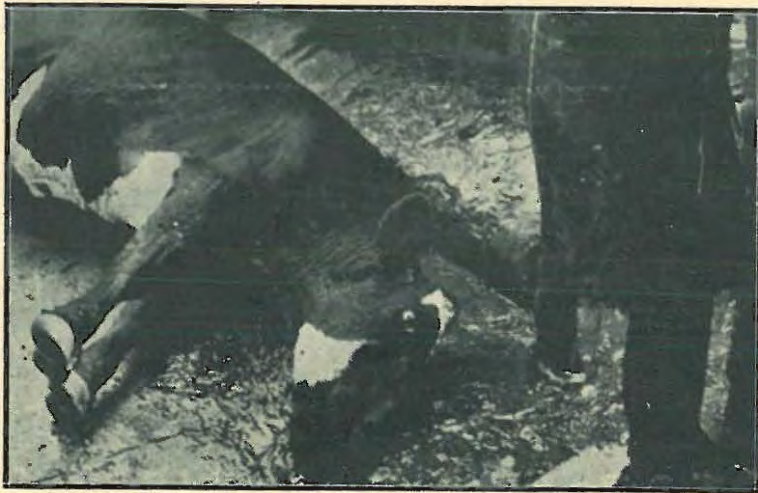


Fig. 12. Animal Lying in a Pool of Blood and Dirt at the Abattoir.

liness, stains on our hides and skins will not easily be eliminated.

Iron in South African solar salt is most commonly present in insoluble form as the carbonate, hydroxide or oxide. Analysis of samples of salt from different parts of the country (see Chapter 14) showed that these salts contained on the average about one part of soluble iron per million, the lowest

figure being 0.1 and the highest 4.1 parts per million. The total iron content of these salts varied between 7 and 1600 parts Fe per million. This would imply that iron stains could only result as a consequence of interreaction between the insoluble iron compounds in the curing salt or in the blood on the one hand, and other impurities of the salt or products of bacterial activities in the hide on the other hand. Since soluble iron is ordinarily not present in solar salt, it need not be considered here. However, experiments which were nevertheless conducted with curing salt to which had been added various percentages by weight of soluble iron compounds all failed to establish the critical amount of soluble iron which could be allowed in curing salt, because of the fact that iron salts easily hydrolyse when dilute, the iron then being again present in the insoluble form.

2. Experimental Stains Caused by Insoluble Iron.

The following experiment was conducted. 100 gram pieces of fresh well washed hide were salted with 33 grams each of salt to which had been added varying amounts of iron salts. The different samples of curing salt were prepared to contain 14, 50, 100, 200, 500 and 1000 parts insoluble Fe per million. In order to get even mixing of the iron with the curing salt, the salt was dissolved in water,

soluble iron compounds added to give the above concentrations and ammonium hydroxide then stirred in to precipitate the iron as the hydroxide, which on heating would partially decompose to form iron oxide. The water was then evaporated off on a water bath, the crystallising salt being stirred continuously until quite dry in order to prevent the insoluble iron from settling.

The salted hide pieces were stacked on raised platforms in glass jars, the piece with the lowest iron content on top and that with the highest at the bottom of each little stack. The test pieces were separated from one another by larger pieces of iron-free salted hide in order to eliminate contamination as far as possible.

One series of hide pieces was dipped in saturated sodium fluosilicate for 30 minutes before salting, the other series acting as untreated control. Two duplicate series were also prepared. Those pieces which had been given the antiseptic sodium fluosilicate treatment would, when compared with the controls, give an indication of the effect of bacterial activities in producing iron stains on salted hides.

The jars were covered and left for three months before examining the pieces. The results, judged

macroscopically, are given in Table 12.

TABLE 12 : CRITICAL IRON CONTENT OF CURING SALT.

| Ppm. Fe in salt | 14 | 50 | 100 | 200 | 500 | 1000 |
|-----------------|----|----|-----|-----|-----|------|
| Dipped (i) | - | - | - | x | xx | xxx |
| Control (i) | - | - | x | xx | xxx | xxx |
| Dipped (ii) | - | - | - | x | xx | xxx |
| Control (ii) | - | - | x | xx | xxx | xxx |

- = Not stained x = Isolated stains

xx = Pronounced stains xxx = Very bad stains

Examination of the slightly stained hide pieces showed that the stains had not penetrated much below the surface. On soaking the pieces, those stains all but disappeared (i.e. pieces designated as x above); the others however retained the stains.

From these results it would appear that stains will develop on well washed hides when the iron content of the curing salt is above about 100 parts of Fe per million. The test pieces were kept for three months to subject them to a severe test, but in practice South African wet-salted hides at present do not stay in stack for longer than a month.

Hides disinfected by a sodium fluosilicate dip prior to curing seem to be less prone to the development of iron stains. This was also experienced with large scale experiments. See Chapter 11. These results therefore substantiate the theories described above, in so far as it would appear that bacteria play an important part in producing iron stains.

SUMMARY.

Iron is responsible for the occurrence of some of the true salt stains encountered upon hides and skins. This iron may be present either in the curing salt or may result from the presence of blood due to inefficient slaughtering and flaying. The stains can develop as a direct consequence of chemical interreaction between iron and other impurities of the salt, particularly calcium sulphate, or they may develop as a result of interreaction between iron and biochemical compounds liberated from the hide proteins by bacterial activities. Provided the hides are well washed before salting, there is no danger of the development of iron stains if the iron content of the salt does not exceed 100 parts per million. On the other hand, even if very pure salt is used, iron stains may result if the blood is not washed off the hide before salting.

Chapter 10.

THE USE OF SODIUM CARBONATE, SODIUM ARSENITE
AND BARIUM FLUOSILICATE IN
PREVENTING RED HEAT.

(i) Sodium Carbonate.

It has been proved that red heat in cured hides and skins is the result of activities of a chromogenic group of halophylic bacteria. These salt-loving bacteria can thrive in high concentrations of salt and it can safely be assumed that sodium chloride is not an exclusive bacteriostatic agent. Most bacteria prefer neutral or slightly alkaline media for optimum propagation, and the rate of growth can be regulated artificially by changing the reaction of the media. A radical change either to the acid or to the alkaline side of the pH scale can therefore result in total inhibition of the growth and even of the life of the particular species involved. The use of many disinfectants is based on this principle.

Jouve was one of the first workers who realised that the action of bacteria responsible for the development of red discolourations in cured hides and skins could be checked by rendering the curing

salt alkaline. Paessler (36) was of the same opinion and recommended the use of 4% sodium carbonate on the curing salt. Bulgakow and Popow (49) claimed that 5% sodium carbonate on the curing salt should be used for good results, but Hausam⁽⁵⁰⁾ stated that 5% sodium carbonate damaged the hides. He recommended the use of 2% Na_2CO_3 on the curing salt, as is the practice in Germany, and maintained that excellent results could be obtained with this method for the elimination of red heat. Although Hausam admitted that sodium carbonate could not prevent all red heat development, since some of the chromogenic bacteria thrive well at a pH of 9, he nevertheless regarded sodium carbonate as the best suitable preventative against the halophylic red heat bacteria.

Experimental.

Although the use of sodium carbonate has led to excellent results in Germany, it was necessary to conduct some experiments for determining its efficiency under prevailing South African climatic conditions, before recommending its use in the curing of local wet-salted hides.

Sixty fresh hides were washed for one hour in running water in a paddle to rid them of adhering blood, dirt and dung which form focal points for the commencement of bacterial development. The hides

were then divided into three lots of twenty each, and the lots cured with the following.

Lot I. 33% clean sodium chloride of medium grain per weight of hide - Control.

Lot II. 33% sodium chloride with which had been mixed 1% by weight of sodium carbonate.

Lot III. 33% sodium chloride with which had been mixed 2% by weight of sodium carbonate.

After salting, the hides were rolled for 48 hours and then stacked open for the period October to July.

Meanwhile sixty more fresh hides were washed as before and divided into three lots of twenty each, i. . lots IV - VI.

Lot IV. Cured with 33% NaCl.

Lot V. Cured with 33% NaCl + 1% sodium carbonate.

Lot VI. Cured with 33% NaCl + 2% sodium carbonate.

After rolling for 48 hours, the three lots of hides were separately stacked and covered with sacking, the stacks being occasionally sprayed with water.

These stacks were left during the period December/January to July and were then examined together with Lots I to III.

Results.

The hides in Lot I had been excellently flattened out and no creases could be seen. Salt stains were

very sparsely scattered on some of the hides. Red heat was more or less limited to the edges, except in the hides near the top of the stack. Violet stains were encountered on some of the hides lower down in the stack, sometimes in areas where no red heat could be seen. The hides looked clean and well cured.

The hides in Lot II were creased to a certain extent and red heat had severely attacked most of the hides over the entire flesh surface. Salt stains were also present. Violet stains were pronounced in most of the hides lower down in the stack near the concrete floor of the store.

In Lot III the same phenomena were encountered as in Lot II, except that the violet stains were even worse. There were slight signs of decay in a few hides at the bottom of the stack.

The hides in Lots IV - VI were somewhat creased and showed red heat on the entire flesh area, the red heat being worse than in Lots I - III. Salt stains were again present. Violet stains were found in Lot IV to the same extent as in I; in Lots V and VI the violet stains were not so pronounced as in II and III. On the whole all the hides looked well cured.

Discussion.

Red heat was found to be present over the entire flesh area of those hides which had been creased, but it was more or less limited to the edges of the hides which had smoothed out well in the stack. This is in agreement with the evidence produced by some workers that the halophylic bacteria causing red heat are aerobic, but that they require only a relatively low oxygen tension for propagation. The same is true of those bacteria causing violet stains.

The degree of discolouration in the covered stacks was higher than in the open stacks. This is probably accounted for by the fact that the former stacks had occasionally been sprayed with water. Since the bacteriostatic value of sodium chloride depends mostly on its dehydrating properties, the addition of water to these stacks can easily be held responsible for the higher degree of red heat development.

The degree of violet stain development in the hides cured with salt to which sodium carbonate had been added and stacked covered was lower than that in the hides identically cured but stacked open. Although no plausible explanation can as yet be given for this phenomenon, it should be kept in mind that the hides stacked covered had been stored only for seven to eight months (December/January to July),

whereas the hides stacked open had been kept for ten months (October to July). The latter hides were therefore exposed to the heat of all the summer months, while the former were exposed only to the heat of the latter half of summer. Moreover, the longer period of storage might perhaps be responsible for the more marked development of violet stains.

The addition of 1% or 2% sodium carbonate to the curing salt led to very disappointing results. It can even be stated that red heat was more pronounced on the hides cured with this mixture than on hides cured with sodium chloride alone. Guthrie and Sastry (40) used 3% sodium carbonate on the curing salt in India and also obtained negative results. It has been stated by Koppenhoefer and Somer (51) that sodium carbonate was effective at low temperatures, but it did not inhibit red heat development at high temperatures. The mean South African summer temperature is, on the whole, higher than that in Europe, and this probably accounts for the inefficiency of sodium carbonate in preventing red heat under prevailing South African conditions. The results obtained by Guthrie and Sastry in India, where the temperature is even higher than here in South Africa, can perhaps also be explained in this way. The table given here represents the official temperature record for the period during which the hides were stored. It should

however be pointed out that the temperature in the store during those months was probably lower than the official figure, and that the average minimum was probably higher..

TABLE 13 : OFFICIAL AVERAGE TEMPERATURES OF MONTHS
DURING WHICH HIDES WERE STORED.

| Month | Mean Max. | Mean Min. | Highest Max. | Date | Lowest Min. | Date |
|----------|-----------|-----------|--------------|------|-------------|------|
| October | 73.3 | 53.2 | 93.7 | 7 | 38.8 | 15 |
| November | 74.4 | 55.1 | 91.0 | 28 | 42.8 | 17 |
| December | 78.4 | 56.7 | 100.0 | 21 | 47.5 | 3 |
| January | 78.3 | 57.7 | 92.1 | 7 | 44.2 | 29 |
| February | 77.8 | 56.4 | 101.6 | 19 | 47.6 | 13 |
| March | 78.0 | 59.9 | 102.1 | 11 | 45.8 | 30 |
| April | 72.0 | 54.0 | 93.9 | 5 | 41.8 | 30 |
| May | 68.9 | 47.8 | 78.8 | 12 | 39.1 | 23 |
| June | 65.1 | 44.3 | 77.1 | 12 | 36.1 | 30 |
| July | 63.9 | 42.0 | 77.9 | 17 | 32.6 | 10 |

Conclusion.

The use of 1% or 2% sodium carbonate for the prevention of red heat cannot be recommended in South Africa, probably owing to climatic conditions. Concentrations higher than 2% have been shown by Hausam (50) and Jordan Lloyd (52) to be deleterious.

(ii) On the Use of Sodium Arsenite.

Experiments conducted by R.V.G. Cutten of this Institute (private communication) revealed that sodium arsenite could be used with good results as a bacteriostatic agent, and the possibility that this chemical could be applied for the prevention of red heat was therefore considered.

Forty green hides were washed in running water in a paddle for one hour to remove blood and dirt, and were then divided into two lots of twenty each. Lot A was salted with 20% clean salt, rolled for 48 hours and then stacked. Lot B. was dipped for 15 minutes in a 5% solution of sodium arsenite and then subjected to the same treatment as Lot A. The two stacks were kept during the period October to July and were then examined.

Results.

The hides in Lot A were very badly cured and showed partial decay in some cases. Red heat flourished over the entire flesh side of those hides near the top of the stack, but lower down only the edges had been attacked. Violet stains and salt stains were encountered on most of the hides, and moulds were found in some cases. The hides in Lot B were better cured and showed no sign of hair slip

or decay. No violet stains were observed and the red heat stains were less pronounced than in the control. Sodium arsenite is therefore not very efficient in preventing red heat and cannot be recommended.

(iii) On the Use of Barium Fluosilicate.

Fluorides as preventatives of bacterial growth and especially of red heat have been recommended by quite a number of workers (Chapter 11), all of whom maintained that better results could be obtained with these chemicals than with most of the disinfectants usually applied.

Twenty fresh hides were washed as before and then salted with sodium chloride to which 0.5% barium fluosilicate had been added. 33% salt was used per hide weight. The hides were stacked during the period January to July.

An examination of the hides at the end of that period showed that they were cured better than any of the other lots referred to above. They looked clean and white and the hair did not show any signs of slip. Although salt stains were present, the hides had developed red heat only in localised spots. Innes (53) has drawn attention to the fact that it is impossible to mix the solid disinfectant and the curing

salt efficiently, and these spots probably resulted from such improper mixing. No violet stains were observed.

0.5% barium fluosilicate on the curing salt gave the best results of the chemicals tried for the prevention of red heat in wet-salted hides.

SUMMARY.

Experiments on pilot scale were carried out to test the efficiency of sodium carbonate, sodium arsenite and barium fluosilicate in preventing red heat on wet-salted hides. Sodium carbonate, when mixed with the curing salt (1% and 2% on the salt by weight), appeared to result in the development of red heat to a more marked degree than in untreated hides. Violet stains were especially abundant. Sodium arsenite was likewise of little use. Barium fluosilicate mixed with the salt gave excellent results, but it was obvious that mixing could not be done efficiently and localised spots of red heat still developed.

Because of the promising results obtained with barium fluosilicate, sodium fluosilicate was experimented with. The results were very good and such a large number of experiments were conducted that it was decided to treat these in a separate chapter.

Chapter 11.

THE USE OF SODIUM FLUOSILICATE FOR THE
PREVENTION OF RED HEAT.

(i) Introduction.

In Chapter 8 a brief bibliographical review of past work on the question of red heat was submitted and the various causes of and methods for the prevention of the stains discussed. In Chapter 10 it has been shown that sodium carbonate is apparently of no value under South African climatic conditions. The same verdict was passed on sodium arsenite, while it was found that barium fluosilicate mixed with the curing salt gave quite promising results. Preliminary experiments with sodium fluosilicate indicated that this chemical, which is used in England and other foreign countries, might also be applied with success under conditions obtaining in South Africa.

Quite a formidable amount of work on the application of fluorides in the curing process has been compiled on record and it might be useful to discuss some of that work here, in order to elucidate some of the aspects of the different problems involved.

1. Application and Bacteriostatic Value.

Romana and Baldracco (54) were apparently the first to realise the value of the fluorides in the curing of hides and skins. As early as 1914 they experimented with salt to which had been added 1% sodium fluoride, 15% of this mixture being applied per hide weight. The fluoride hides showed no sign of red heat after 15 days and were much more supple and whiter than the control set. An objection to their conclusions might be raised on account of the fact that the experiment lasted only fifteen days, since red heat often only develops after one month.

Only in 1926 reference to the application of fluorides is found again when Jovanovits (14) recommended the use of sodium fluoride for the prevention of "salt stains". In the following year the British Leather Manufacturers' Research Association (55) reported favourably on the application of this chemical as a disinfectant for the improvement of the curing process. "In properties it resembles sodium chloride, but its dehydrating power is a little greater. It will coagulate proteins, but ... it is a reversible change, so that on washing the fluoride away the proteins return to their previous uncoagulated condition. It has valuable antiseptic properties ... In fact, sodium fluoride seems to be one of the rare substances

which are antiseptic without damaging the hide." .
This was followed up by experiments in 1928 (56) in which the hides were brined in saturated salt solutions to which had been added 1% of sodium fluoride, sodium bifluoride, sodium bisulphate, sodium carbonate and magnesium chloride. After eight days the fluoride hides were the fullest, softest and whitest of the series and looked almost fresh, the fibres of those treated with sodium bifluoride being the best.

White and Caughley (57) in 1930 reported that the growth of the organisms responsible for the production of red heat in hides could be checked by adding 0.5 to 1% sodium fluoride or sodium fluosilicate to the curing salt. An American patent (58) was taken out in 1932 for the treatment of green hides with a solution containing one or more disinfectants of the group comprising sodium trichlorophenate, sodium fluosilicate and beta-naphthol. Robertson (29) in the same year reported on hides that had been cured in New Zealand with salt containing 0.5% and 1% sodium fluoride and sodium fluosilicate. The hides, together with controls, were shipped to England and it was found that no red heat had developed on the fluoride hides, even after being kept for six weeks at 37°C in a moist atmosphere. These hides showed up somewhat drier than the ordinary.

Bergmann and Hausam (59) in a paper on the use of 1% sodium fluoride as an admixture to the curing salt stated that two out of thirty fluoride hides developed violet stains, but that the hides in this series undoubtedly looked very good. In the same year Guthrie and Sastry (40) conducted experiments in India with marine salt to which had been added 3% sodium fluosilicate. Excess salt was used on the skins and they were stored for 4 - 5 months. On one skin a small spot of red heat was found and all the skins were judged to be in excellent condition. No hair slip or putrefaction could be noticed. They concluded that "none of the additions tried (i.e. zinc chloride, sodium fluosilicate, oxalic acid, sodium bisulphate, sodium bisulphite, perchloron, Atlas preservative and soda ash) is an absolute preventative for red heat", but that sodium fluosilicate undoubtedly yielded the best results in this respect.

Another patent, this time in France, was taken out in 1935 (60) for the use of a casein solution containing sodium fluoride or sodium fluosilicate for the preservation of hides. Jordan Lloyd (52) recommended the use of clean new salt to which had been added 1% sodium fluoride or sodium fluosilicate instead of 5% sodium carbonate + 1% naphthalene as advocated by Bergmann and his co-workers in Germany.

Experiments conducted in 1934 by Stuart and Frey (43) on the value of various chemicals, including sodium fluosilicate, as admixtures to the salt for the prevention of red heat led them to conclude that (p.636) "the fluorides all show pronounced bacteriostatic power but practically no fungistatic property. They increase the acidity of the medium to a marked extent. A greater inhibiting effect against molds would undoubtedly have been indicated with a fungus less acid tolerant than the strain of Aspergillus niger", which they had used in the tests.

In two consecutive reports Grassmann and Hausam, 1935 (61) and 1936 (41), compared the use of 1% sodium fluoride with 5% sodium carbonate + 1% naphthalene and came to the conclusion that the former undoubtedly helped in the prevention of red heat since only 1.6% of the calfskins used showed stains, but that this method was not much better than the sodium carbonate-naphthalene method.

An Australian Committee of the I.S.L.T.C. (62) reported in 1935 that the addition of 1% sodium fluoride to the curing salt yielded hides of excellent condition and appearance after five months, no hair slip, red heat, putrefactive odour or temperature increase being noticed in the stacks. The hides showed 1.8% less shrinkage than a control set, but

they apparently retained more moisture. These results were confirmed by Frey and Stuart (63) who experimented with 1% sodium fluosilicate + 0.1% p-nitrophenol as admixtures to the curing salt. The temperature in this stack was 2° to 4°F higher than the room (68°- 82°F) as compared with 8° to 9°F rise in the control set of hides.

Jordan Lloyd, 1935 (64) and Dempsey, Jordan Lloyd, Robertson, etc. (65) confirmed the earlier findings of the B.L.M.R.A. Laboratories. O'Flaherty and Doherty (66) recommended (p.336) "for the destruction of Foot and Mouth Disease virus that imported skins and hides be soaked in a solution of sodium hydrogen fluoride 1 part in 10,000 of water - that the skin or hide proportion be 1 part skin or hide to not more than 4 parts by weight of water, the temperature 20° - 25°C (68°- 78°F), and the pH of the solution so adjusted that at the end of 24 hours the pH will be 6.2 - 6.5. The skins or hides should remain in the solution for 24 hours." Manthei and Eichhorn, 1941 (67), also experimented on these lines with the virus of vesicular stomatitis and confirmed the work of O'Flaherty and Doherty.

Robertson (68) used 1% sodium fluoride and sodium fluosilicate on the salt, applying different percentages of the mixture by weight of hide. Her

results again confirmed those of earlier experiments. She stressed the fact that the equable English climate does not necessitate the use of such disinfectants, but that their addition would undoubtedly prove a great help in other countries. This was confirmed by Whitemore and his co-workers, 1942 (69), when they used sodium fluosilicate to re-cure Frigorifico hides. The fluoride hides showed no marked deterioration even when stored for four months at 97°F. Innes, 1941 (70) and 1942 (53), experimented with sheepskins and found that at least 2% sodium fluoride or fluosilicate had to be used on the curing salt to obtain good results. The calcium present as an impurity of the curing salt will precipitate as calcium fluoride and thus deprive the fluorides of their bacteriostatic power. He furthermore found that red heat still developed in localised spots even if 2% sodium fluoride was added to the salt, and attributed this to improper mixing.

A review of fourteen papers on the use of fluorides in curing was given in September, 1943 by Robertson and Merry (71). They again recommended the use of 0.5 - 1% fluorine compounds on the curing salt. It has however repeatedly been proved that this method of application does not always lead to the highest efficiency in preventing red heat, despite the excellent bacteriostatic power of these fluorides.

2. Toxicity of Fluorides.

A number of papers have been published from time to time on this question, but it will only be necessary to quote those having a bearing on the use of fluorides in the leather and allied trades.

The danger arising from fluoride treated hides lies in the fact that a certain percentage of the hide substance eventually finds its way into the manufacture of glue and gelatin, and on this account objection was raised against the use of fluorides in curing, especially since these chemicals are cumulative poisons.

According to Jordan Lloyd (52) a lethal dose of fluorine is 0.5 gram per kilogram body weight and she therefore contended that it is highly improbable for a human being to consume gelatine in such quantities as to cause death from fluorine poisoning. It can perhaps be pointed out here that arsenic compounds are, on the whole, nine times as toxic as fluorine compounds to mammals.

Humphreys (72) found that ordinary gelatine contained 20 to 200 parts per million of fluorine as compared with 130 to 160 parts per million in gelatine made from fluoride treated hides, and concluded that "gelatine made from hides which had been cured with

salt to which sodium fluosilicate had been added do not appear to contain appreciably more fluorine than normal edible gelatins."

This work was confirmed by Stuart, Dahle and Frey (73). They determined the fluorine content of commercial edible gelatine as 4 to 10 parts per million. The fluorine content of gelatine from calfskins treated with 1%, 2% and 3% fluorine compounds on the salt was 72, 72 and 64 parts per million respectively when the skin pieces were soaked in still water. With washing the content was reduced to 5 - 7 parts per million. They drew attention to the fact that commercial lime as used for the manufacture of gelatine contains 20 - 800 parts per million and this will affect the ultimate fluorine content of the gelatine. It was also pointed out that when impure salt was used for curing, calcium fluoride will precipitate and render it difficult to wash the fluorine out of the hide pieces.

Bowes (74) summarised her work on the relative toxicity of fluorides and its effect upon crops and livestock as follows : "It may be concluded that the use of salt containing 1% sodium fluoride as a dressing for arable land will have no harmful effects on the crops, but that if livestock are allowed free access to grass land which has recently been treated in this way, there is some danger that direct con-

sumption of the fluorides may result in harmful effects to the animals and indirectly to human beings.

Certain precautions might be taken which would tend to obviate any possible dangers. Firstly care should be taken to safeguard the cattle from any possibility of direct consumption of the salt either while it is in store prior to application or after it has been applied to the land. Again, the addition of lime to the salt would render the fluoride less effective owing to the formation of calcium fluoride. The presence of the lime would also be beneficial to the land."

It therefore seems obvious that, if the necessary precautions are taken, there should be practically no danger of poisoning arising from fluoride treated hides and skins.

The question of dermatitis resulting from fluorine compounds is apparently not settled yet. The writer has had occasion to work with both solutions and solid powder of sodium fluosilicate for long periods at a time during the course of all the experimental work described in this book, and can state quite definitely that no ill effects have ever been experienced yet, although absolutely no precautions were taken to cover the skin of the hands and arms. When working with the solutions, the hands

b came rather soft, but not worse than with clean water. These observations were confirmed by the workman who assisted the writer with the experiments, and it may be assumed that there is little danger of contracting dermatitis when working with sodium fluosilicate. No information seems to be available regarding the effect of sodium fluoride and sodium bifluoride.

(ii) Experimental.

Although the value of fluorides as admixtures to the curing salt for the prevention of red heat has been proved beyond doubt by overseas workers, it still remained to be seen whether the same results could be obtained under prevailing South African climatic conditions which favour the development of the halophilic bacteria causing red heat stains.

Three series of experiments were run during the period July to January to subject the treatments to the test of the summer months when the temperatures often exceed 90°F. In every experiment 20 fresh butcher hides were used.

SERIES A.

In this series the object was to determine the

efficiency of sodium fluosilicate when mixed with the curing salt.

Experiment I. Washed in cold running water to remove blood and dirt, salted with 33% clean salt of medium grain on the tail weight, rolled for 48 hours, then stacked hair to flesh in a battie for the period July to January. Control.

Experiment II. As I, with 0.5% sodium fluosilicate mixed with the curing salt. Stacked July to January.

Experiment III. As I, with 1% sodium fluosilicate mixed with the salt. Stacked July to January.

Experiment VI. As I, with 2% sodium fluosilicate mixed with the salt. Stacked August to January.

Experiment V. As I, with 5% sodium fluosilicate mixed with the salt. Stacked August to January.

Experiment VI. As I, but with 2% sodium fluosilicate mixed with old used salt of very low grade. Stacked August to January.

SERIES B.

This second series was run to investigate the effect of dipping the hides in a cold saturated solution of sodium fluosilicate prior to salting

upon the development of red heat in the stacks. All the workers have found isolated spots of red heat on their experimental hides or skins treated with salt to which various fluorine compounds had been added, probably due to improper mixing. In dipping the entire surface of the hide comes into contact with the chemical.

Experiment VII. Washed, dipped for fifteen minutes in a saturated (1%) solution of sodium fluosilicate, salted with 33% salt on the tail weight, rolled and stacked as before during the period July to January.

Experiment VIII. As VII, but applying dirty used salt. Stacked August to January.

SERIES C.

The effect of used salt and blood on the development of red heat and salt stains was studied in this series of experiments.

Experiment IX. Not washed (so as to retain the blood and dirt), not dipped, salted with 33% clean salt. Stacked September to January.

Experiment X. As IX, using very impure old salt. Stacked September to January.

Experiment XI. Washed, old used salt applied.

Stacked October to January.

Examination of Stacks.

All the stacks were left undisturbed until the end of January, when they were examined.

SERIES A.

Experiment I. All the hides in this stack, except the one on top which had dried out somewhat, showed excessive development of red heat, in some cases covering the entire flesh surface and also showing on the grain side. Only two hides had developed isolated spots of violet stains. No true salt stains could be found, but one hide had a dark spot where a clot of blood had not been well washed off. On the whole the hides were well cured and did not show any hair slip or a tendency to stick together, although there was a putrid smell noticeable.

Experiment II. Five hides, at different positions in the stack, showed a strong development of red heat. On ten hides spots of red heat were found, some covering several square inches, while very small spots were detected on four others. The top hide was dry and did not show any signs of red heat. Apparently no salt stains had developed, but a limited number of small blood stains were present. These hides looked,

felt and smelled better than than the control stack, the flesh being much whiter and cleaner. On those hides which had developed much red heat a slight putrid smell could be detected.

Experiment III. Only five of the hides in this stack showed red heat development, some spots being very small whilst others covered areas of 2 to 8 square inches. All the other hides were completely free from red heat. As before, no salt stains could be seen, and only a few blood stains were found. The general condition of the hides was much better than in the two former experiments. They were white and clean and there was no disagreeable odour.

Experiment IV. Three of these hides had developed red heat in very small spots. The remarks under Experiment III also apply here with regard to the general appearance of the hides.

Experiment V. This stack had the best appearance with regard to colour, cleanliness and red heat development. Only one hide showed two small spots of discolouration of this type. A small number of dark blood stains were present. These hides looked more moist than those in the other sets, but no data on this are available yet. See Chapter 16.

Experiment VI. The hides in this experiment could,

on the whole, be compared with those of Experiment III. Four hides had developed red heat, the spots being scattered over the flesh side. These spots were limited in size, except for one which covered several square inches. Small salt stains of a dark greenish colour were found on all the hides and a number of blood stains were also present. The hides did not look as clean and as white as those of Experiments II, III and IV, and there was a tendency to stick together. A faint disagreeable odour could be detected, and some of the hides had a slimy feel.

Discussion - Series A.

It was evident from these experiments that the addition of sodium fluosilicate to the curing salt undoubtedly resulted in checking the development of red heat on the wet-salted hides. All the fluosilicate hides had a better general appearance than those in the control stack; they were whiter, and cleaner looking, and there was a marked absence of putrid odours although the hides on which the old salt had been applied were apparently not very well preserved, probably owing to the low grade salt which had been applied. See Chapters 13 and 14.

The results obtained confirmed those of other workers with regard to the efficiency of fluorides when mixed with the curing salt. In all the stacks

Discussion - Series B.

The method of dipping the fresh hides in a saturated solution of sodium fluosilicate gave far better results than that of mixing the disinfectant with the curing salt. Red heat is completely prevented from developing and bacterial decay is inhibited since the entire hide comes into contact with the chemical. The dipped hides are therefore less prone to putrefaction and are better cured than hides salted with a mixture of salt and sodium fluosilicate. Furthermore, as was shown in Chapter 6 the latter method proved unsuccessful in preventing insect damage to the hides in store, whereas dipped hides stood up to a very severe test.

SERIES C.

Experiment I, Series A, acted as control.

Experiment IX. All the hides, except the top one, were affected by red heat. Some showed violet stains. Large dark patches were found on areas which had retained the blood in shallow pools. Isolated lumps of clotted blood were scattered over the flesh of most of the hides. They looked very dirty and of a dark colour, and a strong putrid smell was present.

Experiment X. This stack was very badly stained. Red heat, violet stains, blood and salt stains covered

nearly the entire flesh surface of every hide, except the top one, and a strong putrid odour was present. The hides were inclined to stick together and stains could also be seen on the grain side. The hides were extremely dirty and dark coloured compared with those in Experiment I or Experiment VI.

Experiment XI. The general appearance of the hides in this stack was superior to that of Experiment X. Red heat was again very pronounced, salt stains were present on most of the hides, but blood stains were absent. The colour was much better than in Experiment X and could be compared with IX. Here again putrefaction had affected the hides due to the impure salt and they also had a tendency to stick together.

Discussion - Series C.

It became evident from the experiments in this series that all fresh hides should be washed to remove blood and dirt which cause stains on the hides and on the finished leather. The re-use of salt must be discouraged since salt used once is invariably badly contaminated with impurities causing stains, as well as with halophylic bacteria which have become accustomed to living in high concentrations of sodium chloride. In Experiment X it seemed as though blood in conjunction with impure salt led to the development

of more dark stains of small dimensions than when the blood had been washed off prior to curing. This is probably due to the iron content of the blood, as has been pointed out in Chapter 9.

SUMMARY.

Pilot scale experiments aiming at evaluating the efficiency of sodium fluosilicate for the prevention of red heat under South African climatic conditions have been described in detail. In these experiments two methods of application have been compared.

(i) Mixing the sodium fluosilicate powder in different concentrations by weight with the curing salt as advocated by overseas workers.

(ii) Dipping the fresh hides in a cold saturated solution of sodium fluosilicate prior to salting.

The former method undoubtedly helped in preventing the development of red heat, but because it is practically impossible to mix the two substances efficiently localised spots of red heat will still develop on the hides. Hides dipped for fifteen minutes in a saturated solution of sodium fluosilicate prior to salting were completely protected against red heat bacterial attack. It is therefore recommended that, whenever possible, fresh hides should be dipped as described above. In all other cases it will be advantageous to mix the disinfectant with the curing

salt, two to three pounds of solid sodium fluosilicate being used with every 100 lbs of salt.

Experimental results once more stressed the fact that blood and impure or used salt will lead to the development of stains on the hides. Washing of fresh hides and the use of pure salt of good quality are therefore advocated.

SUMMARY OF PART III.

1. A detailed discussion has been given on the stains usually encountered upon hides and skins, with a full list of references of papers which have been published on this problem during the past 35 years. Three types of stains can be distinguished. The first group comprises the so-called true salt stains which are usually limited in size, varying in colour from light yellow to reddish-brown. These stains are caused by chemical reactions between impurities in the curing salt and the biochemical compounds of the hide, probably accentuated by the activities of bacteria. Iron appears to be of importance in the development of such salt stains. The second type includes the more or less localised spots of violet-blue to violet-red stains encountered upon wet-salted hides and skins, these stains being most probably

caused by bacterial action. The third type is the well-known red heat stains on wet-salted material which are caused by the activities of halophylic bacteria of a chromogenic group. All these stains cause troublesome defects on the finished leather and may also be responsible for the loss of valuable hide substance in the case of bacteriological stains.

2. Iron is responsible for many of the true salt stains upon salt-cured hides and skins. This iron may be present either in the curing salt or may result from blood left on the hide or skin after slaughtering and flaying. Proper washing of the hide is therefore necessary to minimize the danger of the development of true salt stains. If the hides are well washed, iron stains will not develop provided the total iron content of the curing salt does not exceed 100 parts Fe per million of salt, as was shown by experimental results.

3. Experiments on pilot scale to test the efficiency of sodium carbonate, sodium arsenite and barium fluosilicate for the prevention of red heat showed that the two former were not of any use. Barium fluosilicate, when mixed with the curing salt, gave very promising results.

4. Detailed descriptions have been given of experiments aiming at evaluating the efficiency of sodium

fluosilicate for preventing red heat. This chemical was successfully applied by two methods.

(i) Mixing the sodium fluosilicate with the curing salt in various concentrations by weight.

(ii) Dipping the fresh hides in a cold saturated solution of sodium fluosilicate prior to curing.

The former method helped in minimizing the danger of red heat development but localised spots of red heat still occurred because of the mechanical impossibility of obtaining even mixing of the curing salt and the disinfectant. Two to three pounds of solid sodium fluosilicate powder should be used on every 100 lbs of curing salt. Hides dipped in a saturated (1%) solution of sodium fluosilicate prior to salting were completely immune from attack by the red heat bacteria.

5. Experimental evidence once more stressed the importance of washing the hides prior to salting and of using pure fresh salt, in order to reduce the number of true salt stains on the hides and the resulting leather.

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