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# Dyeing Wool with Metal-free Dyes – The Use of Sodium Borohydride for the Application of Vat Dyes to Wool

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## 1. Introduction

Vat dyestuffs are pigments that must be pre-treated with a reducing agent, such as sodium hydrosulphite, to make them water-soluble immediately before they are used for dyeing (Latham, 1995; Trotman, 1984). The reduction step converts the pigment form into a leuco compound. This owes its name to the Greek word for colourless, because many vat dyes are very pale in colour when in the reduced state, due to the lower level of conjugation of double bonds. A schematic of this reaction for the dyestuff Vat Red 1 is shown in Figure 1.

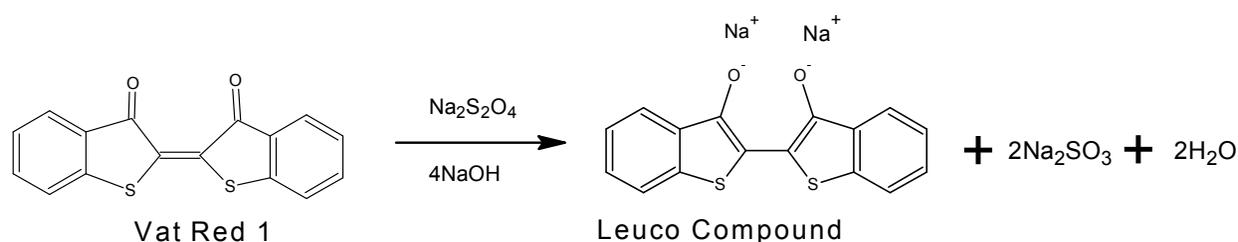


Fig. 1. Structure of Vat Red 1 and formation of the sodium salt of the leuco compound.

In strongly alkaline conditions, the leuco forms of vat dyestuffs are anionic and soluble in water. They can be exhausted onto cotton from long liquors under alkaline conditions in the presence of an electrolyte, such as sodium chloride or sodium sulphate (Latham, 1995; Trotman, 1984). After adsorption by the substrate, the leuco form of the dye is oxidised back to the insoluble coloured pigment inside the fibre. This can be done by exposure to air, or with an oxidising agent such as hydrogen peroxide. Wool is usually dyed with anionic dyestuffs from acidic dyebaths, where the amphoteric wool fibres are positively charged as a result of protonation of amino and carboxyl groups. Under alkaline conditions, however, fewer amino groups are protonated and, depending on the pH, the net charge on the fibres may be neutral or even negative. The effect of this is that conventional acid, premetallised and reactive wool dyes have a lower substantivity for wool under alkaline conditions than under acidic conditions. In contrast to this behaviour, however, even under strongly alkaline conditions, the anionic leuco form of a vat dyestuff has a relatively high substantivity for wool (Bird, 1947; Hug, 1948; Luttringhaus, Flint & Arcus, 1950; Weber, 1951) and wool/cotton blends (Lemin & Collins, 1959). This results in high levels of dyebath exhaustion at pH values as high as pH 9 and above.

Vat dyes are amongst the oldest colouring materials used for textiles, and for many years selected vat dyes were used on both cotton and wool for products requiring very high levels of wet fastness and light fastness. Vat dyes are still used on cotton, where the highly alkaline conditions employed in their application do not damage the fibre. In the case of wool, however, the propensity for alkaline damage during dyeing makes their use less attractive. This resulted in them being replaced by chrome and premetallised dyes, which also give high levels of fastness. Furthermore, chrome and premetallised dyes are applied under pH conditions where fibre damage is less likely to occur. The more recent introduction of reactive dyes for wool also enables excellent wet fastness properties to be achieved with little fibre damage.

Pressure from environmental lobby groups and some major retailers has raised the possibility that wool products that are coloured with metal-containing dyestuffs may become increasingly unacceptable because of concerns about the possible effects of heavy metals on the environment. Although metal-free reactive dyes can be used on wool to give products with high wet fastness, with some shades lightfastness can be a problem. Furthermore, heavy black and navy shades are difficult for many mills to achieve with reactive dyes. This paper investigates the feasibility of using vat dyes as alternatives to reactive dyes to obtain shades with high fastness properties on wool.

The traditional method of preparing the leuco form of a vat dye employs the reducing agent sodium dithionite (sodium hydrosulphite;  $\text{Na}_2\text{S}_2\text{O}_4$ ) and sodium hydroxide. Sodium hydrosulphite has a sufficiently negative reduction potential for it to effectively reduce all vat dyes. Other reducing agents have also been used, but these have not found wide acceptance. Sodium borohydride has been evaluated but, on its own, reacts too slowly with vat dyes for practical usage (Latham, 1995). It has been claimed, however, to improve the stability against atmospheric oxidation of vat dyes reduced with sodium hydrosulphite (Neale, 1961; Harrison & Hinckley, 1963; Medding, 1980; Vivilecchia, 1966), but other workers have disputed this claim (Baumgarte & Keuser, 1966; Nair & Shah, 1970).

A technique has recently been developed for producing sodium hydrosulphite in situ by mixing sodium borohydride and sodium bisulphite (Rohm and Haas Technical Information, 2007) (Figure 2).

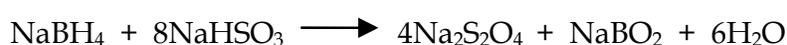


Fig. 2. Reaction between sodium borohydride and sodium bisulphite

Sodium borohydride is supplied commercially as an aqueous solution containing sodium borohydride (12%), stabilised with sodium hydroxide (NaOH). It has been found that a mixture of sodium bisulphite and the sodium borohydride solution in the ratio 4:1 is suitable for the application of indigo to cotton under alkaline conditions (Rohm and Haas Technical Information, 2007; Schoots, 2007). Hydrosulphite produced in this way is claimed to be virtually free of the by-products that result from its decomposition during storage (Rohm and Haas Technical Information, 2007). Furthermore, this reducing system has been found to be more efficient than hydrosulphite alone and it has been claimed to give a dyestuff saving of around 15% in the application of indigo to cotton warps (Schoots, 2007). A borohydride/bisulphite mixture has also been found to be very effective for the reductive bleaching of wool under acid to neutral conditions (Technical Manual, Australian Wool Innovation, 2010; Schoots & Stevens, 2007).

Based on the findings on cotton, it was considered that this reducing system may provide the basis of a new method of dyeing wool with vat dyes. This study describes an evaluation

in which results obtained with a borohydride/bisulphite reducing system are compared with those obtained with a method based on the application of vat dyes using the traditional method with sodium hydrosulphite.

## 2. Experimental

### 2.1 Fabric

A 100% wool, plain weave fabric (weight 193 g/m<sup>2</sup>) was used in this study.

### 2.2 Dyes and chemicals

Commercial samples of the following nine vat dyes were used:

- Vat Red 1
- Vat Red 10
- Vat Red 45
- Vat Green 1
- Vat Green 3
- Vat Yellow 5
- Vat Orange 5
- Vat Violet 18
- Vat Brown 24

A commercial sample of sodium borohydride (SBH) was supplied by Rohm and Haas as a 12% solution in sodium hydroxide. Other chemicals were of laboratory grade.

The following dispersing agents were used:

- Kieralon DB (nonionic/anionic mixture; Dyechem);
- Albigen A (solution of polyvinylpyrrolidone; BASF);
- polyvinylpyrrolidone (Mol Wt 44000; BDH Chemicals);
- Detergent NA-B (blend of anionic and nonionic surfactants: APS/Nuplex).

### 2.3 Equipment

Two types of laboratory machines with different methods of liquor circulation were used to dye samples of wool fabric. The details are described below.

*Ahiba Turbomat.*

Fabric samples were wound onto perforated spindles. The dyebaths were circulated by pumping the liquor through the fabric tube (in to out).

*Mathis Labomat*

With this machine, the fabric samples and dye liquors were sealed inside pots. Circulation was achieved by tumbling the pots inside a heated box. This resulted in both fabric and liquor moving together. As the pots were not completely filled with liquor, the air in the pot was mixed with the liquor.

### 2.4 Preparation of the dye vat by reduction

The vat pigments were converted to the water-soluble leuco form by the following methods.

#### 2.4.1 Hydrosulphite method

The various amounts of sodium hydrosulphite and sodium hydroxide were dissolved in 250 mL of water at room temperature and the solution stirred while the powdered vat dye was slowly added. Stirring was continued while the mixture was heated at 2°C /min to the vating temperature (usually 60-70°C), where it was maintained for 30 minutes.

### 2.4.2 Sodium borohydride/bisulphite method

Sodium bisulphite was dissolved in 250mL of water at room temperature, followed by the addition of the aqueous solution of sodium borohydride (SBH) diluted with ten times its volume of water. After 2 minutes, an aqueous solution of sodium hydroxide (320 g/L or 38°Bé) was added and the mixture stirred until the effervescence had ceased (usually 5-10 minutes). Stirring was continued while the vat dye was added slowly and also while the mixture was heated at 2°C/min to the vatting temperature, where it was maintained for 30 minutes.

### 2.5 Fabric dyeing

After diluting to the required volume, the vatted liquor was added to the dyeing pot containing the fabric. The liquor ratio was 20:1. The liquor was heated at 1.5°C per minute to the required temperature (usually 60°C or 70°C), where it was held for 30 minutes. The fabric was overflow rinsed (cold) for one minute, followed by two five minute rinses at 40°C. Oxidation of the leuco compound to the vat pigment was carried out by treatment with hydrogen peroxide (1g/L) for 10 minutes at 50°C. The fabric was then soaped off (the normal procedure with vat dyes (Latham, 1995; Trotman, 1984; Bird, 1947)) with Detergent NA-B (2g/L), adjusted to pH 9.5 with ammonium hydroxide, for 20 minutes at 98°C. After cooling, the fabric was rinsed and removed from the dyeing machine. It was then rinsed, with hand stirring, for 5 minutes in a beaker containing a solution of Detergent NA-B (1 g/L) at 50°C (liquor ratio 50:1). This treatment was considered to simulate the process of washing-off a fabric in a scouring machine or back-washing wool top after dyeing. It was noted that the gentle mechanical action involved in this step removed a small amount of oxidised, insoluble pigment from between the fibres and yarns in the fabric.

### 2.6 Measurements

Dyebath exhaustion levels were determined by measuring the absorbance of the dyebath on a Jasco V530 UV-Vis Spectrophotometer at the wavelength of maximum absorbance of the dye. Colour yields were determined by measuring the K/S values of the dyed samples on a Datacolor Texflash Spectrophotometer at the wavelength of maximum reflectance of the dye.

Dry and wet rubbing fastness was assessed by *IWS Test Method 165 – Fastness to Rubbing*.

Alkaline perspiration was assessed by *ISO-105-EO4 – Fastness to Perspiration*.

Washing fastness was assessed by *ISO-105-CO2 – Colour Fastness to Washing*.

Grey scale staining and colour changes were measured on a Datacolor Texflash Spectrophotometer. The software supplied with the instrument (Datacolor Iris Version 2.3) enabled ratings to be quoted to 0.1 of a greyscale unit.

Wet burst strength was measured according to *Australian Standard AS2001.2.4A-90, Determination of Burst Pressure of Textile Fabrics, Hydraulic Diaphragm Method* (which is equivalent to ASTM D3787-01 but also includes procedures for wet testing).

## 3. Results and discussion

### 3.1 Determination of optimum concentration of SBH/bisulphite

Important requirements for a satisfactory vat dyeing are:

- i. complete reduction of the dye to the leuco compound during vatting;
- ii. prevention of premature oxidation of the leuco compound;
- iii. maintaining the leuco compound in a soluble form during the dye exhaustion phase.

A conventional vat dyeing system uses a mixture of sodium hydrosulphite and sodium hydroxide to reduce the dyestuff to its leuco compound. It has been estimated that the stoichiometric relationship between sodium hydrosulphite and SBH is that 1g/L hydrosulphite is equivalent to 0.44 g/L of solid SBH (Rohm and Haas Technical Information, 2007). This, however, provides only an approximate guide to the amount of SBH required for vat dyeing, as the dye manufactures' pattern cards contain only general information on the amount of hydrosulphite required (Weber, 1951).

Reagent/Conditions	A	B	C	D
SBH solution (12%) (g/L)	1	2	4	5
Sodium Bisulphite (g/L)	4	8	16	20
NaOH solution (38° Bé) (ml/L)	3	6	12	15
Vatting conditions	30 min at 60°C			
Colour of vat	Purple	Purple	Purple	Purple
pH after fabric added (40°C)	11.4	11.4	11.5	11.5
Dyebath pH at end of dyeing	8.8	8.8	9.5	10.2
Colour of dyebath after 30 min at 60°C	Purple	Purple	Purple	Purple
Absorbance of dye liquor after 30 min at 60°C	0.15	0.16	0.27	0.36
pH of oxidation liquor	9.5	9.2	9.9	9.9
Final soap off pH	9.9	9.9	9.9	9.9

Table 1. Effect of Concentration of Sodium Borohydride and Sodium Bisulphite in the Application of Vat Red 45 (1% oww) to Wool (Dyed in the Turbomat for 30 mins at 60°C)

The optimum concentrations of SBH, sodium bisulphite and sodium hydroxide required to produce a satisfactory dyeing were, therefore, determined experimentally. A ratio of sodium bisulphite to SBS solution of 4:1 was used because, as discussed previously, this has been found to be suitable for the application of indigo to cotton. Table 1 shows the various concentrations of SBH, sodium bisulphite and sodium hydroxide used to reduce the dye Vat Red 45 to its leuco compound prior to exhaustion onto wool. The samples were soaped off after dyeing with 2g/L Detergent NA-B at pH 9.5 (obtained with ammonium hydroxide) for 20 min at 98°C. Although all the formulations reduced the dye to its purple, soluble leuco form, the three mixtures containing the highest concentrations of reagents gave solutions that were more stable than the one containing the least amounts of the chemicals. The stability was judged by observing the formation of partially oxidised (green) pigment on the liquor surface, after stirring had been stopped. The fully oxidised pigment was red in colour. Other experiments with the lowest concentration of chemicals (i.e. 1 g/L SBH and 4 g/L sodium bisulphite) showed some variability in the reproducibility of the vatting process, in particular with respect to the sensitivity to stirring rate. Furthermore, with liquors vatted with 1g/L SBH and 4 g/L sodium bisulphite, there was a tendency for slight oxidation to occur during the dyeing cycle.

Table 2 shows data for colour yield (K/S) and fastness to dry and wet rubbing. There was no significant difference in rubbing fastness between any of the samples (rubbing fastness gives an indication of the amount of oxidised dye remaining on the fibre surface). There was also no significant difference between the K/S values obtained with the two lowest concentrations of SBH and bisulphite. However, the K/S values decreased with increasing concentration of chemicals above these levels. This was possibly caused by destruction of the chromophore by over-reduction of the dye. The highest colour yield consistent with

good stability of the vatted liquor was obtained with a concentration of 2g/L SBH and 8g/L sodium bisulphite.

Conc. SBH (12%) (g/L)	Conc. Sodium. Bisulphite (g/L)	Final Dyebath pH	K/S Value at 520 nm	Rubbing Fastness	
				Dry	Wet
1	4	8.8	6.6	4.7	4.3
2	8	8.8	6.5	4.6	4.6
4	16	9.5	5.2	4.6	4.3
5	20	10.2	4.1	4.5	4.8

Table 2. Colour Yield (K/S Values) and Rubbing Fastness of Wool Fabrics Dyed with Vat Red 45 (1% oww) by the Sodium Borohydride/Bisulphite Method

The combination of 8 g/L sodium bisulphite and 2 g/L SBH, found to be the optimum amounts to effectively reduce Vat Red 45, was used with the dyestuff Vat Green 1. The data in Table 3 show that the blue leuco form of the dye was maintained until the end of the exhaustion phase. This confirmed that these concentrations of SBH and bisulphite were also satisfactory for this dyestuff.

Conc. Dispersing Agent NA-B (g/L)	Dyeing Temp (°C)	Vat Colour	Dyebath pH with Fabric (40°C)	Final Dyebath pH	Final Dyebath Colour	Absorbance of final dyebath	K/S at 640 nm
None	60	Blue	11.0	9.5	Blue	0.68	11.0
None	60	Blue	10.8	9.1	Blue	0.21	6.0
None	70	Blue	10.7	9.1	Blue	0.18	7.8
None	80	Blue	11.0	9.0	Blue	0.21	4.8
None	90	Blue	10.9	9.1	Blue	0.08	4.0
0.25	70	Blue	11.2	8.6	Blue	0.70	10.9
0.25	70	Blue	11.0	11.6	Blue	1.66	10.9

Vatted with : 2 g/L SBH; 8 g/L sodium bisulphite; 6 ml/L caustic soda (38°Bé).  
The dyebaths contained sodium sulphate (5% oww).  
The samples were soaped off for 20 min at 100°C with 2g/L Detergent NA-B at pH 9.5.

Table 3. Vat Dyeing with Vat Green 1 (1% oww) by the SBH Method (Dyed for 30 mins in the Turbomat at various temperatures)

Table 3 shows, however, that in contrast to the result obtained with Vat Red 45, the colour yield for Vat Green 1 was dependent on the final dyebath pH, with the highest value obtained when the pH was greater than 9.5. Diffusion into the fibre did not appear to be a factor, as increasing the dyebath temperature above 60°C did not improve the colour yield. It is also unlikely that this effect was due to premature oxidation of the dyebath, because all the liquors remained blue (indicative of the reduced leuco form) throughout the whole exhaustion stage. Furthermore, the poor colour yields cannot be explained by lower levels of dyebath exhaustion, because the absorbance values in Table 3 show that the samples with the lower colour yields had higher dyebath exhaustions. A possible explanation is that the aggregation state of the leuco compound is an important factor; and that with some dyes

this is very sensitive to pH within the range used in these experiments (in this study we tried to minimise alkaline damage to the wool by keeping the pH as low as possible). In order to test this hypothesis, fabric samples were dyed with Vat Green 1 in the presence of a dispersing agent. Detergent NA-B was used because it was considered that this compound would be an effective dispersing agent for vat dyes as it is recommended for soaping off vat-dyed cotton after oxidation. Table 3 shows that in the presence of 0.25 g/L of Detergent NA-B, a high colour yield was obtained, even when the pH of the dyebath had dropped to pH 8.6 at the end of the dyeing cycle. The results also show that, with a dispersing agent in the dyebath, maintaining the pH to a high value (pH 11.6) by alkali addition had little effect on colour yield. Following these results, the effect of Detergent NA-B and other dispersing agents was examined further.

### 3.2 Effect of dispersing agent in the dyebath

Table 4 shows the effect of various dispersing agents added to the dyebath on the colour yield of Vat Green 1. Polyvinylpyrrolidone (PVP) was included in the evaluation because it is the main constituent of the commercial product Albigen A. The results from Table 3 for two samples dyed without a dispersing agent are included for comparison purposes.

Dispersing agent (g/L)	Initial Dyebath pH	Dyeing Temp.	Sodium Sulphate in dyebath (% oww)	Final Dyebath Colour	Absorbance at 552 nm	Final Dyebath pH	K/S (at 640 nm)
None	11.0	60	5	Blue	0.68	9.5	11.0
None	10.8	60	5	Blue	0.21	9.1	6.0
0.05 A	11.1	70	0	Blue/Green	0.82	9.0	12.3
0.1 A	11.0	70	0	Blue/Green	1.29	8.9	11.2
0.1 A	11.1	70	5	Blue	0.88	8.7	10.1
0.2 A	11.0	70	0	Blue/Green	1.72	8.9	9.7
0.25 A	11.0	70	0	Blue/Green	1.67	8.9	10.3
0.5 A	11.0	70	0	Blue/Green	3.11	8.8	8.3
0.05 PVP	11.1	70	0	Blue	1.40	8.7	10.6
0.1 PVP	11.1	70	0	Blue	2.24	8.6	10.0
0.1 PVP	11.2	70	5	Blue	2.25	8.7	9.5
0.15 PVP	11.0	70	0	Blue	2.73	8.5	8.3
0.20 PVP	11.0	70	0	Blue	3.30	8.4	7.1
0.25 NA-B	11.0	70	0	Blue/Green	0.96	8.9	13.2
0.25 NA-B	11.2	70	5	Blue	0.70	8.6	10.9
0.5 NA-B	11.5	70	0	Blue	1.05	9.1	10.7
1.0 NA-B	11.5	70	0	Blue	0.53	9.2	6.1
0.25 KDB	11.0	70	0	Blue/Green	0.53	8.9	8.6
0.5 KDB	11.6	70	0	Blue	1.51	9.4	8.6
0.5 KDB	11.1	70	5	Blue	0.68	8.7	7.1
1.0 KDB	11.5	70	0	Blue	3.16	9.2	7.1

(Dyed for 30 mins in the Turbomat at various temperatures).

A is Albigen A; KDB is Kieralon DB; NA-B is Detergent NA-B; PVP is polyvinyl pyrrolidone.

Table 4. Effect of Various Dispersing Agents Added to the Dyebath (1% oww Vat Green 1)

Of the four dispersing agents tested, Kieralon DB gave the worst results and was not investigated further. The other three products gave similar results. For these, only a very small concentration of dispersing agent was required in order to counteract the adverse effect of a low final dyebath pH. High concentrations of dispersing agent tended to reduce the colour yields. The optimum concentrations of Albigen A and PVP were 0.05 g/L, whereas for Detergent NA-B, the highest colour yields were obtained with 0.25g/L.

For all the dispersing agents studied, addition of sodium sulphate (5% oww) to the dyebath slightly decreased the colour yield. It appears, therefore, that with the SBH reducing system, there is a marked benefit with some vat dyes in using a small concentration of dispersing agent in the dyebath, in order to avoid the necessity of maintaining a high liquor pH throughout the dyeing cycle. The pH always dropped to some extent when the dyebath, set with the vatted dye, contacted the wool fabric. It was observed that the amount the pH changed varied from dye to dye. Although the reason for this variability is not known, it is possible that the finishing agents used in the formulation of the dyes give a buffering effect, in some cases. It was found that not all vat dyes showed this pH sensitivity when applied to wool. However, in order to offset any adverse effects caused by unpredictable pH changes, a dispersing agent was added to all dye liquors, as a standard part of setting the dyebath.

### **3.3 Application of vat dyes to wool by the conventional sodium hydrosulphite/sodium hydroxide method**

In order to compare the SBH/bisulphite method with the conventional vat dyeing procedure, a series of fabric samples were dyed with either Vat Red 45 or Vat Green 1 (1% oww), following reduction to the respective leuco compound with sodium hydrosulphite and sodium hydroxide. As the dyestuff manufacturers' pattern cards give only very general information on the amounts of sodium hydrosulphite and sodium hydroxide required for effective reduction, the dyes were vatted by the method described in Section 2.2.1 with the two concentrations of the chemicals shown in Table 5. All the dye liquors contained sodium sulphate (5% oww), in accordance with normal practice on wool. Two sets of fabric samples were dyed with each formulation: one without a dispersing agent and one containing 0.25g/L Detergent NA-B. All the samples were soaped off in a similar manner with Detergent NA-B and ammonia.

It can be seen from Table 5 that all the concentrations of sodium hydrosulphite and NaOH reduced Vat Red 45 to the purple leuco compound. However, although the two dyebaths set with the lower concentrations of these chemicals remained purple up to the end of the exhaustion phase, the fabrics changed to a pink/purple during the dyeing cycle. This showed that some oxidation of the leuco compound to the pigment form of the dye had occurred during dye exhaustion, which indicates that insufficient hydrosulphite had been used. The results show that the most stable system regarding resistance to premature oxidation was the one containing 5 g/L hydrosulphite and 12 ml/L of the sodium hydroxide solution. This was considered to be the optimum concentrations of these chemicals for Vat Red 45, because in this case the dye was not oxidised until after the end of the exhaustion/fibre penetration phase of the dyeing cycle. These concentrations are very similar to those recommended for the application of vat dyes to wool/cotton blends (Lemin & Collins, 1959).

Reagent/Conditions	A	B	C	D
Sodium hydrosulphite (g/L)	3	3	5	5
Sodium hydroxide solution (38°Bé) (ml/L)	7	7	12	12
pH of vat	12.2	12.2	12.3	12.3
Colour of vat	Purple	Purple	Purple	Purple
Dispersing agent (Detergent NA-B) (g/L)	0.25	nil	0.25	nil
pH after fabric added (40°C)	11.8	11.8	11.9	11.9
pH after 30 min at 60°C	11.3	11.2	11.5	11.5
Colour of fabric after 30 min at 60°C	Pink/Purple	Pink/Purple	Purple	Purple
Colour of liquor after 30 min at 60°C	Purple	Purple	Purple	Purple
Absorbance of final dyebath at 548 nm	1.08	0.88	0.43	0.71
Water rinse pH	11.0	11.0	11.1	11.2
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	10.0	9.9	10.0	10.0

Table 5. Vat Dyeing with Vat Red 45 (1% oww) by the Conventional Hydrosulphite/NaOH Method (Dyed in Turbomat 30 mins at 60°C)

Table 6 shows K/S and rubbing fastness data for samples dyed with Vat Red 45 and various concentrations of hydrosulphite and sodium hydroxide. The best results were obtained with the highest concentrations of chemicals (5g/L hydrosulphite and 12 ml/L NaOH solution) without a dispersing agent. Table 6 also shows that when Vat Red 45 was applied to wool by the optimised SBH method, the colour yield and rubbing fastness were superior to the values obtained by the conventional hydrosulphite procedure. Another advantage of the SBH method was the lower pH of the dye liquors at the end of the dyeing cycle (pH 8.5 - 9.0 compared with pH 11.5 for the hydrosulphite/NaOH method). This would be expected to result in a lower level of fibre damage, as discussed later.

Conc. Sodium Hydrosulphite (g/L)	Conc. NaOH (ml/L of 38°Bé)	Dispersing Agent (Detergent NA-B) (g/L)	Final pH of Dyebath	K/S Value at 520 nm	Rubbing Fastness	
					Dry	Wet
3	7	Nil	11.3	3.4	4.4	4.3
3	7	0.25	11.2	4.0	4.4	4.3
5	12	Nil	11.5	4.3	4.3	4.1
5	12	0.25	11.5	3.9	4.4	3.7
Dyed with 2g/L SBH; 8 g/L Bisulphite; 6 ml/L 38°Bé NaOH		0.25	9.5	6.5	4.6	4.6

Table 6. Comparison of Colour Yield (K/S Values) and Rubbing Fastness of Samples Dyed with Vat Red 45 (1% oww) by the Hydrosulphite/NaOH and SBH Methods at 60°C (Dyed for 30 mins in the Turbomat)

The results obtained when Vat Green 1 was applied by the conventional hydrosulphite/NaOH method are shown in Tables 7 and 8.

Reagent/Conditions	A	B	C	D
Sodium Hydrosulphite (g/L)	3	3	5	5
NaOH (38°Bé) (ml/L)	7	7	12	12
pH of vat	11.9	11.9	12.0	12.0
Colour of vat	Blue	Blue	Blue	Blue
Dispersing agent (Detergent NA-B) (g/L)	0.25	Nil	0.25	Nil
pH After fabric added (40°C)	11.4	11.4	11.5	11.5
Final dyebath pH	11.0	11.0	11.5	11.5
Colour of fabric after 30 min at 70°C	Green	Green	Blue	Blue/Green
Colour of liquor at after 30 min at 70°C	Green	Green	Blue	Green
Absorbance of final dyebath at 558 nm	1.09	0.63	2.87	1.16
Water rinse pH	10.5	10.6	10.8	10.9
pH of Oxidation	9.5	9.2	9.9	9.9
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	9.9			

Table 7. Vat Dyeing with Vat Green 1 (1% oww) by the Hydrosulphite Method (Dyed for 30 mins in the Turbomat at 70°C)

Conc. Sodium Hydrosulphite (g/L)	Conc. NaOH (ml/L of 38°Bé)	Dispersing Agent (Detergent NA-B) (g/L)	Final pH of Dyebath	K/S Value at 640 nm	Rubbing Fastness	
					Dry	Wet
3	7	Nil	11.0	7.9	4.4	3.4
3	7	0.25	11.0	5.1	3.8	2.6
5	12	Nil	11.5	7.5	4.2	3.2
5	12	0.25	11.5	9.8	4.4	3.5
Dyed with 2g/L SBH; 8 g/L / Bisulphite; 6 ml/L 38°Bé NaOH		0.25	8.6	11.3	4.6	3.8

Table 8. Comparison of Colour Yield (K/S Values) and Rubbing Fastness of Samples Dyed with Vat Green 1 (1% oww) by the Hydrosulphite and SBH Methods at 70°C (Dyed for 30 mins in the Turbomat)

Table 7 shows that all the concentrations of hydrosulphite and NaOH reduced Vat Green 1 to the blue leuco compound. However, as discussed above for Vat Red 45, the dyebaths set with the two lowest concentrations of these chemicals were oxidised to some extent during the

exhaustion phase of the dyeing cycle. This again indicated that insufficient hydrosulphite had been used. The results show that the most stable system regarding resistance to premature oxidation was again the one containing 5 g/L hydrosulphite and 12 ml/L NaOH. In contrast to the finding for Vat Red 45, in this case, the addition of a dispersing agent produced better results for colour yield and rubbing fastness (Table 8). This is similar to the finding for this dye applied with SBH/bisulphite.

Table 8 compares results for Vat Green 1 applied by the hydrosulphite/NaOH method with results obtained by the optimised SBH method. Thus, as found for Vat Red 45, the SBH method gave a much better colour yield and slightly better rubbing fastness than the conventional procedure using hydrosulphite and NaOH. Again, it should be noted that the final liquor pH of the SBH dyebath was significantly less than for the hydrosulphite/NaOH system.

### 3.4 Effect of using a buffered dyebath

Results discussed above show that with some dyes (e.g. Vat Green 1) the colour yield can be adversely affected if the pH of the dyebath falls below a certain value during the exhaustion stage. Despite this effect being decreased by addition of a selected dispersing agent to the dyebath, it was considered that the reproducibility/robustness of the system would be improved by buffering the pH of the dyebath. After examining possible alternatives, trisodium phosphate was selected for further study. This compound has been claimed to produce less fibre damage than other alkalis (Bird, 1947). Table 9 shows the colour yields and rubbing fastness results obtained by adding three concentrations of trisodium phosphate to the dyebath. A concentration of 2g/L trisodium phosphate maintained the pH slightly above pH 9.5 and gave the best colour yield. This amount of trisodium phosphate was used in all further dyeings.

Reagent/Conditions	A	B	C	D
pH of vat	11.9	11.9	11.9	11.9
Colour of vat	Blue	Blue	Blue	Blue
Conc. trisodium phosphate in dyebath (g/L)	1	2	3	4
pH After fabric added (40°C)	11.2	11.2	11.2	11.2
pH after 30 min at 60°C	9.6	9.7	10.1	10.3
Colour of liquor after 30 min at 60°C	Blue	Blue	Blue	Blue
Absorbance of final dyebath at 620 nm	1.5	1.6	2.2	2.4
Water rinse pH	10.5	10.5	10.6	10.7
Soap off	2g/L Detergent NA-B pH 9.5 ammonia 20 mins at 100°C			
Final soap off pH	9.5	9.5	9.4	9.5
K/S at 640 nm	8.8	11.3	9.4	10.2
Dry Rubbing	4.5	4.6	4.5	4.5
Wet Rubbing	4.0	3.8	4.0	3.8

Table 9. Effect of Buffering the Dyebath with Trisodium Phosphate on the Colour Yield and Rubbing Fastness of Vat Green 1 (1% oww) Applied to Wool by the SBH Method (2g/L SBH; 8g/L sodium bisulphite; 6 ml/L of 38° Bé NaOH) (Dyed in Turbomat for 30 min at 60°C; 0.05 g/L Albigen A added to dyebath)

### 3.5 Optimisation of dye fastness

When cotton is dyed with vat dyes, the dyed samples are soaped off to remove oxidised pigment from the fibre surface and to aggregate the pigment particles inside the fibre. Both these effects improve overall fastness properties (Latham, 1995; Trotman, 1984; Bird, 1947; McNeil et al, 2005). It was observed during the early part of this work that some loose pigment remained on the fabric surface, even after wool fabrics had been soaped off for 20 minutes at 98°C. It was also found that this had an adverse effect on fastness properties. Unlike normal wool dyes, vat pigments are insoluble in water after they have been oxidised. It is suggested that a dyeing machine such as the Turbomat is not very effective in removing surface pigment, because its circulation action, which involves pumping liquor through the fabric, will tend to filter any pigment particles removed in the wash off. Washing-off in equipment such as a scouring machine would be expected to be more effective in removing pigment particles trapped within the yarns. In the present study, in order to produce dyed fabrics with optimum fastness properties, after soaping-off in the dyeing machine, all fabrics were rinsed with hand stirring in a beaker containing 1 g/L Detergent NA-B, as described in Section 2. This treatment was considered to provide a laboratory simulation of fabric scouring for piece goods, or backwashing in the case of wool that had been top dyed. Such a treatment should be part of any procedure for applying vat dyes to wool by the new SBH method.

Vat Dye (Colour Index Number)	Method	K/S	Washing Fastness				Rubbing Fastness		Alkaline Perspiration Fastness			
			SC	W	C	N	Dry	Wet	SC	W	C	N
Red 1	Hydrosulphite	5.3	3.7	5.0	4.8	4.9	4.2	3.4	All Rated 5	en		
	SBH	5.7	4.4	5.0	4.7	4.8	4.6	3.9				
Red 10	Hydrosulphite	4.5	4.2	4.9	4.7	4.8	4.3	3.5				
	SBH	5.5	4.3	4.9	4.7	4.7	4.5	4.0				
Red 45	Hydrosulphite	3.9	4.7	4.9	4.7	3.3	4.4	3.7				
	SBH	6.5	4.8	4.9	4.6	3.8	4.6	4.6				
Green 1	Hydrosulphite	9.8	2.4	4.9	4.8	4.8	4.4	3.5				
	SBH	11.3	3.0	4.9	4.8	4.9	4.6	3.8				
Green 3	Hydrosulphite	1.9	4.5	4.9	4.8	4.8	4.4	4.1				
	SBH	2.9	4.1	4.8	4.8	4.8	4.5	4.3				
Yellow 5	Hydrosulphite	1.5	2.8	4.9	4.8	4.9	4.5	4.3				
	SBH	7.6	3.1	4.9	4.8	4.9	4.4	4.3				
Violet 18	Hydrosulphite	8.8	2.9	4.9	4.8	4.9	4.5	3.9				
	SBH	12.9	2.7	4.8	4.7	4.6	4.6	4.0				
Orange 5	Hydrosulphite	6.1	3.5	4.9	4.8	4.9	4.3	3.8				
	SBH	12.4	4.2	4.9	4.8	4.9	4.4	3.4				
Brown 24	Hydrosulphite	0.75	3.4	4.9	4.8	4.7	4.4	4.1				
	SBH	2.2	3.9	4.9	4.7	4.6	4.5	4.3				

SC- Shade Change; W - Stain on Wool; C - Stain on Cotton; N - Stain on Nylon

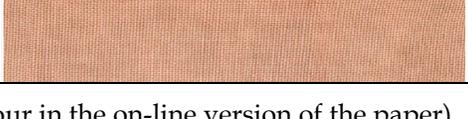
Table 10. Colour Yield and Fastness to Wet Treatments and Rubbing of Vat Dyes Applied by the SBH and Hydrosulphite/NaOH Methods at 60°C (1% oww dye).

### 3.6 Colour yield and fastness of vat dyes applied by the SBH and hydrosulphite methods

The data in Section 3.3 for Vat Red 45 and Vat Green 1 show that the SBH method gave better colour yields and better, or similar rubbing fastness than the conventional method

using sodium hydrosulphite and sodium hydroxide. Table 10 presents results for colour yield and fastness to washing, alkaline perspiration and rubbing for 9 vat dyes applied by the optimised SBH method. For comparison, results are also shown for the dyes applied to wool by the hydrosulphite/caustic soda method.

The data in Table 10 confirm the results obtained with Vat Red 45 and Vat Green 1, discussed above. Thus, for all nine dyes, the SBH/bisulphite system gave better colour yields than were obtained by the conventional method using sodium hydrosulphite and sodium hydroxide. The differences in colour yields can also be seen in Table 11. Furthermore, Table 10 also shows that accompanying the higher colour yields, the SBH/bisulphite system gave similar or slightly better overall fastness properties than hydrosulphite.

Vat Dye (Colour Index Number)	Hydrosulphite Method	SBH Method
Red 1		
Red 10		
Red 45		
Green 1		
Green 3		
Yellow 5		
Violet 18		
Orange 5		
Brown 24		

(Table 11 is shown in colour in the on-line version of the paper)

Table 11. Wool Fabrics Dyed with Vat Dyes (1% oww dye) by the SBH and Hydrosulphite Methods

### 3.7 Effect of type of dyeing machine

In a long liquor dyeing process, interchange of the dyebath liquor with the substrate is important in order to ensure a constant supply of dyestuff molecules to the fibre surface. This can be achieved either by pumping the liquor through a stationary material, moving the substrate through the liquor, or moving both the liquor and material through the machine. Anionic wool dyes applied under acidic conditions have a high substantivity for wool as a result of ionic attraction between the anionic dye molecules and protonated amino groups in the fibre. For this reason, the type of liquor circulation used in the dyeing machine is not an important factor in the uptake of most types of wool dyes. Vat dyes, however, are applied to wool at a relatively high pH, where the fibre is negatively charged. Thus, in this case the substantivity of the dye will be dependent largely on non-polar/hydrophobic interactions rather than on ionic attraction. It is possible, therefore, that the more efficient liquor interchange in the Turbomat, involving pumping the liquor through the fabric, may result in better dyebath exhaustion than in a machine such as the Mathis Labomat, where liquor and fabric are tumbled around together. Another factor that may be important in the Mathis machine is that the constant mixing of air with the liquor could result in premature oxidation of the leuco compound. This could result in precipitation of the dyestuff in the dyebath and, consequently, a lower colour yield.

In order to compare the effects of the SBH vat dyeing system in machines with different actions, fabric samples were dyed with Vat Green 1 by the optimised SBH method in both the Turbomat and Mathis laboratory dyeing machines. The first two sets of data in Table 12 show that the colour yield of the sample dyed in the Mathis was much lower than the one dyed under similar conditions in the Turbomat. Although the exhaustion was slightly better in the Turbomat than in the Mathis, the difference was not great enough to account for the large difference in colour yield. A second possibility, discussed above, is that the reducing power of the SBH system had been adversely affected by oxidation resulting from mixing the dyebath with air during agitation in the Mathis machine. In order to test this possibility, two further samples were dyed in the Mathis machine. Extra SBH, sodium bisulphite and caustic soda were added to one of the pots when the vatted dye liquor was diluted immediately before the fabric was added. This technique, called "sharpening the bath", is used when concentrated stock vats are prepared and then diluted for use over a few days. The extra reducing agent replaces losses due to air oxidation.

Dyeing Machine	Extra SBH/bisulphite and NaOH added	Final Dyebath pH	Absorb. at 558 nm	K/S at 640 nm	Rubbing Fastness	
					Dry	Wet
Mathis	None	9.6	1.03	1.6	4.2	2.5
Turbomat	None	9.0	0.82	12.3	4.5	3.7
Mathis	Yes (a)	9.9	1.37	16.1	4.5	3.2
Turbomat	Yes (a)	8.6	0.57	14.3	4.4	3.3

(a) Bath Sharpened with 1 g/L SBH / 4 g/L sodium bisulphite / 3 ml/L caustic soda (38°Bé)  
All samples soaped off for 20 mins at 98°C in 2 g/L Detergent NA-B

Table 12. Effect of Dyeing Machine Type and of Sharpening the Bath on Dyeing Vat Green 1 (1% oww) by the SBH/Bisulphite Dyeing System (Dyed for 30 min at 70°C; Liquor ratio 25:1; 5% oww Sodium sulphate; 0.05 g/L Albigen A added to the dyebath).

As can be seen from Table 12, the addition of extra reducing agent improved the colour yield of samples dyed in the Mathis machine. The significance of this result is that it provides an indication of the possible behaviour of the SBH system when wool is dyed with vat colours in different types of machines. Thus, the results obtained in the Turbomat can be considered to relate to the behaviour of top, loose stock, package and beam dyeing equipment, where liquor is pumped through the substrate and very little mixing with air occurs. The action of the Mathis, however, can be considered to simulate that of a jet, winch or hank dyeing machine, all of which allow a high degree of contact between the dyebath and atmospheric oxygen. It is clear from these results that when this type of equipment is used, the bath sharpening technique should be employed. It is inadvisable to use extra reagents during the dyestuff vatting step, because with some vat dyes the chromophore can be destroyed by over reduction.

### 3.8 Wool fibre damage caused by SBH and hydrosulphite/NaOH vat dyeing methods

Wool fibre damage was assessed by comparing the wet burst strength (Lewis, 1989) of fabrics after dyeing with vat dyes, by either the optimised SBH or optimised hydrosulphite/NaOH methods, with the values for the undyed fabrics. In a wet wool fabric, ionic interactions (salt linkages) and hydrogen bonds within fibres are largely disrupted and their stabilising effect on wool structure is considerably diminished. Wet burst strength is, therefore, particularly useful because it provides an indication of cleavage of both disulphide and peptide covalent bonds (Lewis, 1989).

The data in Table 13 show that at dyeing temperature of 60°C and 70°C, the optimised SBH method produced less fibre damage than the standard procedure using hydrosulphite and NaOH. This can be attributed largely to the much lower final dyebath pH obtained with SBH. Fibre damage is, however, determined by both temperature and pH; and at a dyeing temperature of 70°C, the difference in fibre damage was lower than at 60°C. As it has been shown that dyed fabrics with good colour yield and fastness properties can be obtained at 60°C, it is concluded that this temperature should be used for the application of vat dyes to wool by the SBH/bisulphite system. For comparison purposes, a fabric sample was also dyed with a pre-metallised dye (1% oww) at pH 5 for 45 minutes at 98°C. The dyed fabric had a bursting force of 286N (equivalent to a strength retention of 86%).

Dyeing Method	Dyeing Temp. (°C)	Final Dyebath pH	Wet Burst Strength	
			Bursting Force (N)	Strength Retention (%)
Undyed	----	----	330	100
Hydrosulphite	60	11.5	193	58
SBH	60	8.9	256	78
Hydrosulphite	70	11.5	223	67
SBH	70	8.9	242	73

Table 13. Wet Burst Strength of Wool Fabrics Dyed with Vat Dyestuffs by Hydrosulphite/NaOH and SBH Methods

## 4. Conclusions

The feasibility of using a reducing system based on sodium borohydride and sodium bisulphite to apply vat dyes to wool has been demonstrated. For a range of nine vat dyes, better colour yields and overall better fastness properties were obtained by the

borohydride/bisulphite method, compared with the conventional procedure involving sodium hydrosulphite/NaOH. Furthermore, the SBH/bisulphite procedure produced less fibre damage than the conventional method.

Sodium borohydride is more expensive than sodium hydrosulphite. However, the cost difference between the auxiliaries is likely to be offset by the better colour yield and, for an expensive substrate such as wool, by the lower fibre damage produced by the SBH/bisulphite reducing system, compared with sodium hydrosulphite/NaOH.

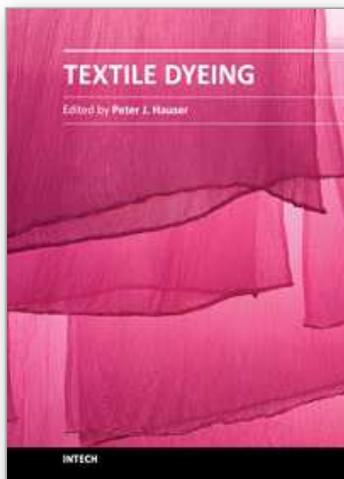
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