

Researches into Dips and Dipping.

A. Lime-Sulphur Dips.

Paper IV. Further Studies on the Colorimetric Method as a Rapid Means of Control of Polysulphide Solutions.*

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

IN a previous study of the colorimetric method as applied to polysulphide solutions—Paper A. III.—it was shown that under certain conditions solutions of the polysulphides of calcium conform to Beers Law, that is that the colour intensity is a linear function of the concentration. It was also shown, however, that field conditions, especially the process of dipping, affect these solutions to such an extent that this relation between colour intensity and concentration no longer holds. As a result of rather intensive dipping all dips become markedly turbid, and of these a very large percentage retains their turbidity even after standing unmolested for some months. Apart from this, dipping invariably results in appreciable amounts of suint alkali constituents entering the dip with the result of a partial base exchange being effected. Thus not only the reaction of the solution is changed, but some of the calcium polysulphides are also replaced by alkali polysulphides.

As a result of these observations it was decided to study the effect of the reaction of the medium on the relation of colour intensity to polysulphide concentration. For this purpose the effect of both sodium hydroxide and sodium carbonate on the colour characteristics of the polysulphides of sodium were studied. A solution of sodium polysulphide was prepared by boiling a concentrated solution of sodium sulphide with excess flowers of sulphur, diluting this concentrate somewhat, filtering, and making up to a fairly large volume. In this way a stock solution containing 5.10 gm. polysulphide sulphur per 100 c.c. was obtained. This stock solution was protected against atmospheric oxidation by covering its surface with a layer of 70-80° benzene. For the experiment under consideration 5.0 c.c. of this stock solution were carefully pipetted into a 50 c.c. measuring flask containing a few cubic centimetres of benzene, the sides of the flask immediately rinsed down with distilled water, and then different

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

COLORIMETRIC METHOD FOR CONTROL OF POLYSULPHIDE SOLUTIONS.

amounts of N/1 NaOH or 9 per cent. sodium carbonate (9 gm. Na₂CO₃—anhydrous—per 100 c.c.) added as required; the solutions were then made up to volume. The thus prepared solutions were allowed to stand at room temperature, and compared colorimetrically from time to time with the polysulphide solution to which no alkali had been added. After this the solutions were analysed by the volumetric cadmium acetate method (Paper II, A.).

Considering first the colorimetric analyses, the "apparent" polysulphide concentrations so obtained at different reaction times and different sodium hydroxide concentrations have been tabulated in Table I. All concentrations have been expressed in gm. polysulphide sulphur per 100 c.c. solution.

TABLE I.
Effect of NaOH on Na₂S_{4,6}—Colorimetric.

C.c. N/1 NaOH added per 50 c.c.	After 19 hrs.		After 66 hrs.		After 115 hrs.		After 236 hrs.	
	Color. reading.	P.S.S. conc. (app.).	Color. reading.	P.S.S. conc. (app.).	Color. reading.	P.S.S. conc. (app.).	Color. reading.	P.S.S. conc. (app.).
0·0 c.c.	20	0·510	20	0·510	20	0·510	20	0·510
0·1 c.c.	21	0·485	22	0·463	22	0·463	22	0·463
0·4 c.c.	25	0·408	28	0·364	29	0·352	28	0·364
1·0 c.c.	30	0·340	35	0·290	36	0·284	38	0·268
2·0 c.c.	32	0·318	37	0·275	40	0·255	43	0·238
10·0 c.c.	36	0·284	45	0·226	48	0·212	52	0·196

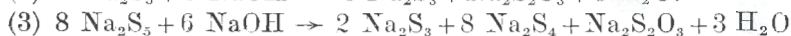
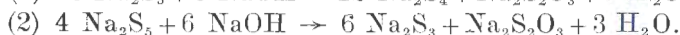
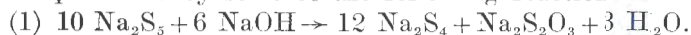
P.S.S. = polysulphide sulphur.

These apparent polysulphide concentrations have been calculated from the colorimetric readings by assuming that the polysulphide concentration remains proportional to the colour intensity. Initially, however, all solutions contained the same concentrations, since in every case 5 c.c. of the same stock solution were diluted to 50 c.c. Hence, judging by the marked fall in the apparent polysulphide concentration—from 0·510 to 0·196—a distinct change in the nature of the initially present polysulphide must have occurred.

Since sodium hydroxide reacts with elementary sulphur according to the equation:—



forming sodium polysulphides and sodium thiosulphate, it may be expected that this alkali will also react with the sulphur of higher polysulphides forming lower polysulphides and thiosulphate, and consequently increasing the monosulphide sulphur equivalent. This type of reaction, which we shall in future refer to as Reaction I, may thus be represented by some of the following reactions:—



etc.

To what extent these reactions influence the figures tabulated in Table I may be determined by considering the analytical data tabulated in Table II.

TABLE II.

Effect of NaOH on $\text{Na}_2\text{S}_{1.6}$ analysed after 236 hours.

C.c. N/1 NaOH per 50 c.c.	Thiosul- phate (gm. S/100 c.c.).	M.S.S.E. (gm. S/100 c.c.).	F.P.S.S. (gm. S/100 c.c.).	Polysul- phide (gm. S/100 c.c.).	Total S (calculated) (gm. S/100 c.c.).	x (in Na_2S_x).
0.0 c.c.	0.020	0.111	0.399	0.510	0.530	4.60
0.1 c.c.	0.024	0.107	0.390	0.497	0.521	4.64
0.4 c.c.	0.031	0.113	0.387	0.500	0.531	4.42
1.0 c.c.	0.033	0.119	0.377	0.496	0.529	4.17
2.0 c.c.	0.045	0.120	0.368	0.488	0.533	4.07
10.0 c.c.	0.045	0.122	0.365	0.487	0.532	4.00

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

F.P.S.S. = Free polysulphide sulphur (see previous reports).

From the figures recorded in the last column of the above table for the atomic ratio of sodium to sulphur we note that there is some decrease in the average order of the polysulphides. There is also a small corresponding increase in the thiosulphate and monosulphide sulphur equivalent. However, as has also been observed by Green (1915), the changes noted are small, the actual polysulphide concentration only decreasing from 0.510 to 0.487 gm. sulphur per 100 c.c. It is clear, therefore, that the chemical interaction described under Reaction I cannot explain why the apparent polysulphide concentration should, under the same conditions, fall from 0.510 to 0.196 gm. sulphur per 100 c.c.

To explain this observation, i.e. why the colour intensity of the polysulphides in solution decreases so markedly on adding sodium hydroxide, there would appear to be only two possible explanations. Either the sodium hydroxide, probably in dissociated form, is in some way or other linked on to the still unsaturated sulphur atoms of the polysulphide molecule forming a new complex compound with a much lower colour intensity, or the inorganic polysulphides in solution, like the organic polysulphides, are capable of existing in different isomeric forms with different colour intensities. The further discussion of this highly interesting observation, however, must be considered beyond the scope of the present paper.

Proceeding now to the effect of sodium carbonate on the polysulphides in solution, a similar state of affairs is revealed. Calculating again the apparent polysulphide concentrations from the colorimetric readings by assuming that the polysulphide concentration remains proportional to the colour intensity, we again find an appreciable fall in the apparent concentrations.

TABLE III.

Effect of Na₂CO₃ on Na₂S_{4.6}—colorimetric.

C.c. 9% Na ₂ CO ₃ added per 50 c.c.	After 45 hours.		After 168 hours.		After 360 hours.	
	Color. reading.	P.S.S. conc. (apparent).	Color. reading.	P.S.S. conc. (apparent).	Color. reading.	P.S.S. conc. (apparent).
0.0 c.c.	20	0.510	20	0.510	20	0.510
0.1 c.c.	21	0.485	21	0.485	21	0.485
0.4 c.c.	21	0.485	22	0.463	23	0.443
1.0 c.c.	23	0.443	24	0.424	24.5	0.416
2.0 c.c.	24	0.424	26	0.392	29	0.352
10.0 c.c.	28	0.364	30	0.340	36	0.284

P.S.S. = Polysulphide sulphur.

Comparing this fall in apparent polysulphide concentration—from 0.510 to 0.284 gm. sulphur per 100 c.c.—with the actual change in the concentration as revealed by chemical analysis, we again find that the appreciable change in apparent concentration cannot be accounted for by the type of reaction grouped under Reaction I.

TABLE IV.

Effect of Na₂CO₃ on Na₂S_{4.6}—analysed after 360 hours

C.c. 9% Na ₂ CO ₃ per 50 c.c.	Thiosul- phate (gm. S/100 c.c.).	M.S.S.E. (gm. S/100 c.c.).	F.P.S.S. (gm. S/100 c.c.).	Polysul- phide (gm. S/100 c.c.).	Total S (calculated) (gm. S/100 c.c.).	x (in Na ₂ S _x).
0.0 c.c.	0.020	0.111	0.399	0.510	0.530	4.60
0.1 c.c.	0.030	0.111	0.390	0.501	0.531	4.51
0.4 c.c.	0.028	0.111	0.390	0.501	0.529	4.51
1.0 c.c.	0.030	0.113	0.386	0.499	0.529	4.41
2.0 c.c.	0.027	0.113	0.388	0.501	0.528	4.43
10.0 c.c.	0.042	0.114	0.380	0.494	0.536	4.33

M.S.S.E. = Monosulphide sulphur equivalent.
F.P.S.S. = Free polysulphide sulphur.

As a result of these observations on the effect of alkali on the colour of polysulphides, the practical application of the colorimetric principle was further studied by adding excess alkali to the calcium polysulphide solutions. For this purpose sodium carbonate was found most useful, since firstly it converts all polysulphide to alkali polysulphide, and secondly precipitates the matter in suspension along with the calcium carbonate. To make this clarification of the solution more complete some absolute alcohol was also added, the polysulphides of the alkali metals being soluble in alcohol.

For the purpose of studying the effect of this treatment on the colour intensity of the solutions, a calcium polysulphide stock solution of known composition was suitably diluted to give a series of polysulphide solutions ranging from 0.14 to 1.44 gm. polysulphide sulphur per 100 c.c. In making up these solutions the required amount of stock solution was pipetted into a 50 c.c. measuring flask containing 10 c.c. of a 9 per cent. sodium carbonate solution and 5 c.c. absolute alcohol, and the mixture immediately made up to 50 c.c. After shaking up thoroughly, the solution was immediately filtered through a dry filter into a dry 50 c.c. bottle containing a few c.c. of benzine. The thus prepared solutions were then immediately compared under the colorimeter against a set of standard pure potassium dichromate solutions. All concentrations have been expressed in gm. per 100 c.c. solution.

TABLE V.

Effect of Na₂CO₃ Treatment on Polysulphide Concentration.

Conc. polysulphide used as CaS _{4.6}	Colorimeter setting.	Concentration of K ₂ Cr ₂ O ₇ standard.	Colorimeter reading (average).	K ₂ Cr ₂ O ₇ corresponding to polysulphide used.
0.14	20	0.03	40.2	0.06
0.14	20	0.06	17.0	0.05
0.29	20	0.06	31.0	0.09
0.29	20	0.09	22.0	0.10
0.44	20	0.09	37.0	0.17
0.44	20	0.12	26.0	0.16
0.57	20	0.12	39.0	0.23
0.57	20	0.18	28.0	0.25
0.72	20	0.18	36.5	0.33
0.72	20	0.24	30.0	0.36
1.00	20	0.24	41.0	0.49
1.00	20	0.30	36.0	0.54
1.15	20	0.30	38.5	0.58
1.15	20	0.42	33.5	0.70
1.44	20	0.42	42.5	0.89
1.44	20	0.54	33.0	0.89

Table V. thus gives the colorimetric relationship between polysulphide concentration and the corresponding potassium dichromate concentration over a range of polysulphide concentrations of 0.10 to 1.44 gm. sulphur per 100 c.c. solution.

Using this relationship, and treating a number of lime-sulphur dips obtained from the field in a similar manner, it was found that the polysulphide concentration of all the dips studied could be determined with a fair amount of accuracy. For this purpose 25 c.c. of the dip sample as received was pipetted into a 50 c.c. measuring flask containing 10 c.c. of 9 per cent. sodium carbonate and 5 c.c. absolute alcohol, the mixture made up to volume, shaken up, and immediately filtered through a dry filter into a dry bottle containing a few cubic centimeters of benzine. By thus decreasing the chances of oxidation to a minimum, a perfectly clear filtrate was obtained in every case. If, during the process of filtering, the filtrate is not

protected against the atmospheric oxygen, it often soon becomes turbid due to the formation of elementary sulphur. Laboratory experience has shown that polysulphide solutions, adulterated by the process of dipping, display a much greater sensitivity towards atmospheric oxygen than pure polysulphide solutions.

In the following table—Table VI—the colorimetric analyses obtained as above have been compared with the actual analyses obtained with the volumetric cadmium acetate method.

TABLE VI.
Colorimetric Analyses of Field Dips.

Dip.	K ₂ Cr ₂ O ₇ standard used (gm./100 c.c.).	Polysulphide found colorimetrically (gm. S/100 c.c.).	Polysulphide actually present (gm. S/100 c.c.).	x (in CaSx).	
Undipped Washes.	1.....	0.06	0.23	0.24	—
	2.....	0.12	0.40	0.46	5.25
	3.....	0.12	0.42	0.45	4.6
	4.....	0.24	0.44	0.44	4.2
	5.....	0.12	0.44	0.47	5.0
	6.....	0.12	0.44	0.52	5.2
	7.....	0.24	0.49	0.47	4.5
	8.....	0.24	0.50	0.46	4.4
	9.....	0.24	0.50	0.54	4.9
	10.....	0.42	0.62	0.50	4.2
	11.....	0.24	0.66	0.59	4.4
	12.....	0.24	0.66	0.76	4.6
	13.....	0.24	0.73	0.86	4.8
	14.....	0.42	1.01	1.15	4.4
Dipped Washes.	15.....	0.12	0.23	0.22	1.9
	16.....	0.12	0.42	0.42	4.0
	17.....	0.24	0.45	0.39	4.4
	18.....	0.24	0.56	0.56	3.9
	19.....	0.42	0.61	0.55	2.8
	20.....	0.24	0.61	0.61	3.5
	21.....	0.24	0.68	0.72	3.9
	22.....	0.24	0.69	0.72	4.6
	23.....	0.42	0.77	0.68	3.9
	24.....	0.24	0.77	0.85	4.5
	25.....	0.24	0.82	0.83	4.0

The results show that for all purposes of field control the colorimetric method as here described gives quite satisfactory results. The accuracy of the method would seem to be influenced neither by the process of dipping nor by the atomic ratio of metal to sulphur in the dipwash analysed. If this finding can be substantiated on a still wider range of dip samples the main difficulty in the rapid analysis of lime-sulphur dip-washes has been overcome, although at this stage we are not in a position to give a full explanation of the observations made, since the true nature of lime-sulphur solutions, their behaviour on oxidation, etc., are all questions awaiting further intensive research. However, the possible adaptation of this colorimetric principle as a basis for evolving a simple field method of control is sufficiently promising to warrant its further study.

SUMMARY.

As a continuation of the preliminary study of the colorimetric method as a rapid means of control of polysulphide solutions, the effect of free alkali on sodium polysulphide solutions at room temperature was studied, since in the process of dipping the washing-out of the suint of the fleece results in the interaction of dipwash with alkali and in the formation of alkali polysulphides. It was found that the chemical interaction, as revealed by ordinary chemical analysis, is slight, though the colorimetric study reveals a marked change in chemical nature. This change was ascribed, either to the formation of a complex compound between the alkali and the polysulphide, or to the existence of different isomers of the polysulphides in solution. The observation that field samples of lime-sulphur cannot be directly compared colorimetrically is thus partially explained.

It was further shown that the addition of excess sodium carbonate and alcohol causes immediate precipitation of all turbidity-forming materials, rendering a perfectly clear solution of the alkali polysulphides which can be matched against a potassium dichromate standard. In this way fairly accurate values were obtained with both used and unused lime-sulphur dip washes. It is proposed to apply this colorimetric principle for evolving a simple field method of control.

REFERENCES.

- GRAF, H., AND JORDEN, T. J. WILKEN (1932). General Introduction. Lime-Sulphur Dips. *18th Rept. Dir. Vety. Serv. and Anim. Indust.* Paper A.I, p. 1005.
- GREEN, H. H. (1915). Upon composition and analyses of polysulphide solutions. *3rd and 4th Rept. Dir. Vety. Res.*, p. 192.
- JORDEN, T. J. WILKEN (1932). A preliminary study of a colorimetric analysis. *18th Rept. Dir. Vety. Serv. and Anim. Indust.* Paper A.II, p. 1015.
- JORDEN, T. J. WILKEN (1932). A Preliminary study of a colorimetric method as a rapid means of control of polysulphide solutions. *18th Rept. Dir. Vety. Serv. and Anim. Industr.*, p. 1029.