Note on the Decomposition of Diluted Polysulphide Dips.

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THE question of possible deterioration of lime-sulphur dipwash is of some economical importance, as this type of dip is very extensively used in the Union for dipping sheep against scab. As the recognized practice is to dip a second time on the tenth day after the first dipping, the question naturally arises whether the wash left over in the tank from the first dipping can be used for the second dipping. Many farmers prefer taking the absolutely safe course of cleaning out the tank prior to the second dipping and using a completely fresh dipping fluid. This is also the course advised by sheep inspectors and insisted upon at compulsory dippings. For the large sheepowner, who has to replenish the tank once or more during the course of a single dipping, and is left with only a few hundred gallons of very dirty dip and sludge when his flock is through, the probable value of the residue is relatively unimportant. In many other cases, however, the residual dip represents a value which the farmer can ill afford to disregard, and it was therefore considered advisable to collect some analytical data bearing on the strength of used polysulphide dipwashes.

Although it was the prevalent opinion in this country that the polysulphides, constituting the active principle of this class of dip, got oxidized fairly rapidly in the open, the writer was aware of cases where farmers claimed good results for the old, used dipwash. In 1921 Mellvill* showed in two experiments that the polysulphide solution lost about 3 per cent. in strength on diluting (with ordinary water and mixing) to tank strength, and a further 8 per cent. during the course of dipping one hundred sheep. From observations made by officers of this Division, it was also surmised that the decomposition was probably less marked than was commonly supposed to be the case. It was therefore decided to obtain some figures to elucidate this point.

During a small scale dipping experiment carried out at the Laboratory in 1921 with the object of ascertaining a possible harmful effect of a certain proprietary soda-sulphur dip, analyses made on various samples of the dipwash gave the following results (iodine method):—

EXPERIMENT No. 1.

	Monosulphide Sulphur. %	Thiosulphate Sulphur. %
(1) Immediately after addition of dip to water and stirring three minutes with plunger	.525	.435
(2) After dipping ten sheep, in pairs, quarter of an hour later than (1)	.510	.486
(3) Sub-surface sample from resting tank, one hour later than (2)	.498	.518
(4) Taken immediately after (3), but after vigorous stirring with plunger	.501	.518

* Mellvill, *Journ. S.A. Chem. Inst.*, V: 15 (1922).

As the figures for monosulphide sulphur can in general be taken as a direct indication of the efficacy of such a "sulphur dip," we see that in the above case there has been a deterioration of under 5 per cent. only. The figures in the second column have no direct bearing on the efficacy of the wash, but they serve to give some indication as to the nature of the decomposition. Unfortunately, proposed further analyses were made impossible as the tank was flooded by rain-water.

A similar experiment carried out a few months later gave the following values (iodine method):—

EXPERIMENT No. 2.

	Monosulphide Sulphur. %	Thiosulphate Sulphur. %
(1) Immediately after mixing	.517	.442
(2) After dipping ten sheep, twenty-five minutes later than (1)	.509	.461
(3) *Skimmed off surface*, one hour later than (2)	.170	—
(4) Taken immediately after (3), but after vigorous stirring with plunger	.485	.486
(5) Tank kept agitated for an hour after (4), and then sampled	.478	.518
(6) Sub-surface sample from resting tank, two and a quarter hours later than (5)	.470	.557
(7) Sampled after vigorous stirring, immediately after (6)	.483	.506
(8) Tank kept agitated for two hours after (7), and then sampled	.477	.525
(9) Sub-surface sample from resting tank, twenty-two hours later	.470	.589
(10) Immediately after (9), after tank well stirred up	.488	.506
(11) After further twenty hours, during which period tank thoroughly agitated five times. Sampled directly after stirring	.488	.506
(12) Three days later, i.e. five days after dipping. Sampled after stirring. Dip diluted about 15 per cent. by rain-water. Results corrected approximately	.467	.515
(13) Nineteen days after dipping. Sampled after stirring. Tank flooded completely and no correction possible	.283	.384

On the basis of the monosulphide equivalent, we again see that the decomposition due to dipping ten sheep and exposing the wash to the action of the atmosphere for an hour afterwards has been slight, i.e. only about 6 per cent. After two days, in spite of repeated, and in some cases prolonged, mixings, the monosulphide value is still the same, indicating that the rate of decomposition has been very slow. Assuming that the results for sample (12) are approximately correct, we see that the five-day-old used dip has only lost about 10 per cent. in strength, although it is possible that, owing to the inflow of rain-water, these values might not be very reliable. Complete flooding of the tank made it quite impossible, unfortunately, to compare the figures for the nineteen-day-old dip with the previous results, but they nevertheless seem to support the evidence in favour of a slow rate of deterioration. It should here be noted that the iodine methods, particularly when applied to partially decomposed dips, probably do not give absolutely reliable results.* Indeed, it seems doubtful if

* For literature, see Green, 3rd, 4th Reports of D.V.R. 175–195 (1915), also Chapin, *Journ. Indus. Eng. Chem.*, **8**, 151, 339 (1916).

any method exists which is satisfactory in all respects. Many of the samples discussed in this report were also analysed by the zinc chloride methods, but as the actual values found were rather different for the two methods, though they indicated much the same rate of decomposition [i.e. in Experiment 2 for sample (4) a deterioration of 7 per cent., for sample (11) 9 per cent., and for sample (12) 11 per cent.], it is not considered necessary to include full analytical figures in a short non-technical paper.

Without entering upon a discussion as to the precise nature and rate of the decomposition, and in spite of possible small errors in the method of analysis, the results obtained in Experiment 2 clearly show that in the resting tank it is only the actual surface layer which is subject to pronounced decomposition, for samples taken from just under the surface show very little change compared to the average composition for the contents of the whole tank (compare e.g. 6 with 7). As would be expected, the increase in thiosulphate sulphur is usually considerably more than the decrease in monosulphide sulphur. The conversion of polysulphide sulphur into thiosulphate sulphur can of course not be quantitative, mainly because there is not sufficient base present. A considerable proportion of the sulphur is liberated as free sulphur, and found either in the sludge at the bottom of the tank or as a protecting layer on the surface. There is also a slight oxidation to sulphate.

The analytical results (iodine methods) recorded under Experiments 3, 4, and 5 were obtained during an actual farm dipping, using a proprietary lime-sulphur dip in a fairly large tank.

EXPERIMENT No. 3.

	Monosulphide Sulphur. %	Thiosulphate Sulphur. %
(1) Dip diluted *in laboratory* to tank strength with air-free distilled water	.284	.102
(2) Actual tank wash, immediately after stirring well. Sub-surface sample	.177	.067
(3) Same as (2), after one hour, and 150 sheep dipped	.254	.131
(4) Same as (2), after two hours, and 300 sheep dipped	.246	.150

EXPERIMENT No. 4.

	Monosulphide Sulphur. %	Thiosulphate Sulphur. %
(1) Dip diluted *in laboratory* to tank strength with air-free distilled water	.282	.113
(2) Actual tank wash, after stirring. Sub-surface sample	.221	.090
(3) Actual tank wash, after fifteen minutes, and eighteen sheep dipped	.272	.115
(4) Actual tank wash, after two hours, and 300 sheep dipped	.258	.179

EXPERIMENT No. 5.

	Monosulphide Sulphur. %	Thiosulphate Sulphur. %
(1) Sample *water* from tank, after dipping 100 sheep	—	(.032)
(2) After proprietary dip added to (1), stirred, and eight sheep dipped	.267	.176
(3) After proprietary dip added to (1), after 200 sheep dipped	.232	.278

The dipping tests referred to in these three cases were carried out within a short time of each other in connexion with an investigation of the effect of the dip on the sheep. The results again show that oxidation is not excessive, though in Experiment 5 it is fairly high, i.e. about 13 per cent. after dipping two hundred sheep. In this experiment it is clearly brought out that the thiosulphate figure is affected by the excreta of, or dirt on the dipped animals. This may be wholly due to reaction of organic matter with the iodine (e.g. sample 1), but it also seems possible that in general the decomposition of the dip will be increased if the amount of foreign material brought into the tank is increased. In the case of Experiments 3 and 4 it is not possible to state precisely what the extent of deterioration has been, as the initial mixing did not give a uniform mixture and the method of measuring the capacity of the tank (with paraffin tins) was not exact. In Experiment 3 there is reason to assume, from observations made at the time, that the tank was initially somewhat under strength (about 5 per cent.). On this assumption the initial strength would have been about .270 per cent. monosulphide equivalent instead of the theoretical .284 per cent., and, therefore, a drop to .246 per cent. after dipping three hundred sheep would mean a decrease in efficacy of 9 per cent. In Experiment 4 the quantity of water necessary was measured off more carefully, so that in this case we can assume that .282 per cent. is roughly correct, which places the loss in strength due to dipping three hundred sheep at about 8 per cent. It is perhaps of interest to note that under ordinary farm conditions it seems a difficult matter to obtain a perfectly uniform mixture by ordinary stirring with a pole or plunger. This is brought out by comparing sample 2 with sample 3 in Experiments 3 and 4 above, both of which were carried out under supervision. This factor is presumably responsible, in part at any rate, for various discrepancies in the analyses recorded in this paper.

After the above results were available it was decided to carry out a rather more elaborate test in which the extent of oxidation on standing for a long time could be followed. With this object in view, the dip which was left over in the tank after the first dipping was used for the second dipping as well, and samples were subsequently taken during a three months' period.

EXPERIMENT No. 6.

(All samples taken from a depth of 6 inches below the surface; results by iodine methods.)

	Depth of tank. in.	Monos. Sulphur. %	Thios. Sulphur. %	Polys. Sulphur. %
(1) Proprietary lime-sulphur dip, 600 gallons of approximately 1 in 20 dilution. Immediately after mixing for five minutes	32*	.368	.125	1.785
(2) After further four minutes, and five sheep dipped	—	.359	.112	1.635
(3) After further forty-five minutes, and 100 sheep dipped	26	.318	.175	1.210
(4) After further one day. Tank at rest	—	.300	.187	1.260

* Tank was found to leak at about 2 feet level, so that at the time of adding dip some water had leaked out and the initial strength was above 1 in 20. Leak repaired prior to second dipping.

	Depth of tank. in.	Monos. Sulphur. %	Thios. Sulphur. %	Polys. Sulphur. %
(5) After further eight days. Tank at rest	22	.312	.162	1.350
(6) Same as (5), but immediately after stirring up vigorously	—	.301	.150	1.120
(7) Tank ready for second dipping, after adding 300 gallons of fresh dip of 1 in 25 strength. Stirred, and five sheep put through	37	.278	.137	1.205
(8) Fifty sheep dipped. Sampled one day later. Tank at rest	35	.275	.187	1.240
(9) One month after second dipping. Tank at rest	31	.276	.306	
(10) Three months after second dipping. Tank at rest	21	.288	.512	1.355

From the monosulphide figures obtained in this experiment, it is again seen that oxidation has not been excessive, although it reaches the relatively high figure of 14 per cent. in dipping only one hundred sheep. As these sheep carried fairly long wool at the time, however, a somewhat higher rate of oxidation than in the previous experiments is not surprising. Longer wool not only means more air carried into the tank, but also more drainage from the pen of partially oxidized fluid from the fleeces. The drop in monosulphide equivalent for the following nine days, during which time the tank was left undisturbed, is only about 5 per cent. The figures for monosulphide sulphur after the second dipping show practically no change, although the increased figure for thiosulphate sulphur is indicative of oxidation.* It is of interest that during the following three months the loss in strength due to decomposition is more than balanced out by the gain in strength due to evaporation of water. The relatively great drop in polysulphide sulphur recorded for the first dipping—the free sulphur and dirt in the turbid sample were allowed to settle out in the tightly corked sample bottle before the analysis was undertaken—would seem to point to the probability that, apart from the change of sulphide sulphur to free sulphur thiosulphate or sulphate, the polysulphide is converted to a lower sulphide (e.g. pentasulphide to tetrasulphide). As the long-woolled sheep dipped in this partially decomposed wash were kept under observation for several weeks and closely compared with the controls, without showing any signs of ill effects to health or wool, it seems permissible to assume that no harmful lower sulphides resulted as a consequence of the oxidation.

Although the recorded work is not comprehensive enough to allow of very definite conclusions, it is indicated that the decomposition of this common scab dip is not so rapid nor of such a nature that the farmer with a small flock (and a small purse) may not use the wash left over from the first dipping for the second dipping as well.

* Comparison of the figures for polysulphide sulphur in samples 7 and 8 show that the mixing was not sufficient.