

Researches into Dips and Dipping.

D. Effects of Dips on Wool.

Paper I. The Effect of Arsenical Dips on Wool.*

By

H. A. HAMBROCK,† B.Sc.(Agric.), Assistant Dip Research
Officer, and

T. J. WILKEN-JORDEN, D.Sc., Dip Research Chemist,
Onderstepoort.

CONTENTS.

- I. INTRODUCTION.
- II. EXPERIMENTAL TECHNIQUE.
 - (a) Moisture Determination.
 - (b) Determination of Arsenic in Wool, Grease, etc.
 - (c) Estimation of Suint, Grease, Dirt and Clean Fibre.
 - (d) Estimation of Chlorine in Wool.
 - (e) Estimation of Chemical Damage.
- III. MATERIAL USED IN INVESTIGATION.
- IV. INVESTIGATION OF GROOTFONTEIN SAMPLES.
 - (a) Effect of Dipping on Hygroscopicity.
 - (b) Adherence of Dip Constituents to Wool.
 - (c) Effect of Dipping on Raw Wool Constituents.
 - (d) Effect of Dipping on Wool Fibre.
- V. IN VITRO STUDIES ON WOOL FIBRE.
 - (a) Effect of Sodium Arsenite and Cooper's Powder Dip on Wool.
 - (b) Influence of Sunlight and Ultra-Violet Radiation on Wool and Dipping.
- VI. SUMMARY.
- VII. REFERENCES.

*This work has been carried out with the aid of a grant from the Empire Marketing Board.

†The substance of this paper was submitted as a thesis in partial fulfilment for the degree of M.Sc.(Agric.) at the University of Pretoria.

I. INTRODUCTION.

The problems relating to the various processes in the manufacturing of woollen materials have during recent years received a great deal of consideration, particularly those processes which involve the use of chemical substances injurious to the wool fibre, and which may modify certain natural properties of wool, thus interfering with the ultimate usefulness of the finished fabric. It is a well-known fact that the main qualities of wool only become fully revealed at the spinning and dyeing stages, while from the wool-grower's point of view the relative resistance to the conditions leading up to those stages is an important factor. Again, the amenability of different wools to such processes must reflect back on their production. The aim of the producer should, therefore, be focussed, not only towards the production of a wool fibre of desired length and general quality, but also towards the preservation of those natural properties which determine its value as a textile material.

Of the various factors which influence or modify the physical and chemical properties of the wool fibre, the wool producer is in the first instance concerned with the effect of various chemical preparations in the form of dipping fluids. It is no exaggeration to state that the very existence of a wool-bearing sheep industry in South Africa is dependent on the effective combating of various external parasites. It was soon realized that the deleterious effect of uncontrolled parasitic infection was a far more serious factor in wool production than the damage which might conceivably be wrought by the chemicals used as dips. To illustrate this, we have reproduced two photographs, one of a sheep badly infected with scab (*Psoroptes communis*) (Fig. 1), and the other (Fig. 2) of a staple of wool showing the effect of scab as also the healthy new growth after the animal had been cured by dipping in a lime-sulphur solution.



FIG. 1.

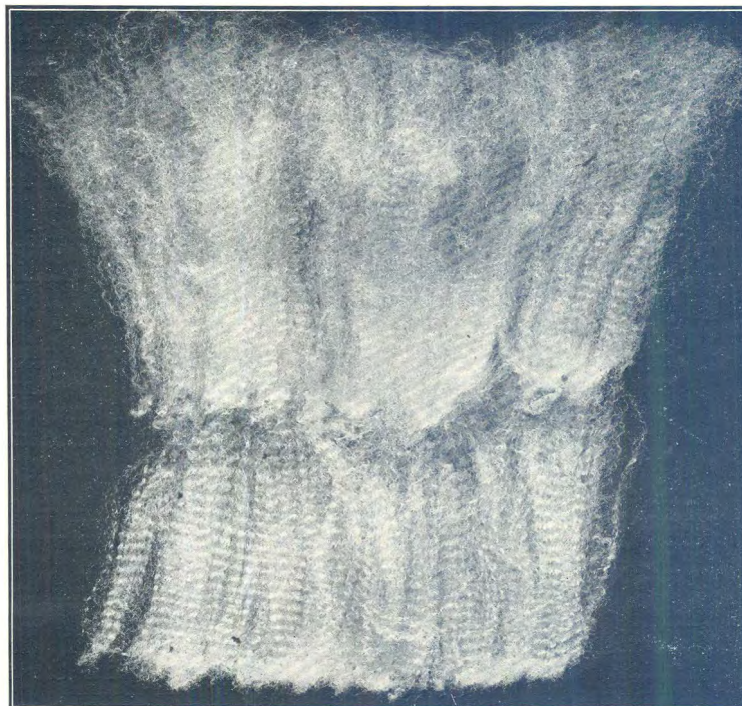


FIG. 2.

These photographs speak for themselves. Hence it is only natural to find that all initial efforts were mainly directed towards the finding of efficacious dips, and that the possible effect of such dips on the fibre was allowed to recede into the back-ground.

The selection of the chemicals used as dips is in the first instance controlled by the nature of the parasite to be exterminated. Thus lime-sulphur is highly efficacious against scab, but quite ineffective against ticks. On the other hand, sodium arsenite is sure to kill the tick, but is not of much use in combating scab. In the present paper we propose to deal only with those arsenical dips most widely used for sheep dipping, namely, arsenite of soda, used for tick destruction (Heartwater), and Cooper's Powder dip used primarily against scab. However, in reviewing the work done on the effect of these dips on the fleece in general and on the wool fibre in particular, it would appear desirable to include also other dips for the sake of comparison.

In 1913 tests were carried out by the Union Department of Agriculture to determine the possible effect of such dips as Cooper's Dip, Lime and Sulphur dips, Little's dip, tobacco extract, etc., on the scouring, combing, spinning, dyeing and finishing properties of the dipped wools. Samples of the dipped and undipped wools were submitted to the Bradford Technical College and Leeds University to be put through the different processes of manufacture. The

completion of the study of the samples submitted was unfortunately delayed for many years, and it was not until 1926 that a report by Hollis was submitted to the Department. The conclusions arrived at by Hollis as a result of this study may conveniently be summarized as follows:—

- (1) Dips have some detectable injurious action on wool.
- (2) Staining action by the dip does occur, and in some cases the discoloration is permanent.
- (3) Dipped wools scour less easily than undipped wools.
- (4) To some extent dipping seemed to affect the affinity of wool for different dyes, though the results were often contradictory.
- (5) Defects in the fibre due to irregular application and penetration of the dipping fluid could not be definitely shown, although it was suggested that this irregularity was probably the cause of irregular dyeing of the finished material.

In 1915, Green, basing his study on macroscopic and microscopic examinations of the pure wool fibre, made some observations on the effect of lime-sulphur dips on wool. Wools subjected to more severe tests in which clean wool samples were steeped into solutions of lime-sulphur of varying concentrations (1-8 per cent. polysulphide sulphur), showed rapid swelling and pronounced structural changes with the higher concentrations and long exposure; while the usual concentrations and the short immersion period of two minutes showed no detectable effect on the wool, no difference being noticeable between dipped and undipped samples.

In 1931 further sheep and wool dipping experiments were carried out at the Bathurst Experimental Farm, these experiments extending over a period of 12 months. During this time groups of 30 sheep were dipped regularly every week, one group being dipped in a 0.16 per cent. solution of sodium arsenite, another group in pure water, and the third group remaining undipped for the purpose of control. The object of this experiment was to determine (1) whether Merino sheep could withstand and adapt themselves to such regular dipping, and (2) the effect of such dipping on the fleece. It was found that the process of regular dipping had no effect on the condition of the sheep, but produced marked changes in the wool. The staples from the dipped sheep were for the most part harsh and inelastic to the feel. The foreign matter consisting of sand and dirt also extended more or less throughout the length of the staple instead of being restricted to the tip, producing a general discoloration and dullness. This effect appeared to be as marked with the water dipped sheep as with the arsenite dipped animals. On the other hand, dipping appeared to have no effect on fibre fineness and contour, although the arsenite of soda did appear to lower the breaking strength of the fibre. Samples of these wools were forwarded to us for the chemical study of damage, but unfortunately the samples were found to be useless since not sufficient care had been exercised in classification and sampling.

From this brief review it will be seen that very little attention has been paid to the possible effect of dipping on the wool fibre. Regarding the chemical effects of dip constituents on the fibre we know practically nothing. It is true that at one time certain buyers and manufacturers in the textile trade raised a great outcry against the use of certain dips in South Africa, but this outburst can only be ignored since it was based on misunderstanding and ignorance regarding the most elementary chemical principles. In the present paper we have concerned ourselves only with the chemical examination of dipped fibres. Physical measurements such as elasticity, breaking strength, etc., have not been undertaken, since other arrangements have been made for such physical studies.

II. EXPERIMENTAL TECHNIQUE.

Several aspects of the effect of dips on the wool fibre have been studied. These include the effect of dipping on hygroscopicity, the adherence of dip constituents to the wool fibre, the effect of dipping on the yield of clean wool, and the effect of such dips on the soundness of the wool fibre.

(a) MOISTURE DETERMINATION.

The analytical sample was obtained by taking small sub-samples from the original sample. One or two grams of the sample thus obtained were weighed out into a small weighing bottle with ground glass stopper. Three to four of these weighing bottles were then slipped into the vacuum tube of the apparatus reproduced below (Fig. 3).

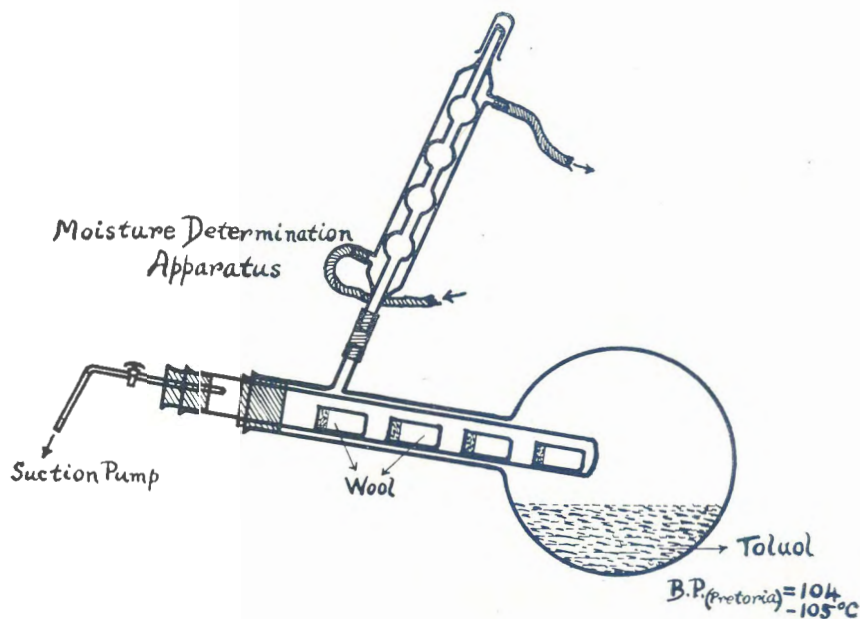


FIG. 3.

The moisture was expelled under vacuum by heating to 104-105° C. by means of toluol vapour. Constant weights were usually obtained after about 16 hours heating. The weighing bottles were then closed, allowed to cool in a desiccator, and weighed, the moisture being calculated from the loss in weight.

(b) ESTIMATION OF ARSENIC IN WOOL.

The same method of sampling was used for determining the arsenic in the wool. The method used was that described by Green (1918) for the determination of arsenic in organic materials. Five gram samples were weighed out into a silica dish, and thoroughly wetted with ca. 30 c.c. of a 20 per cent. magnesium nitrate. The dish was then kept on a sand-bath until complete dryness and then ignited in an electric oven at a temperature just approaching a dull red heat. The ash was dissolved in ca. 20 c.c. of a 1 in 3 sulphuric acid, transferred to a 100 c.c. measuring flask, and made up to volume. Of this solution 10 to 50 c.c. aliquots were used for the actual arsenic determinations. The arsenic was evolved as AsH_3 , and absorbed in a ca. N/50 solution of silver nitrate. In this solution the arsenious acid formed was then titrated with N/495 iodine, after disposing of the silver nitrate by adding sodium bicarbonate and excess potassium iodide.

1 c.c. N/495 I thus gives 0.1 mgm. As_2O_3 .

(c) ESTIMATION OF WOOL GREASE, SUINT AND DIRT.

The method using a soxhlet extractor as described by Bonsma (1930) was tried out. It was found, however, that this method was inapplicable especially to sub-samples taken from dipped wools, since the dirt became distributed throughout the entire wool mass. Even removal of the sample from the soxhlet and washing in a basin with water failed to give a perfectly clean wool. It was, therefore, decided to go back to the older and perhaps more crude method of washing the wool in open basins. The results were certainly more satisfactory for our purpose. A 25 gm. sample was dried for 24 hours in a steam oven, and then placed in a large porcelain dish and covered with benzol which had been redistilled. The wool was carefully triturated with a forceps, thoroughly squeezed out, and the process repeated in a second dish with fresh benzol. Usually this washing process was repeated a third time. The washings were then collected in a distillation flask and the large excess benzol removed by distillation, thus concentrating the grease extract down to about 100 c.c. This concentrated solution was then filtered through a weighed quantitative filter into a 250 c.c. measuring flask, and the sludge remaining on the filter well washed with benzol. The filtrate was then made up to volume with benzol. In this solution the grease was determined by pipetting out 100 c.c. into a weighed evaporating dish, driving off the benzol on the steam bath, and weighing the residue. In another aliquot the arsenic was determined by evaporating off the benzol, evaporating down with magnesium nitrate, and igniting. For the rest the same procedure was followed as described under the determination of arsenic in wool. In the case of wool dipped in Cooper's dip the free sulphur extracted with the grease was further determined in a third aliquot by using both the Rimington-Benedict-Denis (1930) and peroxide fusion methods.

Having removed the grease, the dried wool was next washed several times with distilled water as above, the washings collected, evaporated down to about 100 c.c. and again made up to a definite volume after filtering through a second weighed quantitative filter. In an aliquot of this solution the suint was determined by evaporating down on a steam oven to constant weight. In a second aliquot the arsenic was determined by the same method as described for the wool.

For determining earth, sand and other impurities the two weighed filters containing these substances, as well as any remaining plant material subsequently removed by hand, were transferred to a weighed platinum dish, and heated in a steam bath to constant weight. The arsenic in this residue was determined as already described by evaporating down with a solution of magnesium nitrate and igniting.

The clean wool obtained by this process is allowed to dry in the atmosphere, and then weighed. At the same time its moisture content is determined on a small sample. All figures may thus be calculated, either on an absolutely dry basis, or on a basis of the same moisture content throughout.

(d) ESTIMATION OF CHLORINE.

The chlorine in the raw wool was determined by the usual micro-titration method in use in this Institute (Malan and v. d. Lingen, 1931) by evaporating down 2 gm. wool in a platinum dish with 10 c.c. of a 10 per cent. calcium acetate (chlorine-free) solution and igniting at a low temperature. The extract of the ash in a 5 per cent. nitric acid solution was filtered through a small filter and made up to a convenient volume. Of this an aliquot was titrated by adding excess N/25 silver nitrate, shaking briskly to coagulate the silver chloride formed, and then titrating back with N/50 ammonium sulphocyanide, with a solution of ferric alum as indicator.

(e) CHEMICAL ESTIMATION OF DAMAGE.

In considering the methods available for determining quantitatively the degree of damage of wool fibres, several methods were studied, including that of Sauer (1916) and the two D.I. methods described by Kraus and Schleber (1929). Of these the Pauly-Rimington diazometric method and the borax method as described by Kraus and Schleber (1929) were found to give the most reliable results.

The method of Pauly (1904) is based on the coupling of certain amino-acid residues with p-phenyl diazonium sulphonate thereby producing an intense reddish-brown coloration. This reaction has been made quantitative by Rimington (1930) by dissolving the diazo colouring formed in alkali, and matching the solution thus obtained against a standard solution of "New Acid Brown S".* In this way the number of units of damage could be determined for each wool.

*We are indebted to the Wool Industries Research Association, Torridon, Leeds, for placing a quantity of this dye at our disposal.

In the borax method as modified for our purpose, 25 c.c. of a boiling 2.5 per cent. borax solution was allowed to act for half an hour on 100 mgm. wool, and the amount of nitrogenous material thus extracted calculated as a percentage of the total nitrogen present. The extract was filtered, made up to a known volume, and the nitrogen in a suitable aliquot determined by the micro-kjeldahlization method of Folin (1919). The ammonia so formed was micro-distilled over with caustic soda by the method used by Folin and Svedberg (1930) for urea determinations, and determined by nesslerization in the usual way. The total nitrogen in the wool was determined by the ordinary macro-Kjeldahl method, using copper sulphate as catalyst.

In the Sauer method described by Kraus and Schleber (1929) the amount of extractable nitrogen is determined by allowing a mixture of N/2 potassium hydroxide and a 1 per cent. hydrogen peroxide to act on the wool for 3 days at room temperature. In our micro-modification of the method 100 mgm. wool was allowed to soak for a period of three days in a solution consisting of 8 c.c. water, 10 c.c. of a 1 per cent hydrogen peroxide, and 2 c.c. of a N/2 potassium hydroxide contained in small Erlenmeyer flasks, the flasks being closed with thistle funnels containing a very dilute solution of sulphuric acid. The extract was again filtered, the solution in the thistle funnel added, made up to a definite volume, and the nitrogen in an aliquot determined by micro-kjeldahlization, distilling over with caustic soda, and nesslerization. The "soluble nitrogen" was again calculated as a percentage of the total nitrogen.

III. MATERIAL USED IN INVESTIGATION.

Two sets of materials were used in the present investigation—viz. wool samples obtained from actual dipping trials, and wool samples from undipped sheep for in-vitro studies.

The first set of samples was obtained from dipping experiments carried out at the Grootfontein School of Agriculture. Seven groups, each consisting of 50 unshorn Merino wethers, uniform in age and wool, were subjected to the following treatment:—

Lot CC3—dipped 3 times in Coopers.

Lot C3—dipped 3 times in Coopers.

Lot C2—dipped 2 times in Coopers.

Lot As3—dipped 3 times in Arsenite of Soda.

Lot As2—dipped 2 times in Arsenite of Soda.

Lot C (100 animals) used as control and not dipped.

No definite order was observed in dipping the various groups, except that Lot CC3 were always put through the dip prior to Lots C2 and C3. The dips were prepared freshly for each dipping, the interval between the first and second dipping being 10 days, and that between the second and third 14 days.

With both the sodium arsenite and the Cooper's dip the strength of the bath was regulated to show 0.16 per cent. As_2O_3 , throughout the experiment, six animals being lowered into the bath at a time

and kept immersed for $1\frac{1}{2}$ minutes. The weather conditions remained good, bright sunshine prevailing throughout the course of the experiment. Two days after the third and last dipping, however, heavy rains were experienced amounting to 2.8 inches. Just prior to the first dipping a shoulder sample was taken from each sheep. A similar set of samples was taken three months after the first dipping, or more than two months after the last dipping. Thereupon the sheep were shorn, the wool yields noted, and each fleece examined in the usual commercial way, observations being made as to soundness, colour, quality and feel. The live weights of the animals were also controlled by weighing the animals just prior to dipping, 10 days after the last dipping, and again just prior to shearing. The shoulder samples taken were forwarded to us for chemical examination. Unfortunately the individual sheep were not numbered, so that it was impossible for us to determine the relation of the dipped wool to the undipped sample from the same animal.

This omission on the part of those responsible for the experiment at Grootfontein made an accurate determination of the effect of dipping on the wool most difficult. The results of this part of our investigation must, therefore, be regarded merely as preliminary and indicative. For more accurate data these and other dipping experiments will be repeated at Onderstepoort in the near future.

The second set of samples, which were used for in-vitro studies in the laboratory, were obtained from sheep at Onderstepoort which had not been dipped, at least not during the period of growth of the fleece in question. These samples were selected most carefully, in a manner to be described more fully later.

IV. INVESTIGATION OF GROOTFONTEIN SAMPLES.

Before proceeding to deal with the results of our chemical investigation of the samples submitted, it is perhaps advisable to state briefly what observations were made at Grootfontein.* In Table I the average live weights of the different groups throughout the course of the experiment have been recorded.

TABLE I.
Live Weights in Pounds.

Date.	CC3.	C3.	As3.	C2.	As2.	Control.
4.12.31.....	57.4	59.0	59.7	59.2	59.2	58.7
8.1.32.....	56.9	58.2	59.6	60.7	60.9	59.8
14.3.32.....	65.3	65.9	67.4	68.6	68.3	66.7

It will thus be seen that the process of dipping had no noticeable effect on the animals themselves. In Table II have been recorded certain observations made on the fleece at shearing.

* The dipping experiments as well as the examination of the fleeces at Grootfontein were made by Mr. G. S. Maré, Sheep and Wool Research Officer, Grootfontein.

TABLE II.

Shearing Results.

Lot.	Average yield per animal (grease wool in lb.).	Soundness.	Colour.
CC3.....	7.34	Some fleeces showed break	Least attractive.
C3.....	7.50	Sound	Fairly attractive.
As3.....	7.41	„	Very attractive.
C2.....	7.44	„	Fairly attractive.
As2.....	7.53	„	Very attractive.
Control.....	7.95	„	Most attractive.

The yield in raw wool from the control group thus exceeds the yields from all the other groups, the difference, however, being very small. In fact, the loss of suint due to dipping may, under circumstances, account for a more marked loss in raw yield than that expressed in the above table. The more unattractive appearance of the fleeces from lot CC3 may be ascribed to the deposit of sulphur and arsenic sulphide especially noticeable in a freshly prepared bath of Cooper's dip, the animals emerging from it being quite yellow. As dipping proceeds this staining effect gradually diminishes, probably due to the chemical action of the suint in solution on the arsenic sulphide forming soluble thio-arsenites. It will be remembered that lot CC3 were always put through the freshly prepared wash prior to lot C3. Whether the breaks in the staples noted in some fleeces from lot CC3 can be ascribed to the effect of the yellow deposit on the fleece cannot be answered at this stage, as obviously further study is necessary.

Having thus briefly referred to the observations made at Grootfontein, we may now proceed to describe more fully our chemical study of the samples.

(a) EFFECT OF DIPPING ON HYGROSCOPICITY OF WOOL.

Duplicate moisture determinations were made on samples of raw wool from both dipped and undipped fleeces by the method already described. After complete "dryness" the wool samples in the weighing bottles were placed open in a desiccator containing water, and left to condition in this saturated atmosphere for two days. The fluctuations in room temperature were small. These results have been tabulated in Table III, columns 2 and 4 representing the percentage regain at normal atmospheric temperature and humidity, and columns 3 and 5 representing the percentage of reabsorbed moisture at 100 per cent. humidity and atmospheric temperature.

TABLE III.

Effect on Hygroscopicity—Raw Wool.

Group.	Before dipping.		After dipping.	
	Percentage regain.	Percentage water reabsorbed at 100 per cent. humidity.	Percentage regain.	Percentage water reabsorbed at 100 per cent. humidity.
CC3.....	6.63	30.30	6.21	21.68
C3.....	6.89	27.30	5.60	18.75
As3.....	6.55	26.30	6.44	19.10
C2.....	6.64	28.50	6.99	18.85
As2.....	6.34	28.65	5.95	20.08
Control.....	6.50	30.63	6.36	29.38

Except in the case of lot C3 there is no appreciable difference between dipped and undipped samples at atmospheric humidity. However, at 100 per cent. humidity raw wools show a decided change in their absorptive capacity for moisture on being dipped. The absorption capacity for undipped wools is here more than 30 per cent. higher than that for dipped wools. The main reason for this change may be ascribed to the fact that some of the more hygroscopic constituents of the suint are removed from the wool in the process of dipping. As will be shown later, most of the more readily removable suint constituents are removed by the second dipping, there apparently being no appreciable difference in the suint content of twice and thrice dipped wools. In parallel with this, there is no appreciable difference in hygroscopicity between twice and thrice dipped raw wools.

Apart from the effect of suint and other constituents of raw wool, there is also the possibility that the wool fibre itself is so affected by the dip that its hygroscopicity may be changed. According to Tänzer (1930) the treatment of wool with alkalis and acids results in a loss of weight, together with a loss in affinity for moisture. Speakman (1931) showed that the treatment of wool with sodium sulphide does not result in any noticeable change in hygroscopicity for humidities below 100 per cent.; at 100 per cent. humidity, however, a small change in moisture affinity was noted, the untreated wool absorbing less moisture than the treated wool.

In order to determine whether any such change in the absorptive capacity of the wools had occurred as a result of dipping, the wool samples under investigation were carefully degreased and desuinted by washing in benzol and distilled water respectively. The moisture content of the atmosphere conditioned samples were again determined, and the dry wool again allowed to reabsorb moisture in a desiccator at 100 per cent. humidity. The results so obtained have been tabulated in Table IV.

TABLE IV.
Effect on Hygroscopicity—Clean Wool.

Group.	Before dipping.		After dipping.	
	Percentage regain.	Percentage water reabsorbed at 100 per cent. humidity.	Percentage regain.	Percentage water reabsorbed at 100 per cent. humidity.
CC3.....	10.19	27.0	9.63	26.3
C3.....	8.87	27.0	9.26	26.5
As3.....	9.55	27.4	9.42	25.5
C2.....	9.60	27.2	9.79	26.8
As2.....	9.57	27.5	9.37	27.0
Control.....	10.08	27.2	10.06	27.5

The relatively small changes in hygroscopicity shown by the variously treated wools measured at atmospheric humidity we do not propose to discuss here, since such changes can be stressed only when working under carefully regulated conditions of humidity in a specially equipped laboratory. The results at 100 per cent. humidity, however, show that the effects of dipping on the wool fibre were so small or of such a nature that they are not reflected by its affinity for moisture.

(b) ADHERANCE OF DIP CONSTITUENTS TO WOOL.

Arsenic determinations were made on the raw wool, on the suint, grease, sand and other impurities, and on the clean fibres by the methods already described. In Table V these determinations have been recorded, all figures being expressed as mgm. As_2O_3 per 100 gm. of the original raw wool.

TABLE V.
Arsenic Adhering to Wool.

Wool constituent.	CC3.	C3.	As3.	C2.	As2.	Control.	
						Before dipping.	At shearing time.
Suint.....	109.0	97.0	53.0	52.5	45.0	0.0	5.0
Grease.....	30.0	27.0	15.0	24.8	10.0	0.0	0.0
Impurities.....	21.8	18.3	29.0	6.5	6.2	0.0	0.0
Clean fibre.....	21.0	14.0	16.0	16.0	19.0	0.0	0.0
TOTAL.....	181.8	156.3	113.0	99.8	80.2	0.0	5.0
Raw wool.....	190.0	150.0	115.0	100.0	80.0	0.0	5.0

These results are significant, especially if it be remembered that the wool samples were taken more than two months after the last dipping. The fact that the CC3 sample shows the highest arsenic content is in agreement with the suggestion that the free arsenic sulphide suspended in a freshly prepared wash of Cooper's dip is deposited as such in the fleece. In fact, the samples dipped in Cooper's are throughout higher in arsenic than those dipped in arsenite of soda, due mainly to this deposition of the insoluble ingredients of Cooper's dip powder. The small quantity of arsenic found in the control sample taken at the conclusion of the dipping experiment, suggests that the undipped sheep of the control group had come into contact with freshly dipped sheep, thus causing slight contamination. It should further be noted that at least half of the total arsenic in the raw wool is in a fairly soluble form, being removed along with the suint. A fairly appreciable percentage, however, is or becomes very closely associated with the clean fibre, being fixed in such a way that it cannot be removed by mere washing in water. Whether this arsenic enters the fibre during the actual dipping process, or whether it enters during the period between dipping and shearing, or whether it becomes fixed in the fibre only in the actual process of suint extraction in the laboratory, it is most difficult to say.

In order to determine how this apparently fixed arsenic is affected by the process of scouring, 25 gm. samples of the raw wools were put through three successive baths of about 10 litre capacity, containing in order solutions consisting of 0.36 per cent. soap and 0.17 per cent. Na_2CO_3 , 0.30 per cent. soap and 0.10 per cent. Na_2CO_3 , and pure water respectively. The temperatures of the first two baths were 49° and 45° C. respectively, the third bath containing water being at ordinary temperature. The wool was washed for two minutes in each of these baths, and subsequently thoroughly rinsed with clean water. The amounts of arsenic remaining fixed in the fibre have been tabulated in Table VI.

TABLE VI.
Arsenic in Scoured Wools.

<i>Sample.</i>	<i>Mgm. As₂O₃ per 100 gm. scoured wool.</i>
CC3.....	14.0
C3.....	14.0
A3.....	13.0
C2.....	12.0
As2.....	11.5
Control.....	—

Comparing the results thus obtained with those tabulated in Table V for the clean fibre, and remembering that in these wools the clean fibre only amounts to about 50 per cent. of the raw wool, we observe that more than half of the apparently fixed arsenic is removed by the scouring process. However, speaking relatively, a still fairly appreciable quantity remains fixed even in the scoured fibre. The fate of this arsenic we hope to investigate still further.

if possible tracing it throughout the whole of the manufacturing process up to the finished and worn product. We feel it our duty, here, to sound a note of warning to buyers, manufacturers, and others concerned in the wool trade, not to resort to rash speculations regarding the interpretation of this arsenic in the textile trade. It is entirely unjustified to rush to the conclusion that this arsenic is bound to have some ill effect on the person wearing garments made from such wool. Such a conclusion can only be justified when based on the experimental facts of further research into the problem. What is more, South African wool-bearing flocks are not, as a rule, dipped in arsenical preparations, the official dip recommended against scab being a solution of calcium polysulphides containing no arsenic. The argument of ill effects to human health, if it *should* be proved by further research, would be applicable, as far as scab eradication is concerned, only to arsenic-containing preparations.

In examining the grease obtained from wools dipped in Cooper's dip, it was observed that this grease was to an appreciable extent contaminated with free elementary sulphur. On analysis the following results were obtained:—

Sample CC3	3.10 per cent. sulphur.
Sample C3	2.22 per cent. sulphur.
Sample C2	1.09 per cent. sulphur.

TABLE VII.

Effect on Wool Constituents.

	Group CC3.		Group C3.		Group As3.	
	Before.	After.	Before.	After.	Before.	After.
Moisture.....	5.85	6.23	5.30	6.45	6.05	6.15
Grease.....	14.27	16.38	14.38	15.42	15.40	13.20
Suint.....	6.77	3.51	6.86	3.20	7.66	3.19
Impurities.....	25.68	23.46	24.90	23.74	22.50	25.90
Clean fibre.....	46.16	50.48	49.07	50.92	48.83	50.66
TOTAL.....	98.73	100.06	100.51	99.73	100.59	99.10

	Group C2.		Group As2.		Control.	
	Before.	After.	Before.	After.	Before.	After.
Moisture.....	6.54	6.23	5.62	5.96	6.17	5.98
Grease.....	13.90	13.88	13.60	14.02	13.96	14.65
Suint.....	7.11	3.17	7.29	3.22	6.94	6.77
Impurities.....	23.88	28.32	24.53	27.60	24.15	26.72
Clean fibre.....	47.80	49.91	48.27	49.60	46.27	48.28
TOTAL.....	99.23	101.51	99.31	100.83	99.47	101.40

The sulphur contents here given were calculated on a raw wool basis, so that the grease obtained from the dipped CC3 sample contained close on 20 per cent. of free sulphur. As will be shown presently this sulphur causes a quite noticeable rise in the apparent grease content of the wool as determined by the usual solvent extraction method. It is also interesting to note that normal raw wool, yielding around 50 per cent. of clean fibre, contains only from 1.5 to 2.0 per cent. sulphur consisting chiefly of cystine sulphur, while in the case of wool CC3 the free sulphur alone amounts to over 3 per cent.

(c) EFFECT OF DIPPING ON RAW WOOL CONSTITUENTS.

The grease, suint, impurities, and clean fibre contents in raw wool were determined by the methods already described. The results obtained have been tabulated in Table VII.

All the figures in the above table have been calculated on a raw wool basis. It will be seen that there is no significant difference in the analysis of the samples before dipping. The process of obtaining samples, representative of the group as a whole, by the method of sub-sampling thus far used, is therefore apparently fully justified. It would further appear that the selection of the sheep for the dipping experiments was highly efficient, since all groups show a fairly uniform fleece analysis (shoulder portion). It is also evident that there is little, if any, difference in the yield of clean fibre between the dipped and undipped wools. The small increase in the grease content of wools dipped in Cooper's dip is in all probability due to the sulphur contaminating the grease, as we have already pointed out. There is, however, a marked decrease in the suint content of all the dipped wools, this decrease roughly amounting to about 50 per cent. There is, therefore, no doubt that the process of dipping results in the washing-out of some of the suint in the raw wool. However, this leaching out process is apparently limited, since it is not appreciably greater for wools dipped three times than for wools dipped twice.

Exactly the same effect is observed when the chlorine contents of the different wools are compared. This can best be illustrated by grouping together the suint and chlorine contents with the hygroscopicity of the different wools at 100 per cent. humidity—

TABLE VIII.
Leaching Effect of Dipping.

Group.	Before dipping.			After dipping.		
	Percentage Suint.	Percentage Chlorine.	Hygroscopicity.	Percentage Suint.	Percentage Chlorine.	Hygroscopicity.
CC3.....	7.19	0.22	30.30	3.74	0.14	21.68
C3.....	7.24	0.21	27.30	3.42	0.12	18.75
As3.....	8.15	0.20	26.70	3.39	0.13	19.10
C2.....	7.61	0.20	28.50	3.38	0.13	18.85
As2.....	7.72	0.21	28.65	3.42	0.13	20.08
Control.....	7.39	0.20	30.63	7.19	0.21	29.38

(d) EFFECT OF DIPPING ON WOOL FIBRE.

The wool samples in question were investigated for soundness or damage by both the Rimington-Pauly diazometric method and the Sauer method. Due to the fact that the individual samples comprising the larger group samples had not been numbered, and also on account of certain important sampling considerations to be discussed later, twenty individual sub-samples, carefully degreased and desuinted, were examined from each group. The results obtained by the Rimington-Pauly method—expressed in Rimington units of damage—have been tabulated in Table IX as average figures for each set of 20 determinations.

TABLE IX.
Damage by Rimington Method.

Group.	Before dipping.	After dipping.
CC3.....	45.0	63.2
C3.....	47.1	48.7
As3.....	41.0	54.0
C2.....	40.2	41.2
As2.....	45.0	40.0
Control.....	44.2	40.0

If these average figures can be relied on to give anything like an exact reflection of the true state of affairs, we must conclude that only the wools CC3 and As3 show any detectable damage. However, considering the remarkable sensitivity of the Rimington method under certain conditions, this damage would appear to be insignificant, and it is highly doubtful whether it can ever be recognized in industrial processing and manufacture. In the case of the As2 wool the fibre has rather been improved than damaged.

The results obtained by the Sauer method confirm these observations. Damage was here calculated to represent the percentage of the extractable nitrogen of the total nitrogen in the wool. The results thus obtained have been tabulated in Table X, representing average figures from 20 determinations obtained as above.

TABLE X.
Damage by Sauer Method.

Groups.	Before dipping.			After dipping.		
	Total N per cent.	Extracted N per cent.	Damage per cent.	Total N per cent.	Extracted N per cent.	Damage per cent.
CC3.....	14.0	1.75	12.5	13.9	2.00	14.2
C3.....	14.8	1.74	11.8	14.9	2.03	13.6
As3.....	14.0	1.84	12.7	14.5	2.91	20.1
C2.....	14.0	1.65	11.4	14.6	1.35	9.5
As2.....	14.1	1.85	13.4	14.1	1.90	13.4
Control.....	14.0	1.75	12.5	14.0	1.85	13.2

The fluctuations in the total nitrogen content must be ignored since the different groups were analysed at different periods under different humidity conditions. For each group, however, all the samples, including those for the determination of damage, were weighed out at the same time, so that the percentages of damage are still strictly comparable.

V. IN-VITRO STUDIES ON THE WOOL FIBRE.

With the object of obtaining a somewhat clearer insight into the various factors which might be responsible for damage to the fibre in the process of dipping in the usual arsenical dips, the matter was further followed up, testing out some of the more obvious factors under laboratory conditions of control. For this purpose a special parent sample of undipped wool was used. Even then various difficulties were at first encountered, it being impossible to obtain reproduceable results. Having satisfied ourselves that the methods of determining damage were highly reliable, our attention was next directed to the difficult question of wool sampling. It was soon found that the chemical methods used were so sensitive that they were able to reflect appreciable differences in the fibre, not only in different parts of the fleece, but also in the different staples from the same part of the fleece. In addition to this, all tips are normally far more seriously damaged than the rest of the fibre. This difficulty of sampling was eventually overcome by the following method:—

From a carefully removed shoulder portion of the fleece one gram staples were selected and the tip portions removed by cutting about half an inch from the tip, all staples being cut the same length as measured from the skin end. These staples were tied up with cotton thread, and carefully cleaned in benzol and distilled water, avoiding as far as possible all felting of the fibres. The individual analytical samples were obtained from these staples by taking small sub-samples from each staple in such a way that the thus obtained composite analytical sample amounted to about 0.10 gram. That such samples are representative and reproduceable, the following table will show.

TABLE XI.
Uniformity of Samples of Rimington Method.

Sample.	Colorimetric readings.		Rimington units of damage.
	Standard.	Wool.	
1.....	5.0	9.5	52.6
2.....	5.0	10.5	47.6
3.....	5.0	10.5	47.6
4.....	5.0	10.0	50.0
5.....	5.0	9.0	55.5
6.....	5.0	9.5	52.6
7.....	5.0	10.5	47.6
8.....	5.0	10.0	50.0
AVERAGE.....	5.0	9.81	50.4

EFFECTS OF ARSENICAL DIPS ON WOOL.

(a) EFFECT OF SODIUM ARSENITE AND COOPER'S POWDER DIP ON WOOL.

A series of experiments was made by treating 0.1 gm. samples of the wool with 20 c.c. solutions of pure sodium arsenite (approximately Na_2HAsO_3) and Cooper's Powder Dip at the concentrations normally employed in the field. The results obtained with the usual two minute immersion revealed no measurable damage, and need not be given here. In a second series of experiments the wool samples were immersed in these solutions for two hours, and the damage studied by the Rimington method. The results have been tabulated in Table XII.

TABLE XII.

Influence of Cooper's and Sodium Arsenite.

Treatment.	Strength of solution (Percentage As_2O_3).	pH of solution.	Damage (Rimington units).
Untreated sample.....	—	—	50.4
Sodium arsenite.....	0.08	9.57	52.6
" " 	0.16	9.90	52.6
" " 	0.24	10.24	55.5
Cooper's powder.....	0.13 (soluble)	—	50.0
" " 	0.07 (")	—	50.0

It will thus be seen that no damage can be demonstrated, not even after two hours immersion. The above results, however, have been obtained with a fairly pure sample of sodium arsenite. In order to determine whether these results may in any way be influenced by the proprietary brands of sodium arsenite in use, the effect of various brands of sodium arsenite was further studied, using solutions containing 0.16 per cent. As_2O_3 , and immersing for two hours.

TABLE XIII.

Effect of Proprietary Arsenite Brands.

Brand.	Percentage As_2O_3 in solution.	pH of solution.	Damage (Rimington units).
Kynoch.....	0.16	9.3	58.7
Protea.....	0.16	9.3	52.6
Conquest.....	0.16	8.9	50.0
Steward.....	0.16	8.9	50.0

These figures show that all the proprietary brands studied are quite safe as far as damage to the wool fibre is concerned.

It might, however, be argued that under certain conditions, due to faulty preparation of the dipping bath, the concentration of the dip wash may rise above the specified strength. Accordingly this point was also investigated, the concentration of the solutions being increased from 0.08 to 1.6 per cent. As_2O_3 , and the wool samples in each case being immersed for two hours.

TABLE XIV.
Influence of concentration on Damage.

Concentration (Percentage As_2O_3).	pH of solution.	Damage (Rimington units).
0.08	9.6	52.6
0.16	9.9	52.6
0.24	10.2	55.5
0.80	11.0	77.0
1.60	11.1	83.0

These results show that as a result of immersion for two hours in a solution of sodium arsenite containing 0.8 per cent. and more As_2O_3 , the wool is clearly damaged. But even then it is extremely doubtful whether any measurable damage will occur when the wool is immersed for the usual two minutes. What is of definite interest, however, is the observation that this increase in damage coincides with a definite increase in pH or hydroxyl ion concentration. It is a well-known fact that caustic alkalis have a deleterious effect on the wool. It is, therefore, very important that the effect of increasing hydroxyl ion concentration on the wool fibre should be further studied. The importance of this aspect of the matter is not limited to the use of substances with alkaline reaction such as dips, but applies with equal force to certain stages in the industrial processing of the wool.

For this and other reasons a series of experiments was made using solutions of sodium arsenite of increasing hydroxyl ion concentration. The concentration of the arsenite was kept constant at 0.16 per cent. As_2O_3 , but the pH of the solutions was so changed by the addition of sodium hydroxide as to vary from 9.9 to 12.4. In order to determine the possible effect of the arsenite ions on the wool, these experiments were repeated with solutions of pure sodium hydroxide of hydroxyl ion concentrations covering the same range as the arsenite solutions. The hydroxyl ion concentrations of the arsenite solutions were determined electrometrically using the modified quinhydrone electrode described by Davis (1931). The hydroxyl ion concentrations of the solutions of pure sodium hydroxide were calculated theoretically assuming solutions weaker than tenth normal to be completely dissociated. All samples were immersed for two hours at room temperature. The determination of damage was made both by the Rimington diazometric method and by the D.I. borax method. The results thus obtained have been tabulated in Tables XV and XVI.

TABLE XV.
Effect of NaOH on Wool.

Treatment.	pH.	Rimington method damage.	Borax method *damage.
1.....	10·4	49·5	4·0
2.....	11·9	60·6	4·3
3.....	12·4	166	4·4
4.....	12·6	250	5·8
5.....	13·0	500	6·8
Untreated.....	—	50·4	4·0

TABLE XVI.
Effect of Arsenite + NaOH on Wool.

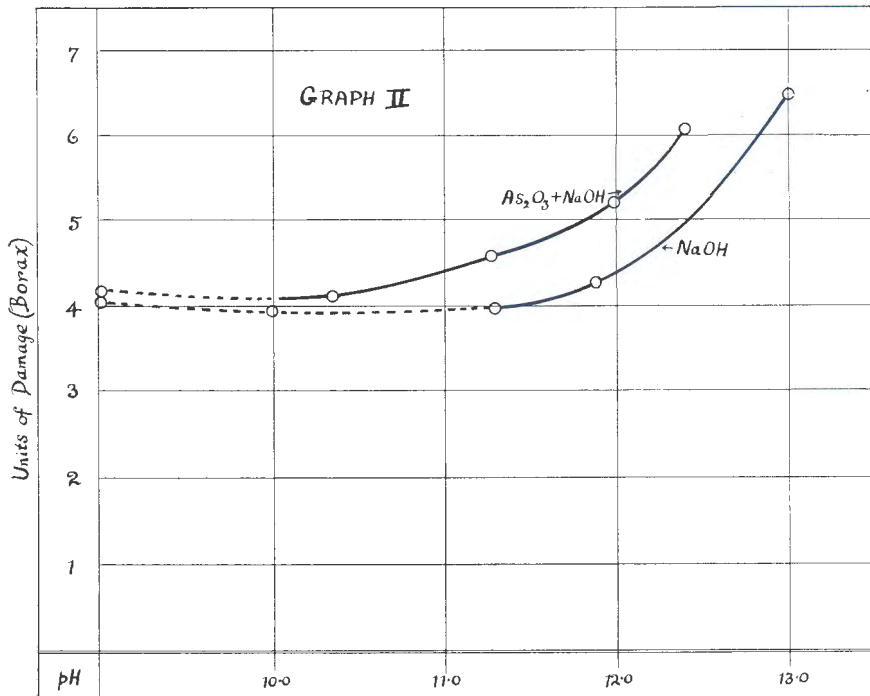
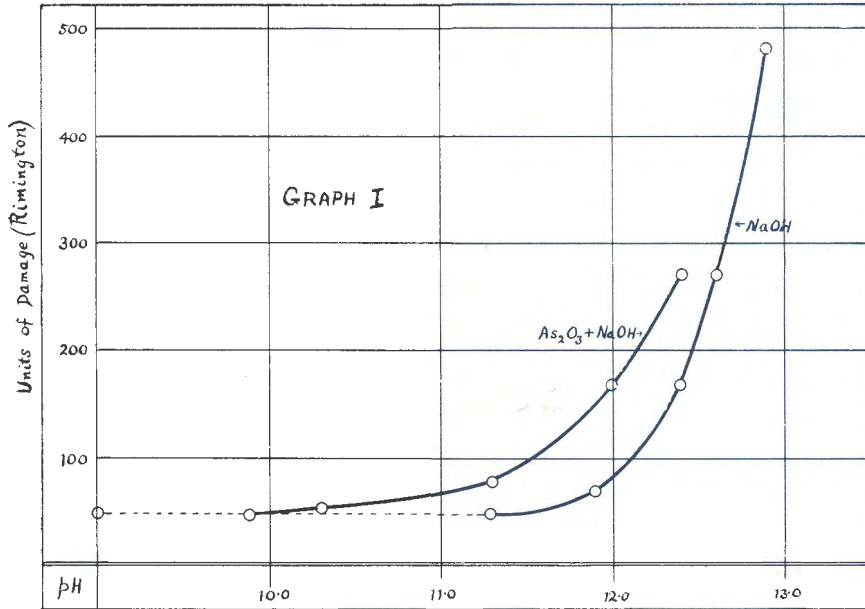
Treatment.	pH.	Rimington method damage.	Borax method *damage.
1.....	9·9	47·6	3·9
2.....	10·3	55·5	4·3
3.....	11·3	76·9	4·7
4.....	12·0	166	5·2
5.....	12·4	250	6·1
Untreated.....	—	50·4	3·8

We note that both the Rimington and the Borax methods demonstrate a steady rise in damage with rise in pH. The tables also show that this increase in the units of normal damage becomes noticeable only after the pH rises above a certain critical limit lying in the neighbourhood of 10·3. These results are thus in agreement with the observed† relation between hydroxyl ion concentration and tensile strength.

In graphs I and II the influence of pH on the soundness of the fibre has been illustrated graphically. Both graphs, i.e., both the Rimington and the Borax method, present the same picture. We note that both methods show that in a medium of equal pH the solution of arsenite plus sodium hydroxide shows a greater damage effect than the sodium hydroxide alone. It would, therefore, appear as if the negative arsenite ions exert some effect of their own. We suggest that this behaviour of the arsenite ions is closely connected with the absorption and apparent fixing of some of the arsenic by the wool fibre. Whether we are here dealing with mere absorption, or whether the arsenic enters into chemical combination with certain free amino-acid groups of the keratin molecule it is most difficult to say.

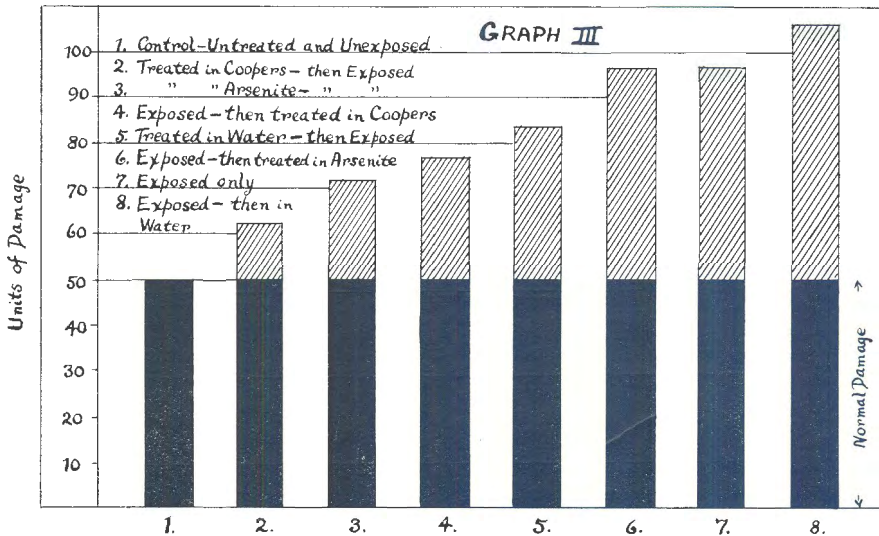
*This nitrogen includes that extracted by the sodium hydroxide and sodium arsenite solutions.

†Compare: Bulletin of Wool Industries Research Association, Torridon, Vol. 3, No. 1, p. 23 (1932).



(b) THE INFLUENCE OF SUNLIGHT AND ULTRA-VIOLET RADIATION AS A FACTOR IN DIPPING RELATED TO FIBRE DAMAGE.

In considering the effect of dipping on the soundness of the wool, there is one very important factor which must not be lost sight of. Up to the present we have been studying the direct effect of certain dips on the wool fibre, concentrating on the direct effect of such dips as the primary cause of fibre damage. There is, however, also the possibility that the dipping effect may be only a secondary factor in wool damage. By this is meant that the process of dipping may serve to bring out certain dormant changes in the fibre which had been caused by influences other than dipping. As one of the most potent of these outside influences we venture to suggest the effect of sunlight, or more particularly the ultra-violet portion of the sun's spectrum, on the fleece. From measurements on the ultra-violet radiation intensity of South African sunlight by Osborn (1932), it has been found that the ultra-violet radiation in South Africa is decidedly high, particularly so on the high inland plateaux. Naturally such radiation would in the first instance effect the outermost exposed portion of the fleece, and it is by no means improbable that the photo-chemical action thus produced is the primary cause of the intense weathering of the tip portions of the fleece. In how far such radiation might affect the more inner portions of the fleece is most difficult to say, since we do not know to what extent the raw wool mass is opaque to ultra-violet radiation. Naturally the degree of penetration would depend on the nature and structure of the fleece.



That sunlight, and more particularly the ultra-violet radiations, do affect wool and woollen goods is a daily observed occurrence and well known. What is not generally realized, however, is the close bearing this effect of sunlight may have on dipping questions in relation to fibre damage. To stress these considerations more

effectively, we have studied the effect of sunlight and ultra-violet radiation in conjunction with the arsenical dips. For this purpose two sets of experiments were made. In the first set samples of the clean fibre were exposed for an hour to the radiations of a quartz mercury-arc lamp at a distance of 18 inches, and subsequently immersed in solutions of Cooper's (0.13 per cent. soluble As_2O_3), and sodium arsenite (0.16 per cent. As_2O_3) as well as in pure water for two minutes.

In the second set the wool samples were first immersed in the same solutions of Cooper's, sodium arsenite, and water for two minutes, and then while still wet subjected to the ultra-violet radiation for an hour. The results obtained in duplicate have been tabulated in Table XVII and illustrated graphically in Graph III.

TABLE XVII.
Relation of Ultra-Violet to Dipping.

Experiment.	Treatment.	Damage (Rimington units).
1.....	Control—not exposed and not treated.....	50.4
2.....	Exposed, but not treated.....	86.8
3.....	Exposed and then treated with water.....	105.3
4.....	Exposed and then treated with Cooper's.....	76.9
5.....	Exposed and then treated with arsenite.....	86.8
6.....	First treated with Cooper's and then exposed.	62.5
7.....	First treated with arsenite and then exposed.	71.4
8.....	First treated with water and then exposed...	83.3

Comparing these figures for damage with those for the same dips in Table XII, it immediately becomes evident that the ultra-violet treatment of the wool definitely affects the soundness of the fibre. Experiment 2 shows that mere exposure alone already affects the fibre, although this effect may be latent, and Experiment 8 shows that this radiation effect remains the same, whether the wool is exposed in the dry or wet state. Considering the wools first exposed and subsequently treated with the dips, we observe the most interesting fact that the treatment with pure water produces appreciably more damage than either the Cooper's dip or the sodium arsenite. Exactly the same phenomenon is observed with wools first treated and then exposed. This observation gains in practical importance when we recall that the dipping experiments carried out at Bathurst showed that the wool suffered at least as much by dipping in water as by dipping in sodium arsenite. We are not in a position at the moment to give a full explanation of this highly interesting observation. However, it seems feasible to assume that the exposure of the wool fibre to ultra-violet radiations directly affects the keratin molecule. We venture to suggest that these radiations, probably by resonance, set up abnormally violent oscillations within certain parts of the molecule, the more disturbed groups in the molecule becoming either totally detached or greatly loosened. This would explain the observation of Barritt and King (1929) that the mere exposure of wool to ultra-violet radiation causes a loss in the sulphur-content of the wool. Apart from the sulphur totally detached, a still greater

EFFECTS OF ARSENICAL DIPS ON WOOL.

proportion becomes loosened to such a degree that the exposed wool was found to lose about 11 per cent. of its sulphur on subsequent treatment with a very dilute alkali. We have shown the same to hold true for at least a portion of the nitrogen in the keratin molecule, as the following results will show:—

Exposure.	Percentage N. extracted (Sauer method).	Percentage of total N. in wool.
Unexposed.....	3.0	21.4
Exposed $\frac{1}{2}$ hr. at 1 ft.....	4.0	29.3
Exposed $\frac{1}{2}$ hr. at 1 ft.....	4.2	30.0
Exposed 1 hr. at ca. 1 $\frac{1}{2}$ ft.....	4.6	32.9

The explanation why water affects the exposed fibre to a much greater extent than solutions of sodium arsenite and arsenate also follows readily enough from this theory. By loosening certain parts or radicals of the keratin molecule, the exposed molecules obviously exist in a state of metastability. Assuming now this destabilising action of the molecule to be reversible, it is obvious that under certain conditions the metastable form may be reconverted into the stable form. Thus pure water detaches and dissolves the loosened portions of the molecule, whereas the presence of arsenite and arsenate ions in the water impedes this detaching action of the water, exerting their influence in the direction of restabilising the metastable molecules. Apparently this restabilising effect is not limited to the anions of the arsenic acids, since in the course of our experiments it was found that the anion of borax exerts a similar effect.

From Table XVII it will also be seen that the damage to the fibre is least in the case of Cooper's dip, especially where the wool was first treated and then exposed. It has already been pointed out that immersion in freshly prepared Cooper's dip results in an appreciable deposit of sulphur and arsenic sulphide on the fibres. It was therefore suspected that the yellow film thus covering the fibres might conceivably act as an ordinary filter, greatly impeding the penetration of the ultra-violet to the actual fibre. This suspicion was easily enough confirmed by treating a wool sample with a clear filtered solution of Cooper's dip, thus preventing the formation of a yellow film on immersion.

TABLE XVIII.

Influence of Staining Effect on Ultra-Violet Action.

Treatment.	Damage (Rimington units).
Not treated and exposed.....	77.7
Treated with Cooper's and exposed.....	66.6
Treated with Cooper's clear filtrate and then exposed..	90.9

The fact that the wool sample treated with the clear filtrate of Cooper's dip showed appreciably more damage than the sample treated with the full dip in its original state, thus shows the light filtering effect of the yellow deposit formed, and explains why wools thus treated become more resistant to ultra-violet radiations. Similar observations have been made by Kertesz (1919) by protecting the fibres with a film of chromium salts.

Having thus shown that the wool fibre can be protected to some extent against the action of ultra-violet light by the application of an artificial film, it appeared highly interesting to determine to what extent the natural grease and suint on the raw wool fibre would impede the penetration of such radiations. With this object in view the influence of ultra-violet radiations on the wool in different stages of the process of cleaning was compared with that on the raw wool, the samples being exposed for one hour at a distance 18 inches from a mercury-arc lamp. After exposure the raw and desuinted wools were degreased by washing in ether, the degreased wool being desuinted with water. All the samples were finally washed in pure water. The results obtained in Rimington units of damage have been tabulated in Table XIX.

TABLE XIX.
Protective Influence of Grease, Suint, etc.

Experiment.	Wool treatment.	Damage.
1.....	Raw wool—unexposed.....	53
2.....	Raw wool—exposed.....	ca. 83
3.....	Degreased wool—exposed.....	ca. 83
4.....	Desuinted wool—exposed.....	ca. 83
5.....	Degreased and desuinted wool—clean fibre—exposed	ca. 100

The results show that the raw and partially cleaned wools were slightly less affected by the ultra-violet treatment than the clean fibres. However, it is doubtful whether this apparent protective influence on the part of the grease and suint can be ascribed exclusively to their absorptive action of the ultra-violet. The possibility is by no means excluded that the suint *in solution* may reverse the initial photo-chemical effect already referred to. We conclude, therefore, that the protective influence of grease and suint against ultra-violet is, if anything, exceedingly small.

The exposure of wool to actual sunlight produces exactly similar effects. In the first set of experiments both clean and raw wool samples were immersed in solutions of Cooper's (0.13 per cent. soluble As_2O_3), sodium arsenite (0.16 per cent. As_2O_3), and water for two minutes, and kept out of contact with direct sunlight. After three days the wools were again immersed in Cooper's, sodium arsenite and water, and kept for another three days. In the second set of experiments the wool samples were exactly similarly treated by immersing twice at an interval of three days, with the exception that these samples were for the whole of the six days during which

EFFECTS OF ARSENICAL DIPS ON WOOL.

the experiment lasted exposed to the direct rays of the sun. The degree of damage was again measured in Rimington units, and the results illustrated graphically in Graph IV.

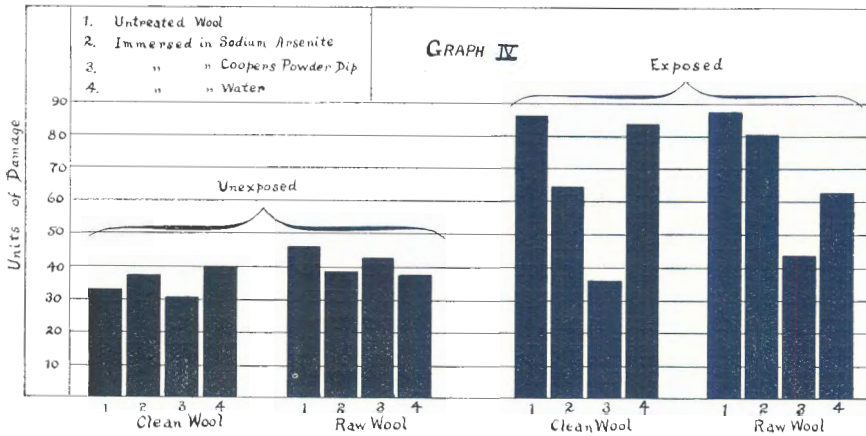


TABLE XX.
Effect of Sunlight on Wool.

Experiment.	Treatment.	Unexposed.		Exposed.	
		Clean wool.	Raw wool.	Clean wool.	Raw wool.
1.....	Not immersed—control.....	32.3	45.5	86.9	86.9
2.....	Immersed in sodium arsenite.....	37.0	37.7	64.5	80.0
3.....	Immersed in Cooper's.....	30.3	42.5	35.1	43.5
4.....	Immersed in water.....	40.0	37.0	83.3	62.5

We note that in Experiment 1, 2 and 4 the exposed wools show a much greater damage than the unexposed wools, the damage in the case of the former being about double that of the latter. In the case of Cooper's powder dip—experiment 3—exposure to sunlight seems to have had no effect. The reason for this we have already explained. These results also show that the protective influence of grease and suint is insignificant, the raw wool often showing slightly more damage than the clean fibres.

VI. SUMMARY.

The effect of the two arsenical dips, viz.: Cooper's powder dip and sodium arsenite, on the fleece has been studied from several angles. The process of dipping results in the leaching out of suint constituents, thereby influencing the hygroscopicity of the raw wool, especially at 100 per cent. humidity. The use of arsenicals as dips results in the contamination of the fleece with arsenic, some of this arsenic remaining in the fibres even after scouring. When using the

correct concentrations, the dips themselves do not cause any noticeable damage to the fibre, except that Cooper's dip tends to stain the fleece yellow by depositing its insoluble constituents. Should, however, the alkalinity of the dips rise above pH 10.3, the soundness of the fibres may be seriously affected. Under normal conditions, however, the undesirable effect of dipping on the fibre soundness must be ascribed to the process of dipping as such, and not to the use of the chemicals here studied. In-vitro studies have shown that this dipping effect in turn is merely a secondary cause of damage, the initiative and primary cause of fibre damage being the effect of the ultra-violet radiations of ordinary sunlight. In this respect arsenates and arsenites would appear to protect the fibre, rather than causing further damage, since pure water is appreciably more deleterious to such radiated wools than arsenite solutions. Cooper's dip renders additional protection to the fibre, the yellow film staining the fibres impeding the penetration of the ultra-violet rays to the fibre itself. The theoretical implications of these observations have been discussed and explained. The natural grease and suint on the fibres were not found to afford sufficient protection against the effects of sunlight. In how far these observations affect the fleece on the sheep's back must still be further investigated. It may be expected, however, that repeated dipping would aggravate this photo-chemical effect, since the staple-formation is thereby destroyed, thus exposing a greater portion of the fleece to direct radiation.

VII. REFERENCES.

- BARRIT, J., AND KING, A. T. (1929). 18, The Sulphur Content of Wool. Part II. Distribution of Sulphur along the Fibre, Variation with Colour and the Effect of Exposure to Ultra-Violet Light. *Jnl. Text. Inst.*, Vol. 20, No. 7, p. T.153.
- BENEDICT, S. R. (1909). The Estimation of Total Sulphur in Urine. *Jnl. Biol. Chem.*, Vol. 6, p. 363.
- BONSMA, F. N. (1930). Yolk—Its Economic Importance. A Technique for the complete Analysis of a sample of greasy wool. *Wool Record and Textile World*, July 24th, p. 235.
- DAVIS, J. C. (1931). A Simple, Inexpensive Quinhydrone Cell for Rapid Work. *Analyst*, Vol. 56, No. 664, p. 449.
- DENIS, W. (1910). The Determination of Total Sulphur in Urine. *Jnl. Biol. Chem.*, Vol. 8, p. 401.
- FOLIN, O., AND WU, H. (1919). A System of Blood Analysis. *Jnl. Biol. Chem.*, Vol. 38, p. 87.
- FOLIN, O., AND SVEDBERG, A. (1930). An Improved Distillation Method for the Determination of Urea in Blood. *Jnl. Biol. Chem.*, Vol. 88, p. 77.
- FOLIN, O., AND SVEDBERG, A. (1930). Micro Methods for the Determination of Non-Protein Nitrogen, Urea, Uric Acid, and Sugar in Unlaked Blood. *Jnl. Biol. Chem.*, Vol. 88, p. 85.
- GREEN, H. H. (1915). The Sulphur Sheep Dips. *Dir. Vet. Res., U. of S.A., 3rd and 4th Repts.*, p. 148.
- GREEN, H. H. (1918). The Micro-Titration of Arsenic. *Dir. Vet. Res., U. of S.A., 5th and 6th Repts.*, p. 539.
- KERTESZ, A. (1919). Über die Wirkung der atmosphärischen Einflüsse auf Wolle und Tuche, *Textile Forschung*, Vol. I, No. 3, p. 65.
- KRAIS, P., AND SCHLEBER, V. (1929). Die Erkennung chemischer Wollschädigungen *Textile Forschung*, Vol. 11, No. 2, p. 99.

EFFECTS OF ARSENICAL DIPS ON WOOL.

- MALAN, A. I., AND V. D. LINGEN, G. W. B. (1931). Studies in Mineral Metabolism, XVI. The Micro-Determination of Some Inorganic Elements in Blood and Vegetation. *Dir. Vet. Serv. and An. Ind., U. of S.A., 17th Rept.*, p. 443.
- OSBORN, T. W. B., AND RAFTERY, J. D. (1932). The Ultra-Violet Content of South African Sunlight. *S.Afr. Jnl. of Sc.*, Vol. 29, p. 607.
- PAULY (1904). *Zeitschr. Physiol. Chem.*, Vol. 42, p. 508. Cf. Rimington: *Jnl. Text. Inst.*, Vol. 21, p. T.237.
- PAULY AND BINZ (1904). *Zeitschr. Farben- u. Textilindustrie*, Vol. 3, p. 373. Cf. Rimington, *loc. cit.*
- RIMINGTON, C. (1930). A Quantitative Method for the Determination of "Soudness" in Wool and Cloth. *Jnl. Text. Inst.*, Vol. 21, p. T.237.
- RIMINGTON, C. (1930). A Method for the Determination of Sulphur in Wool and Similar Materials. *Jnl. Soc. Chem. Ind.*, Vol. 49, p. T.140.
- SAUER (1916). *Zeitschr. angew. Chem.*, Vol. 29, p. 424. Cf. Kraus and Schleber (1929), *loc. cit.*
- SPEAKMAN, J. B. (1931). The Action of Sodium Sulphide on Wool. *Jnl. Soc. Chem. Ind.*, Vol. 50, p. T.19.
- TANZER, E. (1930). Physikalisch-chemische Studien über den Feinbau des Wollhaares an mit Alkalien und Chlor behandelte Wolle. *Wissenschaftliches Archiv für Landwirtschaft*, Vol. 4, No. 2, p. 297.