

Researches into Dips and Dipping.*

A. Lime-Sulphur Dips.

VI. A Survey of the Behaviour of Lime-Sulphur Dips under Field Conditions.†

By

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

I. INTRODUCTION.

As has been pointed out in Paper A.I of the series, a field study of lime-sulphur dips was undertaken in order to answer various practical questions which had arisen from time to time. Such questions include the rôle played by various qualities of commercial lime samples used in the preparation of home-made lime-sulphur concentrates, the influence of farm water in its dilution, the liability to oxidation of lime-sulphur solutions on standing, the effect of dipping on such solutions, e.g. the diminution in strength after passing a known number of animals through a bath of known initial concentration and volume, etc. An adequate answer to such and other questions would be of definite assistance to field veterinarians, farmers and dip inspectors.

In the course of this study about 160 full analyses of field dips and concentrates have been made, the method of analysis employed being the volumetric cadmium acetate method as described in Paper II of this series. The lowest concentration of polysulphide shown by the home-made concentrates was 9.6 gm. polysulphide sulphur per 100 c.c. concentrate, the highest concentration being 30.4 gm. The minimum strength of the diluted dips or dipwashes before and after dipping was 0.43 and 0.16 gm. sulphide sulphur per 100 c.c. dipwash respectively. In Table I average figures have been compiled for 84 field dips, all analyses for dips showing faulty sampling or being otherwise doubtful, having been discarded.

TABLE I.
Field Dipping Strengths.

P.S.S. limits (gm. S. per 100 c.c. dipwash).	Before dipping.		After dipping.	
	No. of samples.	Average.	No. of samples.	Average.
Between 0.00 and 0.20.....	0	—	1	0.16
„ 0.20 and 0.40.....	0	—	6	0.33
„ 0.40 and 0.60.....	2	0.47	9	0.51
„ 0.60 and 0.80.....	2	0.66	10	0.71
„ 0.80 and 1.00.....	11	0.92	5	0.86
„ 1.00 and 1.20.....	3	1.15	6	1.14
„ 1.20 and 1.40.....	5	1.32	5	1.31
„ 1.40 and 1.60.....	7	1.46	1	1.54
„ 1.60 and 1.80.....	6	1.72	2	1.67
„ 1.80 and 2.00.....	2	1.90	0	—
„ 2.00 and 2.20.....	1	2.15	0	—
AVERAGE.....	39	1.26	45	0.81

P.S.S. = Polysulphide sulphur.

Under the present regulations of the Department of Agriculture, as recorded in Paper I of this series, the specified initial concentration of lime-sulphur dipwashes is laid down to be 1.5 gm. sulphide sulphur per 100 c.c. dipwash. From the above table about 75 per cent. of the dipwashes examined fall below this specified strength, although the

true average (1.26) of all samples examined does not fall very much below this limit. The average concentration of the washes after dipping is shown to be 0.8, a figure Green (1915) accepted as still adequately effective against scab. On the other hand, in some samples the concentration does fall as low as 0.47 for the fresh wash, and even as low as 0.33 and 0.16 in the case of washes after dipping. If the departmental figure of 1.5 were anywhere near the minimum effective limit, this state of affairs would naturally cause grave concern. However, from the experiments reported in the previous paper (Paper V), a dip of strength 0.33 might still be effective. Of all the dips examined only one falls below this minimum effective limit, which means that the last batch of sheep to pass through this particular wash was not effectively cured of scab if infected.

What is important, however, is the wide range of variations revealed by Table I. In other words, Table I shows how necessary it is to use a considerable safety factor by fixing the recommended dipping strength appreciably above the minimum effective limit in order to make all dipping effective. Even then this safety factor reflects only the better half of the true field picture, since all field work for the present study was done by specially selected men. To this must further be added the effect of the psychological factor, in as much as all field work done for this investigation was to be controlled in the laboratory, whereas under normal field practice no such direct control is anticipated. On the other hand, in the interests of economy, and from the point of view of possible damage to the wool, a lowering of the recommended strength of 1.5 would be highly desirable, especially in view of the observation that concentrations as low as 0.3 may still be effective. It is clear, however, that such steps will be justified only if a greater measure of control can be exercised, with a subsequent lowering of the deviation from the recommended strength.

If, for the purpose of this study, we leave the actual analytical control of samples taken from time to time during the course of dipping out of consideration, the all important question to be answered is in how far the various factors operating during the process of dipping are capable of control or manipulation under field conditions. Obviously, it would be of considerable practical importance if the factors concerned can be so controlled, that it would become possible to tell farmers and dip inspectors to what extent the strength of a bath of known volume and initial concentration would diminish after a certain number of animals had passed through. On the other hand, this diminution in strength per animal may, as a result of factors over which we have little or no control, vary so greatly from one set of conditions to another, that its practical usefulness may be zero.

II. THE PREPARATION OF THE CONCENTRATE.

In the preparation of home-made concentrates, the boiling up of the lime and sulphur in an aqueous medium results in the action of the free sulphur on the active lime with the formation of the polysulphides of calcium and calcium thiosulphate. For determining

the chemical reactions involved, a definite weight of different lime samples was boiled up with excess flowers of sulphur, the solution made up to a definite volume and then analysed. The results obtained have been tabulated in Table II.

TABLE II.
Reaction of Lime with Sulphur.

Lime sample.	Dipping Coeff. II of lime % Ca(OH) ₂ .	M.S.S. Eq. per 2.5 gm. lime (gm.S).	Thiosulphate per 2.5 gm. lime (gm.S).	x in CaS _x .	Ratio Thios. S/M.S.S. Eq.
K. 12	19.9	0.135	0.147	5.37	1.08
K. 3	37.5	0.265	0.280	4.83	1.06
K. 9	48.9	0.356	0.344	4.87	0.97
K. 10	61.2	0.433	0.464	4.98	1.07
K. 4	66.0	0.495	0.500	4.72	1.01
K. 11	67.2	0.495	0.480	4.42	0.97
F. 6	67.8	0.485	0.495	5.11	1.02
K. 7	75.3	0.545	0.540	4.78	0.99
K. 5	76.5	0.545	0.550	4.78	1.01
Tvl. 5	76.8	0.549	0.560	5.12	1.02
K. 6	77.1	0.545	0.540	4.66	0.99
TKi. 1	80.6	0.585	0.590	4.80	1.01
F. 2	82.8	0.595	0.560	4.73	0.96
Tvl. 7	84.4	0.610	0.605	4.62	0.99
K. 1	84.5	0.600	0.610	4.93	1.02
Tvl. 12	86.1	0.634	0.592	5.37	0.93

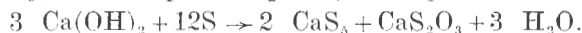
M.S.S.Eq. = Monosulphide sulphur equivalent.

For the polysulphides formed the atomic ratio of calcium to sulphur was found to be over 5.0 in at least four cases, so that, in accordance with the findings of Patel, Sen-Gupta and Chakravarti (1930) for organic polysulphides, an inorganic polysulphide of the order CaS₆ or higher must be present. What other polysulphides are present, and how they are distributed to make up the average value of CaS_{4.6} to CaS_{4.8} we shall not endeavour to discuss here. It would suffice to state that the higher polysulphides in solution are extremely unstable, and that it is quite possible for an initial solution represented by CaS_{5.0} to depreciate to CaS_{4.8} by the time it is analysed, unless all due precautions are taken. It is possibly for this very reason that all proprietary concentrates and home-made dips never show a composition appreciably above CaS_{4.6}.

However, what is of importance as far as the reactions involved are concerned, is the observation that the ratio of thiosulphate sulphur to monosulphide sulphur equivalent is unity, as shown in the last column of Table II. Hence, for every atom of sulphur going into solution as monosulphide sulphur equivalent, there is formed half a molecule of thiosulphate; or, what amounts to the same, for every two atoms of calcium attached to sulphur to form polysulphides there is used one atom of calcium for the formation of calcium thiosulphate. Taking, as an example, the formation of the tetrasulphide from calcium hydroxide and sulphur, the equation for the reaction may be represented as follows:



Similarly, for the pentasulphide, the equation becomes:—



In the case of proprietary preparations and also in the case of home-made concentrates in the field, the thiosulphate content may be appreciably lower than these equations demand. This, however, is due to the relative insolubility of calcium thiosulphate in concentrated solutions of calcium polysulphide, and its subsequent removal with the sediment in the process of clarifying the concentrate.

If now we assume that the directions for the preparation of the concentrate are too simple to allow of faulty preparation, any fluctuation in the quality of concentrate obtained can only be ascribed to the impurity of the ingredients used. The sulphur is excluded from the considerations under review since flowers of sulphur of a high quality is generally used. Considering the relative quantities of lime and water used, the effect of any impurities in the water cannot be expected to be appreciable. As an experimental verification of this conclusion the following data * have been collected in Table III.

(a) EFFECT OF WATER ON CONCENTRATE.

TABLE III.

Effect of Water on Concentrate.

Lime and water sample.	Origin of water.	Dipping coefficient with this water.	Dipping coefficient with Onderstepoort water.
1.....	Beaufort West.....	22.1 % CaO	22.7 % CaO
2.....	" "	47.1 % "	46.0 % "
3.....	" "	39.7 % "	39.7 % "
4.....	Gordonia.....	34.0 % "	37.0 % "
5.....	" "	26.6 % "	27.3 % "
6.....	Williston.....	42.0 % "	42.0 % "
7.....	Carnarvon.....	38.0 % "	36.0 % "
8.....	Van Wyksvlei.....	38.0 % "	36.0 % "
9.....	Calvinia.....	19.1 % "	19.1 % "
10.....	Concordia.....	38.4 % "	38.4 % "
11.....	" "	17.9 % "	18.3 % "
12.....	Namaqualand.....	36.0 % "	36.0 % "

If the above table shows that the effect of the water used in boiling up the concentrate is negligible, it also shows that the limes used vary greatly in purity. For the purpose of the present investigation 19 lime samples, used in the field for preparing home-made lime-sulphur concentrates, have been studied in the laboratory. Besides the determination of the sulphate sulphur, total calcium and free calcium hydroxide content of these limes, their "dipping coefficients" have also been determined by allowing a known quantity to react with excess sulphur at boiling point. 2.5 gm. lime were mixed with ca. 10 gm. flowers of sulphur and boiled with water for 40 minutes, immediately afterwards filtering off into a 500 c.c. measuring flask, washing, and filling up to volume in the cold. By analysing the thus obtained lime-sulphur solution, two dipping

*Data from a departmental report, 1931.

coefficients were determined, once by expressing the total calcium found in the solution as the percentage $\text{Ca}(\text{OH})_2$ of the total lime used—Coefficient I—and secondly, calculating the $\text{Ca}(\text{OH})_2$ equivalent of the sulphur in solution as calcium polysulphides and calcium thiosulphate, and expressing this $\text{Ca}(\text{OH})_2$ content as a percentage of the total lime used—Coefficient II. In Table III these results have been tabulated in ascending order of lime purity. The figures given under Coefficient I. will of course rise above the true values when the lime contains other soluble calcium salts, as for example calcium chloride, and to some extent calcium sulphate. This explains why the figures under Coefficient I are always slightly above those under Coefficient II. On the other hand, any free alkali or earth alkali other than calcium oxide and/or calcium hydroxide present in the lime will result in Coefficient II. falling out too high.

(b) PURITY OF LIME SAMPLES.

TABLE IV.
Purity of Lime Samples.

Lime sample.	Origin and Brand of Lime.	% SO_4 sulphur in lime.	% Ca in lime.	% Active or free $\text{Ca}(\text{OH})_2$	Dip coeff. I.	Dip coeff. II.
K. 12	Not known.....	0.16	38.2	—	23.8	19.9
K. 3	Native Reserve, Rooifontein, Namaqualand.....	0.20	38.6	34.8	37.7	37.5
Tvl. 1	MacKenzie Siding—local.....	0.52	40.6	36.7	41.0	39.1
K. 9	Piquetberg and Bredasdorp Lime Works.....	0.70	36.6	49.9	51.7	48.9
K. 1 and 2 Sp.	„ „ „	0.37	48.7	—	53.2	52.3
K. 10	„ „ „	0.70	42.1	62.5	61.6	61.2
K. 11	Taungs Afric. Lime Works Afric. Brd.....	0.38	45.1	—	67.8	67.2
K. 4	Namaqualand—local.....	—	42.1	—	68.2	66.0
F. 6	White Lime, Ltd., Johannesburg.....	—	—	—	68.7	67.8
K. 7	Taungs.....	—	—	—	76.0	75.3
Tvl. 5	Not known.....	1.06	44.7	78.1	78.2	76.8
K. 5	Northern Lime Co., Taungs..	0.33	46.8	—	78.3	76.5
K. 6	White Lime, Ltd., Johannesburg.....	0.70	46.3	—	78.4	77.1
TKi. 1	Taungs Afric. Lime Works, Afric. Brd.....	0.27	50.2	—	83.8	80.6
F. 2	Buxton Lime Works, Taungs..	0.37	50.8	—	84.5	82.8
K. 1	Northern Lime Co., Taungs..	0.42	48.6	—	84.9	84.5
Tvl. 7	Not known.....	0.28	48.4	—	85.2	84.4
Tvl. 12	Uitloop—Potgietersrust District	0.15	49.5	88.6	86.4	86.1
Tvl. 11	„ „	0.56	49.8	84.1	90.3	87.8
Lab. sample	E. Merck, Darmstadt.....	trace	49.4	92.3	91.8	90.1

From the table it will be seen that the limes used in the preparation of home-made concentrates vary in purity from 20 per cent. to 90 per cent., though the higher purity samples frequently include limes only partially slaked or hydrated. But even a lime of purity approximately 20 per cent. should still yield a dipwash of 0.6 to

0.7 per cent. polysulphide sulphur when prepared according to standard specification. However, in considering this matter from the point of view of field practice, there is at least one important factor to be borne in mind, and this is the factor of field efficiency. By this is meant the efficiency with which the official specifications can be carried out under actual field conditions, taking into account all possible contributing factors. These contributing factors are various, and range from the mere mechanical measurement of quantities to the uncontrollable chemical effect of the water used for the dilution of the concentrate. As regards field efficiency, Green (1915) as early as 1915 pointed out that field samples invariably fail to come up to the strength attainable in the laboratory with the same lime; that is, that the field efficiency apparently invariably falls out below 100 per cent. What this field efficiency actually amounts to under South African conditions we shall attempt to deduce from the data now available.

In trying to determine this efficiency, the amounts of sulphur brought into solution when operating under optimum conditions in the laboratory, must be compared with the amounts brought into solution (in diluted dip) under actual field conditions, using the same quantity of the same lime. As all results for the laboratory work in the determination of the dipping coefficients of the various lime samples were calculated on the basis of the amount of polysulphide sulphur brought into solution by 2.500 gm. lime, the analyses of the diluted dip samples (before dipping) obtained from the field were all recalculated to this basis of 2.500 gm. lime. For this conversion the simple formula $F = 25x \times \frac{1}{a}$ applies, where:—

F is the amount of polysulphide sulphur (in gm. in the diluted dip) brought into solution by 2.500 gm. lime under field conditions;

x is the concentration of the diluted field dip in gm. polysulphide sulphur per 100 c.c. solution; and

a is the weight of lime (in lb.) used per 100 gallons of diluted dip.

The comparison on a purely polysulphide sulphur basis is here necessary, since this is apparently the chief ingredient of a lime-sulphur dip actually responsible for its effectivity against scab, whether this be directly or indirectly. The results thus obtained have been tabulated in Table V.

TABLE V.
Field Efficiency.

Dip.	Dipping coeff. II.	Lb. lime/ 100 gals. diluted dip.	Conc. of concentrate. %.	Polysulphide in dil. dip. (gm. S/100 c.c.).	x in CaS _x .	Field efficiency.
						%
K. 12	{ Lab. sam. Field ,, }	19.9	19.0	12.4 { 0.725 0.573 }	5.37 4.05	79.0
K. 3	{ Lab. sam. Field ,, }	37.5	25.0	17.4 { 1.279 0.971 }	4.83 4.78	75.9
K. 9	{ Lab. sam. Field ,, }	48.9	22.0	17.1 { 1.733 1.316 }	4.87 4.71	75.9
K. 10	{ Lab. sam. Field ,, }	61.2	20.0	26.2 { 2.156 1.545 }	4.50 4.21	71.6
K. 4	{ Lab. sam. Field ,, }	66.0	30.0	30.4 { 2.335 1.581 }	4.72 4.04	67.8
K. 11	{ Lab. sam. Field ,, }	67.2	19.0	27.1 { 2.185 2.130 }	4.42 4.21	97.5
F. 6	{ Lab. sam. Field ,, }	67.8	23.0	14.9 { 2.480 1.871 }	5.11 4.79	75.4
K. 7	{ Lab. sam. Field ,, }	75.3	20.0	22.3 { 2.605 1.240 }	4.78 3.45	47.5
K. 5	{ Lab. sam. Field ,, }	76.5	20.0	24.1 { 2.605 1.591 }	4.78 4.34	61.0
Tvl. 5	{ Lab. sam. Field ,, }	76.8	20.0	21.9 { 2.808 2.360 }	5.12 4.74	84.0
K. 6	{ Lab. sam. Field ,, }	77.1	20.0	23.1 { 2.540 1.794 }	4.66 3.78	70.6
TKi. 1	{ Lab. sam. Field ,, }	80.6	20.0	16.2 { 2.805 2.038 }	4.80 4.06	72.6
F. 2	{ Lab. sam. Field ,, }	82.8	20.0	9.6 { 2.815 2.205 }	4.73 4.22	78.3
Tvl. 7	{ Lab. sam. Field ,, }	84.4	20.0	22.0 { 2.820 1.803 }	4.62 4.68	63.9
K. 1	{ Lab. sam. Field ,, }	84.5	20.0	27.3 { 2.960 1.899 }	4.93 3.87	64.2
Tvl. 12	{ Lab. sam. Field ,, }	86.1	20.0	20.0 { 3.408 2.096 }	5.12 3.90	61.5

The minimum field efficiency found was 47.5 per cent., the maximum efficiency closely approximating 100 per cent. However, on the whole the normal field efficiency seems to lie around 70 per cent., the average of all the values tabulated being 71.7 per cent. Considering the possibility of a very appreciable fraction of this 30 per cent. loss in efficiency being caused by the effect of the dilution water on the polysulphides in solution, an all-round efficiency of 70 per cent. is certainly very satisfactory.

(c) DILUTION OF THE CONCENTRATE.

In order to study the possible effect of the water in the dilution of the concentrate, some of the waters received from the field were subjected to partial analysis in the laboratory. The analyses for non-volatiles or total solids, ash, sulphate sulphur, and total calcium have been tabulated in Table VI.

TABLE VI.
Water Analysis.

Water.	District.	Farm.	Solids (mgm/ 100 c.c.).	Ash (mgm/ 100 c.c.).	SO ₃ (mgmS/ 100 c.c.).	Ca (mgm/ 100 c.c.).
Tvl. 5	Ermelo.....	Wyntoun.....	8.2	2.6	0.0	0.0
Tvl. 1	Pretoria.....	La Rochelle No. 610	17.4	8.2	0.0	0.0
K. 6	Gordonia.....	Swemkuil.....	19.8	13.2	1.3	2.4
K. 9	Sutherland.....	Agterplaas.....	42.0	17.2	2.0	5.1
K. 10	Sutherland.....	Jakhalsfontein....	48.4	24.4	3.1	6.7
Tvl. 12	Pietersburg.....	Klipdam.....	59.2	42.6	1.9	1.7
Tvl. 11	Pietersburg.....	Klipdam.....	70.2	54.4	4.0	4.8
Tvl. 6	Ermelo.....	Tafelkou No. 36..	184	136	23.2	18.4
K. 1	Calvinia.....	Taaiboshoek.....	313	126	17.3	23.7
K. 11	Jansenville.....	Soutpansnek.....	400	301	36.2	26.5
K. 12	Jansenville.....	Soutpansnek.....	410	312	39.0	26.8
K. 2	Van Rhyndorp.	Vredendal.....	444	217	35.6	14.0
K. 5	Kenhardt.....	Mariasput.....	478	252	131	37.5
K. 3	Namaqualand..	Soutvlei.....	530	383	44.7	35.1
K. 4	Namaqualand..	Holgat.....	640	414	60.1	22.9
K. 1 & 2 Sp.	Calvinia.....	Downes.....	662	347	38.2	60.0
K. 7	Carnarvon.....	Eendefontein.....	—	—	7.1	5.1
Tvl. 7	Belfast.....	Houtenbek.....	—	—	0.0	1.9
TKi. 1	Cathcart.....	Rockford.....	—	—	0.0	1.7
N. 7	Greytown.....	Umvoti Location	—	—	0.0	0.0
N. 3	Umzinto.....	Farm No. L/A477	—	—	—	3.4
TKi. 3	Kingwilliams- town	Farm No. 309....	—	—	—	2.3
TKi. 4	Kingwilliams- town	Nonibe Location..	—	—	—	10.4
F. 2	Barkly West....	Witfontein.....	—	—	—	6.8

In every case the water sample was filtered before analysis. In spite of this the total solids in solution were found to rise as high as 0.6 gm. per 100 c.c. and higher, while the maximum ash value exceeded 0.4 gm. per 100 c.c. The sulphate sulphur fluctuated between zero and 0.13 gm. SO₃ per 100 c.c., while the total calcium fluctuated between zero and 0.06 gm. per 100 c.c. Some of the waters contain relatively large concentrations of magnesium and sodium sulphate, while others again apparently contain appreciable concentrations of calcium bicarbonate, since the total calcium exceeds by far the sulphate sulphur necessary for the formation of calcium sulphate. It may thus be expected that, in the case of some of the waters at least, an appreciable reaction between the constituents of the water and the calcium polysulphide will set in, resulting in the decomposition of some of the polysulphide.

To illustrate some of the more important reactions concerned, a few typical water samples were selected, and their effect upon the polysulphides of calcium studied experimentally. For this purpose 5 c.c. of a proprietary concentrate was diluted to 250 c.c. with the water concerned, atmospheric oxygen excluded, and the diluted dip

allowed to stand until complete sedimentation of the precipitate occurred. The perfectly clear solutions were then analysed. These were compared with similar dilutions made by using distilled water. On observing the visible changes, the following was noticed:—

Water sample.	Characteristics.	Sedimentation.
K. 1.....	High in solids and ash ; high in sulphate and Ca ; high in bicarbonate	Appreciable.
K. 5.....	High in solids and ash ; high in Na and Mg sulphate ; high in calcium	Fairly appreciable.
Tvl. 1.....	Low in solids and ash ; no sulphate and no calcium	Slight.
Onderstepoort water....	High in calcium ; high in bicarbonate	Fairly appreciable.
Distilled water.....	Pure.....	None.

The chemical analyses have been collected in Table VII.

TABLE VII.
Effect of Dilution Water.

Dip analysis.	Distilled water.	Tvl. 1 water.	K. 1 water.	K. 5 water.
M.S.S.E. (gm./100 c.c.).....	0.157	0.157	0.157	0.157
Thiosulphate S. (gm./100 c.c.)...	0.012	0.012	0.012	0.012
Total S found (gm./100 c.c.)....	0.776	0.778	0.720	0.794
S in water (gm./100 c.c.).....	0.000	0.000	0.007	0.052
∴ Total dip S.....	0.776	0.778	0.713	0.742
∴ Per cent. S lost.....	0.0	0.0	8.2	4.5
Total Ca found (gm./100 c.c.)...	0.206	0.206	0.202	0.246
Ca in water (gm./100 c.c.).....	0.000	0.000	0.024	0.038
∴ Total dip Ca.....	0.206	0.206	0.178	0.208
∴ Per cent. Ca lost.....	0.0	0.0	14.0	0.6

These results show that the dilution water apparently has no influence on the thiosulphate and monosulphide sulphur equivalent content. On the other hand, both calcium and polysulphide sulphur may be precipitated.

The results obtained in the laboratory have also been substantiated by field samples. In the following table—Table VIII— the results on a number of proprietary concentrates diluted one in twenty-five have been recorded. A sample of the same concentrate was diluted to the same extent in the laboratory with distilled water, and the analysis compared with that of the diluted dip received from the field. Only proprietary concentrates were considered, since the volume of home-made concentrates cannot be relied on.

TABLE VIII.
Effect of Water in Field Dilution.

Dip.	Polysulphide (gm. S/100 c.c.).	x in CaS _x .	Per cent. loss on dilution in field.
TKi. 7 Lab. sample.....	1.456	4.45	} 3
Field ,,	1.406	4.16	
TKi. 9 Lab. sample.....	1.452	4.54	} 12
Field ,,	1.279	4.50	
TKi. 4 Lab. sample.....	1.528	4.66	} 23
Field ,,	1.179	4.46	
TKi. 8 Lab. sample.....	1.447	4.55	} 24
Field ,,	1.105	4.44	
N. 3 Lab. sample.....	1.016	4.68	} 26
Field ,,	0.822	4.70	
N. 11 Lab. sample.....	0.939	4.58	} 28
Field ,,	0.672	4.58	
N. 9 Lab. sample.....	0.955	4.63	} 32
Field ,,	0.647	4.49	

Here again there is a distinct loss on dilution, due to the reaction of the water, some of the higher polysulphides being decomposed with a resultant fall in the atomic ratio of calcium to sulphur. If we accept the field measurements to be correct, that is if the dilution in the field was actually one in twenty-five, then the loss on dilution of up to 30 per cent. would appear to account for the loss in field efficiency of 30 per cent. as recorded in Table V. This loss is, of course, incapable of control, since the field worker cannot normally obviate the effect of the impurities in the water except in cases where rain water is available.

III. THE EFFECT OF DIPPING ON THE TANK FLUID.

During the process of dipping various foreign substances are brought into intimate contact with the constituents of the dipping bath. In the order of their influence on the composition of the bath they may be arranged as the influence of atmospheric and loosely-bound oxygen and carbon dioxide, the effect of suint constituents going into solution, and the adulteration with dirt, animal excrements, and earth. Owing to the air occluded in the fleece and the intensive mechanical agitation of the bath accompanying dipping, large volumes of air are brought into intimate contact with the dip, and accordingly appreciable oxidation and carbon dioxide disintegration may come into play. This atmospheric effect we shall discuss more closely in a following paper.

The dipping of wool-bearing animals, however, also results in an appreciable washing-out of the suint of the wool, these suint constituents effecting the composition of the dip in various ways. The alkali carbonate of the suint will react precipitating the calcium and forming alkali polysulphides.



The alkali soaps in the suint will precipitate the calcium as calcium soaps, again forming the alkali polysulphides. On the other hand, the entering of certain suint constituents into solution may improve the dip in so far as its surface tension towards the wool and the skin may be diminished, thereby increasing its wetting power and consequently its efficacy. In fact, this phenomenon is claimed to have been actually observed in field practice. This is a most important observation from a practical point of view, and we hope to be able to study it more closely in the near future. As far as the present paper is concerned we shall confine ourselves to a study of the collective effect of dipping on the composition of the dip in the field.

In the process of dipping it is found that the polysulphide sulphur in solution decreases, and the thiosulphate increases as has been shown by Van Zyl (1926). Here two questions chiefly deserve consideration, viz. the manner in which the polysulphide decreases, and the manner in which the thiosulphate increases at the expense of the polysulphide. For the sake of simplicity we shall consider the formation of the thiosulphate first.

In proceeding to investigate the manner in which the thiosulphate increases at the expense of the polysulphide, and also to consider such factors as initial polysulphide concentration, bath volume, and the number of animals dipped, it must be remembered that in the process of dipping there is, in addition to a progressive decrease in polysulphide and increase in thiosulphate concentration, also a progressive loss in dipwash, as each animal carries with it a certain volume of dip on emerging from the bath. Naturally, the volume of the dip, thus lost mechanically, will depend on the size of the animal, the weight and nature of its fleece, the manner of dipping, and the design and construction of the dipping outfit. However, to take due account of all these factors would make a field study well-nigh impossible. The only practicable solution here seems to be to resort to averages.

(a) DIPWASH REMOVED DURING DIPPING.

In several cases fairly accurate information was obtained regarding the quantity of dip carried off on dipping a certain known number of animals. In the following table (Table IX) the results of dipping close on to 12,000 animals have been recorded.

TABLE IX.
Dip Lost on Dipping.

	Number of animals dipped.	Initial volume of bath (gals.).	Final volume of bath (gals.).	Volume lost on dipping (gals.).	Volume lost per animal (gals.).
Case 1.....	562	455	325	130	0.23
Case 2.....	197	390	535	45	0.23
Case 3.....	560	395	265	130	0.23
Case 4.....	737	520	325	200	0.27
Case 5.....	536	390	225	165	0.31
Case 6.....	536	485	275	210	0.39
Case 7.....	900	800	350	450	0.50
Case 8.....	805	700	275	425	0.53
Case 9.....	3,813	2,500	475	2,025	0.53
Case 10.....	982	1,300	600	700	0.71
Case 11.....	822	1,600	650	950	1.15
Case 12.....	1,262	1,900	400	1,500	1.19
TOTAL.....	11,712	—	—	6,930	0.59

From the 11,712 animals dipped the average mechanical loss of dip is found to be 0.59 gallons per animal, the minimum and maximum limits being 0.23 and 1.19 gallons respectively.

(b) THE EFFECT OF DIPPING ON THIOSULPHATE CONTENT.

For every animal immersed into the bath a certain quantity of thiosulphate is formed. On leaving the bath the animal, however, carries off with it a certain quantity of thiosulphate, depending on the concentration of thiosulphate in the bath at that moment. When the second animal enters, it enters a bath somewhat smaller in volume, but with a somewhat higher thiosulphate and somewhat lower polysulphide concentration. For the rest it repeats the process executed by the former animal. If, now, the amount of thiosulphate formed per animal varies, in the first instance, with the nature of the animal which in turn is a function of various unknown variables, and in the second instance with the composition of the bath at the time of immersion, the process, considered mathematically, becomes highly involved. However, taking into consideration the various limits placed on the accuracy of all field measurements, and also the various unknown factors influencing dipping such as nature and weight of fleece, design of dipping plant, etc., it would be of little use to stress unduly the strict mathematical treatment of the problem.

What is actually measured is the initial concentration of the thiosulphate in a bath of known volume, and the final concentration of thiosulphate in the wash remaining in the tank, the volume of which is also measured or known. The simplest method of approach here is to consider the quantity of thiosulphate mechanically removed from the bath during the process of dipping; for obviously, once we know the quantity removed mechanically, the initial quantity and the final quantity, the calculation of the quantity formed chemically

is a simple matter. Given a definite set of dipping conditions under which a known number of animals are dipped, the concentration of thiosulphate in the dipwash mechanically removed from the bath, will rise progressively from a concentration practically equal to the initial concentration, to a concentration practically equal to the final concentration. If, therefore, the initial concentration is T_1 and the final concentration T_n , the average concentration may, for all practical purposes, be taken to be:—

$$T_a = \frac{(T_1 + T_n)}{2}$$

If these concentrations be expressed in gm. S. per 100 c.c., and if the initial volume of the bath be V_1 , decilitres and the final volume V_n decilitres, the amount of thiosulphate, expressed in gm. sulphur, mechanically removed from the bath may be expressed by:—

$$\sigma = \frac{(T_1 + T_n)}{2} \times (V_1 - V_n) \text{ gm. sulphur.}$$

If n animals are dipped then the amount of thiosulphate removed mechanically per animal will be:—

$$\delta\sigma = \frac{(T_1 + T_n)}{2} \times \frac{(V_1 - V_n)}{n} \text{ gm. sulphur.}$$

Expressing the volume V_1 and V_n in gallons, this equation becomes:—

$$\begin{aligned} \delta\sigma &= 10 \times 4.54 \times \frac{(T_1 + T_n)}{2} \times \frac{(V_1 - V_n)}{n} \\ &= 22.7 (T_1 + T_n) \times \frac{(V_1 - V_n)}{n} \text{ gm. sulphur.} \end{aligned}$$

Using this method of calculation, and considering in the first instance only those dips where the final dip volume after dipping was definitely known, Table X was compiled.

TABLE X.

Effect of Dipping on Thiosulphate Content.

Dip.	Initial Thios. conc. (gm.S/100 c.c.).	Final Thios. conc. (gm.S/100 c.c.).	Initial volume (gals.).	Final volume (gals.).	Initial Thios. in bath (gm.S.).	Final Thios. in bath (gm.S.).	Thios. lost (gm.S.).	Number animals dipped.	Thios. formed per animal (gm.S.).
N. 7.	0.150	0.165	395	265	2,690	1,986	933	560	0.4
TKi. 7.	0.018	0.083	520	325	425	1,225	463	737	1.7
K. 7.	0.141	0.384	700	275	4,481	4,794	5,057	805	6.7
Tvl. 6.	0.243	0.621	2,500	475	27,580	13,400	39,730	3,813	6.7
K. 10.	0.262	0.588	800	350	9,517	9,346	8,684	900	9.5
K. 1 and 2 Sp.	0.115	0.416	1,900	400	9,922	7,556	18,110	1,262	12.5
TKi. 1.	0.352	0.640	1,300	600	20,770	17,440	15,770	982	12.6

The results obtained for the quantities of thiosulphate formed per animal under different sets of dipping conditions are somewhat unexpected. It could hardly have been expected that as much as 12.6 gm. thiosulphate sulphur would be formed by dipping a single animal; on the other hand, the great fluctuation from 0.4 to 12.6 gm. thiosulphate sulphur per animal indicates the variety of factors operating under different conditions of dipping.

To serve as a further check on these results, use has been made of the average and minimum loss in gallons of dip per animal, as given in Table IX, to determine analogous figures for those dips where the actual measurement of the final volume in the tank at the end of dipping was not available. These results have been tabulated in Table XI. The figures in column 6 were determined by taking the volume of dip removed per animal equal to the average figure of 0.59 gallons; the figures in column 7 were obtained by employing the minimum loss of 0.23 gallons per animal, and as such represent the maximum amount of thiosulphate formed per animal.

TABLE XI.

Dip.	Initial Thios. conc. (gm. S/100 c.c.).	Final Thios. conc. (gm. S/100 c.c.).	Initial volume (gals.).	Number animals dipped.	Thios. formed per animal (0.59 basis). (gm. S.)	Thios. formed per animal (0.23 basis). (gm. S.)
K. 9.....	0.211	0.358	600	2,181	—	1.1
TKi. 4.....	0.075	0.225	500	1,600	—	1.3
TKi. 5.....	0.012	0.096	400	775	—	1.5
N. 12.....	0.095	0.144	500	549	1.4	1.8
N. 9.....	0.135	0.201	390	458	1.7	2.2
K. 2.....	0.089	0.143	600	508	2.1	2.6
N. 3.....	0.111	0.128	625	160	2.3	2.9
K. 3.....	0.141	0.326	1,700	2,739	3.1	4.2
Tvl. 7.....	0.270	0.450	950	1,487	3.2	4.3
K. 6.....	0.230	0.473	800	1,444	—	4.9
K. 5.....	0.230	0.409	600	723	4.3	5.8
F. 2.....	0.360	0.540	800	600	8.4	9.9

On the whole this table substantiates the results recorded in Table X, the maximum amount of thiosulphate here formed being represented by 9.9 gm. sulphur. It is significant that the figures recorded in columns 6 and 7 do not differ to any great extent. This means that the effect of the final volume on the figures calculated for the amount of thiosulphate formed per animal is small, so that the normal inaccuracies inherent in all field measurements cannot influence the thiosulphate values in Tables X and XI to any appreciable extent. This implies that the wide fluctuations in the quantities of thiosulphate formed per animal under different conditions, cannot be ascribed to any normal inaccuracy in field measurement.

(c) EFFECT OF DIPPING ON POLYSULPHIDE.

The effect of dipping on the polysulphides of calcium in solution can conceivably be twofold; (a) in reducing the total amount of polysulphide sulphur in solution, and (b) in changing the nature of the polysulphides in solution.

If the higher polysulphides are less stable than the lower members of the group, obviously these higher polysulphides will be decomposed at a much greater rate, with a resulting fall in the atomic ratio of calcium to sulphur. The results in Table XII have been collected to show that this change in the nature of the polysulphides actually occurs as a result of dipping.

TABLE XII.

Effect of Dipping on Nature of Polysulphide.

Dip.	Polysulphide concentration before dipping (gm. S/100 c.c.).	X in M_2S_x before dipping.	Polysulphide concentration after dipping (gm. S/100 c.c.).	X in M_2S_x after dipping.
<i>Group A.</i>				
TKi. 4.	1.18	4.46	0.46	1.34
TKi. 5.	0.89	4.46	0.44	1.45
K. 12.	0.43	4.05	0.16	1.50
K. 3.	0.97	4.78	0.25	1.70
TKi. 3.	2.15	4.62	0.36	1.71
N. 9.	0.65	4.49	0.30	1.93
K. 9.	1.16	4.71	0.32	1.94
K. 2.	0.99	4.61	0.38	2.20
TKi. 7.	1.41	4.16	0.65	2.20
K. 7.	0.99	3.45	0.76	2.38
K. 1.	1.52	3.87	0.60	2.57
K. 10.	1.24	4.21	0.68	2.58
K. 6.	1.43	3.78	0.81	3.00
K. 5.	1.27	4.34	0.55	3.12
TKi. 8.	1.10	4.44	0.95	3.29
F. 2.	1.76	4.22	1.16	3.45
K. 11.	1.60	4.21	1.16	3.90
TKi. 1.	1.63	4.06	1.39	3.97
Tvl. 7.	1.44	4.68	0.85	4.04
N. 12.	0.84	4.66	0.53	4.20
N. 3.	0.82	4.70	0.77	4.38
<i>Group B.</i>				
TKi. 3.	0.95	—	0.44	1.83
TKi. 4.	0.52	2.07	0.52	2.03
K. 2.	0.99	4.61	0.38	2.17
TKi. 7.	0.84	2.35	0.46	2.22
TKi. 8.	1.11	3.66	0.65	2.41
K. 1.	—	—	0.65	2.46
K. 7.	1.30	3.54	0.80	2.60
N. 9.	1.38	4.52	0.85	3.29
TKi. 5.	1.42	4.40	0.73	4.01

The results under Group A represent dips which had been freshly prepared before dipping; the results under Group B represent dips which had been previously used for dipping, but which had been re-strengthened for the occasion by adding fresh concentrate to the

bath. The table shows clearly that there is both a decrease in the polysulphide sulphur concentration and a marked change in the nature of the polysulphide. The greatest change in the nature of the polysulphides is shown by dip TKi.4 where the ratio of alkali metal to sulphur had fallen as low as 1.34. This depreciation in the order of the polysulphides in solution is of course dependent on various factors such as initial polysulphide concentration, the volume of the bath, the number of animals dipped, etc. However, from the wool-producer's point of view this change is most important, and must be studied very closely. There can be little doubt that a polysulphide solution represented by $\text{CaS}_{1.3}$ —which by its very nature must contain an appreciable concentration of HS ions due to hydrolysis—must, provided the concentration is high enough, be far more injurious to the wool fibre than a polysulphide solution represented by $\text{CaS}_{1.2}$. In this connection a comparison of dip TKi.4 with dip N.12 (after dipping figures) with respect to their possible effect on the wool would be most interesting and instructive. However, the further discussion on this point must be allowed to stand over until we have completed our investigation on the effect of different polysulphide solutions on wool. In passing it would suffice to stress its fundamental importance, and to point out that the question of excessive dipping must be viewed not only from the point of view of an effective final concentration, but also from that of a safe final composition.

The problem of calculating the amount of polysulphide lost per animal on dipping is in its nature very similar to that of calculating the amount of thiosulphate formed per animal. Again, as each animal passes through the bath it causes a certain amount of polysulphide to be decomposed forming partially thiosulphate—chemical loss—and as it leaves the bath it carries away with it an additional amount of polysulphide—mechanical loss. In solving this problem we shall again first consider the mechanical loss.

If the initial concentration of polysulphide be P_1 gm. sulphur per 100 c.c. in an initial bath volume of V_1 deciliters, and if the final concentration be P_n in a final bath volume of V_n deciliters, the mean concentration of polysulphide sulphur in the dip wash mechanically removed from the bath will be:—

$$P_v = \frac{(P_1 + P_n)}{2} \text{ gm. sulphur per 100 c.c.}$$

The weight in gm. mechanically removed by n animals will therefore be:—

$$\pi = \frac{(P_1 + P_n)}{2} \times (V_1 - V_n) \text{ gm. sulphur.}$$

And measuring the volumes in gallons we have:—

$$\pi = 22.7 (P_1 + P_n) (V_1 - V_n) \text{ gm. sulphur per } n \text{ animals.}$$

If now, the initial weight of polysulphide sulphur be Q_1 gm. and the final weight be Q_n gm., then the weight of polysulphide sulphur lost by chemical means will be:—

$$Q_c = Q_1 - (Q_n + \pi) \text{ gm. sulphur for } n \text{ animals}$$

Hence,

$$\delta Q_c = \frac{[Q_1 - (Q_n + \pi)]}{n} \text{ gm. sulphur per animal.}$$

BEHAVIOUR OF LIME-SULPHUR DIPS UNDER FIELD CONDITIONS.

Calculated on this basis, and considering in the first instance only those dips where the final dip volume after dipping was definitely known, the chemical loss per animal under different conditions of dipping has been tabulated in the following table—Table XIII.

TABLE XIII.
Effect of Dipping on Polysulphide Content.

Dip.	Initial P.S. conc. (gm. S/100 c.c.).	Final P.S. conc. (gm. S/100 c.c.).	Initial volume (gals.).	Final volume (gals.).	Initial P.S. in bath (gm. S).	Final P.S. in bath (gm. S).	P.S. lost mechanically. (gm. S).	Number animals dipped.	P.S. lost per animal chemically (gm. S).
TKi. 8..	1.10	0.95	390	225	19,480	9,705	7,679	536	3.9
K. 7....	0.99	0.76	700	275	31,470	9,488	16,890	805	6.3
K. 10...	1.24	0.68	800	350	45,040	10,810	19,600	900	16.3
TKi. 7..	1.41	0.65	520	325	33,290	9,592	9,118	737	19.8

From the few results recorded here the amount of polysulphide decomposed per animal dipped varies from 3.9 to 19.8 gm. sulphur. In order to study this decomposition, also in the case of those dips where the final volume of the bath was not directly given, this final volume was again calculated on the basis of an average and minimum mechanical loss per animal of 0.59 and 0.23 gallons respectively. This minimum loss basis again gives maximum figures for the chemical loss of polysulphide per animal. The results so obtained have been tabulated in Table XIV.

TABLE XIV.

Dip.	Initial P.S. conc. (gm. S/100 c.c.).	Final P.S. conc. (gm. S/100 c.c.).	Initial volume (gals.).	Number animals dipped.	P.S. decomposed per animal (0.59 basis) (gm. S).	P.S. decomposed per animal (0.23 basis) (gm. S).
K. 9.....	1.16	0.32	600	2,181	—	6.1
TKi. 5.....	0.89	0.44	400	775	—	8.2
N. 3.....	0.82	0.77	625	160	8.2	8.6
N. 12.....	0.84	0.53	500	549	8.6	11.2
N. 9.....	0.65	0.30	390	458	9.5	11.7
K. 6.....	1.43	0.81	800	1,444	—	12.4
Tvl. 7.....	1.44	0.85	950	1,487	10.4	14.1
K. 3.....	0.97	0.25	1,700	2,739	12.1	16.5
K. 5.....	1.27	0.55	600	723	17.4	23.4
K. 2.....	0.99	0.38	600	508	24.5	29.5
F. 2.....	1.76	1.16	800	600	28.1	33.2

Using the value of 0.23 gallons for the loss of dip per animal, the maximum figures for the amounts of polysulphide decomposed per animal under different sets of dipping conditions vary between 6.1 and 33.2 gm. polysulphide sulphur.

As the polysulphide thus decomposed in the process of dipping is partially oxidized to thiosulphate and partially precipitated as elementary sulphur, the data thus far obtained may be grouped together to show how the sulphur of the decomposed polysulphide is distributed between thiosulphate and elementary sulphur under different dipping conditions.

TABLE XV.

Distribution of Decomposed Polysulphide Sulphur.

Dip.	Number animals dipped.	P.S. decomposed per animal (gm. S).	Thios. formed per animal (gm. S).	Free S. precipitated per animal. (gm. S).	Per cent. P.S. converted into thio-sulphate.
K. 10.....	900	16.3	9.5	6.8	58.3
K. 7.....	1,444	12.4	4.9	7.5	39.9
N. 3.....	160	8.6	2.9	5.7	33.7
Tvl. 7.....	1,487	14.1	4.3	9.8	30.5
F. 2.....	600	33.2	9.9	23.3	29.8
K. 3.....	2,739	16.5	4.2	12.3	25.4
K. 5.....	723	23.4	5.8	17.6	24.8
N. 9.....	458	11.7	2.2	9.5	18.9
TKl. 5.....	775	8.2	1.5	6.7	18.3
K. 9.....	2,181	6.1	1.1	5.0	18.0
N. 12.....	549	11.2	1.8	9.4	16.1
K. 2.....	508	29.5	2.6	26.9	8.9
Average.....	12,524	14.6	4.0	10.6	27.3
Limits.....	—	6.1-33.2	1.1-9.9	5.0-26.9	8.9-58.3

Table XV shows that the average amount of polysulphide decomposed per animal, calculated on a total number of animals of over 12,000, amounts to 14.6 gm. sulphur, varying between 6.1 and 33.2 gm. sulphur per animal. Of this decomposed polysulphide sulphur 1.1 to 9.9 gm., or an average of 4.0 gm., is converted into thiosulphate, forming on the average 27.3 per cent. of the polysulphide decomposed. The remaining sulphur, varying from 5.0 to 26.9 gm. and averaging 10.6 gm. per animal, is chiefly precipitated as free elementary sulphur.

Apart from the general decrease in the concentration of total polysulphide sulphur in solution, the process of dipping also causes a change in the nature of the polysulphides, as we have already shown. To some extent this change is affected by certain suint constituents reacting with the polysulphides of calcium in solution. With a view to tracing the effect of the partial base exchange due to reaction with the suint, and also with the object of studying the change in the nature of the polysulphides more closely, the effect of dipping on the monosulphide equivalent, the free polysulphide sulphur, and the calcium in solution was also studied. In Table XVI the analyses of several dips for these constituents have been tabulated.

TABLE XVI.

Dip.	M.S.S.E. initial (gm. S/ 100 c.c.).	F.P.S.S. initial (gm. S/ 100 c.c.).	Ca. initial (gm. Ca/ 100 c.c.).	M.S.S.E. final (gm. S/ 100 c.c.).	F.P.S.S. final (gm. S/ 100 c.c.).	Ca. final (gm. Ca/ 100 c.c.).
N. 12.....	0·131	0·711	0·280	0·126	0·403	0·250
N. 9.....	0·144	0·503	0·301	0·158	0·147	0·270
N. 3.....	0·175	0·647	0·318	0·175	0·593	0·310
TKi. 5.....	0·200	0·693	0·283	0·299	0·136	0·260
K. 3.....	0·203	0·768	0·460	0·149	0·104	0·316
K. 2.....	0·215	0·777	0·329	0·174	0·208	0·278
K. 9.....	0·246	0·912	0·496	0·165	0·155	0·320
K. 10.....	0·294	0·942	0·683	0·262	0·416	0·613
K. 5.....	0·294	0·979	0·705	0·175	0·372	0·280
Tvl. 7.....	0·308	1·134	0·595	0·210	0·638	0·506
K. 6.....	0·379	1·056	0·717	0·274	0·544	0·521
F. 2.....	0·418	1·346	0·792	0·308	0·756	0·555

M.S.S.E. ... Monosulphide sulphur equivalent.

F.P.S.S. ... Free polysulphide sulphur.

The table shows that in all cases the process of dipping results in a decrease in the concentration of free polysulphide sulphur and calcium. This also holds for the monosulphide sulphur equivalent, except in the case of dips TKi.5 and N.9 where a small increase in the monosulphide sulphur equivalent occurs as a result of dipping.

Applying the same method of calculation as used for the total polysulphide sulphur in Tables XIII and XIV, the loss in monosulphide equivalent, free polysulphide sulphur and calcium per animal has again been calculated, the results being expressed in Table XVII.

TABLE XVII.

Dip.	Number animals dipped.	M.S.S.E. lost per animal (gm. S).	Ca. lost per animal (gm. Ca).	F.P.S.S. lost per animal (gm. S).
TKi. 5.....	775	— 1·8	0·4	10·0
N. 9.....	458	— 0·5	1·0	12·2
N. 3.....	160	+ 0·0	1·4	8·6
N. 12.....	549	0·2	1·1	11·0
K. 9.....	2,181	0·6	1·3	5·5
K. 10.....	900	0·9	2·0	15·4
K. 3.....	2,739	1·2	3·3	15·3
K. 2.....	508	2·0	2·5	27·5
K. 6.....	1,444	2·1	3·9	10·3
Tvl. 7.....	1,487	2·3	2·1	11·8
K. 5.....	723	3·8	13·8	19·6
F. 2.....	600	6·1	13·3	27·1
Average.....	12,524	1·4	3·4	13·2
Limits.....	—	—1·8-6·1	0·4-13·8	5·5-27·5

M.S.S.E. = Monosulphide sulphur equivalent.

F.P.S.S. = Free polysulphide sulphur.

The table shows that the quantity of calcium lost per animal is persistently greater than the loss in monosulphide sulphur equivalent, except in the case of dip Tvl.7. This excess of calcium loss over loss in monosulphide equivalent also holds when considered on a basis of chemical equivalent. Since the loss of this excess calcium must be counterbalanced if further loss in monosulphide equivalent as sulphuretted hydrogen is to be avoided, we have here proof that the loss in calcium on dipping must in part be affected by a process of base exchange with the alkali in the suint, the calcium being precipitated as calcium carbonate and calcium salts of suint acids, and the sulphide sulphur becoming attached to potassium. That this process of base exchange is appreciable is shown by the fact that for an average loss of 1.4 gm. in monosulphide sulphur equivalent there is a corresponding average loss in calcium of 3.4 gm.

(d) THE EFFECT OF IMMERSION TIME ON COMPOSITION.

The table also shows that there apparently exists no parallelism between the loss in monosulphide sulphur equivalent and the loss in free polysulphide sulphur. From this we may conclude that the decomposition of polysulphide on dipping is not due to oxidation to the extent one might primarily be led to expect. This point is brought out still more clearly if we consider the amount of thiosulphate formed in comparison with the loss in polysulphide. If oxidation were par excellence the dominating factor causing loss in polysulphide sulphur, then the longer the bath remained in agitation during the dipping, the greater would be the amount of thiosulphate formed, since the effect of other factors would then be minimal. That this is not so, the data tabulated in Table XVIII will show. In this table the total time taken (in minutes) for actual dipping divided by the number of animals dipped has been given as the average time per animal. This average time is taken to serve as an index of bath agitation. It must not be taken to represent the time each animal remained in the bath, since from two to five animals were immersed simultaneously. The actual immersion time per animal was two minutes as officially laid down. All figures have been given in gm. sulphur per animal.

TABLE XVIII.
Effect of Immersion Time on Composition.

Dip.	M.S.S.E. lost.	F.P.S.S. lost.	P.S.S. lost.	Thiosulphate formed.	Average time per animal (minutes).
F. 2.....	6.1	27.1	33.2	9.9	0.40
TKi. 5.....	— 1.8	10.0	8.2	1.5	0.43
Tvl. 7.....	2.3	11.8	14.1	4.3	0.44
K. 5.....	3.8	19.6	23.4	5.8	0.54
N. 12.....	0.2	11.0	11.2	1.8	0.60
K. 10.....	0.9	15.4	16.3	9.5	0.63
N. 9.....	— 0.5	12.2	11.7	2.2	0.65
K. 3.....	1.2	15.3	16.5	4.2	0.67
K. 6.....	2.1	10.3	12.4	4.9	0.70
K. 2.....	2.0	27.5	29.5	2.6	0.71
K. 9.....	0.6	5.5	6.1	1.1	1.07
N. 3.....	0.0	8.6	8.6	2.9	1.50
Average.....	1.4	13.2	14.6	4.0	—

(e) THE EFFECT OF OXIDATION ON DECOMPOSITION.

If, according to the equation



the decomposition of the polysulphide as a result of dipping were due solely to atmospheric oxidation, then the percentage of decomposed polysulphide sulphur converted into thiosulphate must remain constant and equal to about 43 per cent., unless the thiosulphate formed is also partially decomposed. We have found, however, no indication that such decomposition of already formed thiosulphate actually occurs. On the other hand, this thiosulphate conversion constant is a linear function of the atomic ratio of calcium to sulphur in the initial polysulphides present.

If we start with a polysulphide CaS_5 , then, according to the equation:—



the conversion to thiosulphate will be 40 per cent. If, again we start with a polysulphide $\text{CaS}_{2.5}$, then, according to the equation:—



the conversion will be 80 per cent. As the atomic ratio of calcium to sulphur falls continually during the course of dipping, a comparison of the amount of polysulphide sulphur actually converted into thiosulphate, with the amount that should be converted theoretically if oxidation were the only cause of decomposition of the polysulphide, becomes possible only if we take into consideration the initial and final values of this ratio.

In the equation:



where x_1 and x_2 are the initial and final atomic ratios respectively, average or mean figures for a definite set of dipping conditions will be obtained when x is taken to be equal to $\frac{1}{2}(x_1 + x_2)$. We thus obtain the figures recorded in Table XIX.

TABLE XIX.
Effect of Oxidation on Decomposition.

Dip.	Initial X.	Final X.	Average X.	Theoretical per cent. conversion.	Per cent. conversion found.	Per cent. of theoretical conversion.
K. 2.....	4.61	2.20	3.40	59.0	8.9	15.1
TKi. 5.....	4.46	1.45	2.95	67.8	18.3	27.0
K. 9.....	4.71	1.94	3.32	60.2	18.0	30.0
N. 9.....	4.49	1.93	3.21	62.3	18.9	30.3
N. 12.....	4.66	4.20	4.43	45.1	16.1	35.7
K. 3.....	4.78	1.70	3.24	61.7	25.4	41.2
K. 5.....	4.34	3.12	3.73	53.3	24.8	46.5
F. 2.....	4.22	3.45	3.83	52.2	29.8	57.1
TvL. 7.....	4.68	4.04	4.36	45.8	30.5	66.6
K. 6.....	3.78	3.00	3.39	59.0	39.9	67.6
N. 3.....	4.70	4.38	4.54	44.0	33.7	76.6
K. 10.....	4.21	2.58	3.40	59.0	58.3	98.8

From the above table it will be seen that the amount of thio-sulphate actually formed in the course of dipping varies from 15 per cent. to almost 100 per cent. of the amount theoretically possible if all polysulphide decomposition were due to oxidation. Thus in dip K.10 the dominant cause of decomposition of the polysulphides was almost exclusively limited to oxidation; on the other hand, in the case of dip K.2 the rôle played by oxidation is small; by far the major part of the decomposition actually found must be ascribed to other influences. As we have already pointed out, these other influences are various. To some extent the polysulphide decomposition is due to the effect of carbon dioxide and suint constituents. To what extent chemical equilibria and composition as well as concentration exert their influence cannot be determined from such a field study. It would appear, however, that to some extent the factors causing such wide fluctuations are intimately and inseparably connected with the material dipped, which again are controlled by various factors of stock-breeding and stock-raising and all they imply. As far as oxidation of the dip is concerned, it appears to us that this oxidation is primarily caused by the oxygen brought into the bath with the animal; the effect of free atmospheric oxygen due to agitation would appear to be of minor consequence. As to the form in which the oxygen, imparted to the dip by the fleece, exists, we can at present only speculate. However, it seems feasible to suppose that the fleece may contain loosely bound oxygen, attached to suint and fat constituents in a form similar to the peroxide linkage, in addition to ordinary free atmospheric oxygen. These aspects are under consideration.

IV. SUMMARY.

1. The results of analyses of lime-sulphur dipwashes, the lime and water used in their preparation, received from various parts of the Union, have been summarized and discussed. The samples referred to were all obtained from actual dippings undertaken by officials in the combat of sheep scab.
2. The preparation of lime-sulphur solutions and factors influencing its composition are detailed.
3. The effects of the processes involved in the actual dipping on the dipwash itself have been studied.
4. Additional evidence that considerable changes occur in the tankwash as a result of dipping have been obtained.
5. Factors producing these changes have been touched upon.

V. ACKNOWLEDGMENTS.

The authors wish to express their appreciation of and indebtedness to the senior veterinary officers, Government veterinary officers and dip inspectors, in the various areas of the Union whose enthusiastic efforts in the collection of specimens and the detailed information asked for, have made this research possible; to Dr. P. J. du Toit, Director of Veterinary Services and Animal Industry, for placing all facilities at their disposal, and to the Empire Marketing Board for the grant enabling the work to be undertaken.

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