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**Advances in the Mordant Bleaching of  
Karakul**

**Part I: The Effect of Different Reducing Agents  
when Mordanting with Ferrous Sulphate**

by

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# ADVANCES IN THE MORDANT BLEACHING OF KARAKUL PART I: THE EFFECT OF DIFFERENT REDUCING AGENTS WHEN MORDANTING WITH FERROUS SULPHATE

by N.G. TROLLIP and A. BERECK\*

## ABSTRACT

*An investigation has been performed, the results of which provide evidence for the preferential use of phosphorus based reducing agents in place of the traditionally used sulphur based reducing agents in the first stage of mordant bleaching processes using ferrous sulphate. These two classes of reducing agent have been compared with respect to their ability to stabilise ferrous sulphate solutions, their influence on the amount of iron retained following a selective desorption rinse, and their influence on the ultimate bleaching results achieved in terms of whiteness realised and damage incurred. It has been shown that the use of phosphorous based reducing agents is essential for optimising fabric whiteness while minimising fibre damage. These results are explained in terms of disulphide bond cleavage by sulphur based reducing agents.*

## INTRODUCTION

The bleaching of dark, pigmented keratin fibres requires the selective destruction of the melanin pigment responsible for the dark coloration, while minimising damage to the fibre protein. For this purpose, the goods to be bleached are subjected to successive mordanting and bleaching treatments, a process applied to the selective bleaching of dark hair contaminants in white wool<sup>1-4</sup> as well as to the general bleaching of pigmented animal furs and hair, including karakul<sup>5-8</sup>.

The first stage in mordant bleaching processes normally involves treatment with ferrous sulphate, during which the metal reacts preferentially, presumably via chelation, with the melanin pigment within the fibres<sup>9,10</sup>. During subsequent bleaching with hydrogen peroxide, oxidative activity is largely confined to the pigment in view of the high effectiveness of iron as a peroxide catalyst, thereby destroying the pigment without excessively damaging the fibre protein. Fibre damage can be further minimised by including a hot acid rinse between the mordanting and bleaching stages. Such a rinse has been termed "selective desorption" since it appears to remove the iron bound to the fibre protein while leaving the iron-pigment interactions largely intact<sup>1</sup>.

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Workers at the Deutsches Wolforschungsinstitut (DWI) have recently optimised the treatment conditions for mordanting with ferrous sulphate. Thus, a large excess of the metal salt in a solution at pH3 and 80°C was found to produce the best results following subsequent rinsing and bleaching<sup>1,11,12</sup>. Such treatment conditions, as well as those suggested elsewhere<sup>4-6</sup>, require the presence of a reducing agent in the mordanting bath in order to maintain the iron in the ferrous state and prevent its precipitation as ferric oxide. In addition, sulphur based reducing agents, such as sulphites, hydrosulphites and disulphites have been claimed to facilitate the diffusion of the metal to the sites of the melanin pigment by making the fibre interior more accessible through disulphide bond cleavage via sulphitolysis<sup>5</sup>. Bereck has, however, recently reported improved bleaching results following mordanting in the presence of phosphorous based reducing agents, such as hypophosphorous acid<sup>13</sup>. The present paper expands on this finding and attempts to explain the mechanisms involved.

## EXPERIMENTAL

### Materials

A plain fabric of density 320 g/m<sup>2</sup> was knitted from 160 tex yarns spun from brown karakul (SAWB type 625), and treated following Soxhlett extraction with dichloromethane (30 cycles). All chemicals were of commercial grade quality.

### Treatments

An Ahiba laboratory dyeing apparatus was used for all the treatments. Liquor ratios were 50:1 throughout. All solutions were made up in de-ionised water.

### *Mordanting*

4,0 g of material was wet out for 20 minutes in an acidified solution of the reducing agent at 70°C. The pH of the solution was then adjusted, when necessary, by the dropwise addition of dilute sulphuric acid until constant at the required value. Ferrous sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was then added to give a concentration of 5,0 g/l. Mordanting was allowed to proceed for 90 minutes at 70°C.

### *Selective desorption*

Following mordanting, all samples were rinsed for 20 minutes with 0,4 ml/l of 50% hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) at 70°C, followed by a 10 minute rinse with water at the same temperature.

### *Bleaching*

Bleaching was carried out in 10 g/l sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) solutions maintained at 55°C, following addition of hydrogen peroxide (35%) to give 10 ml/l. The pH, which in all cases was 8,6 at the onset of bleaching, was not re-adjusted during the treatment. After bleaching for 120 minutes, the samples were rinsed twice with water at 55°C.

### **Analytical procedures**

#### *Cysteine analysis*

Small amounts of white (unpigmented) karakul loose stock (~200 mg) were treated simultaneously with the fabric and analysed for cysteine content according to the method of Meichelbeck *et al*<sup>14</sup>. The pigmented fabric could not be analysed directly in view of interference by the pigment with the colourimetric measurements on which this method is based. Prior to acid hydrolysis, the samples were thoroughly rinsed with 0,1 N HC in order to remove excess reducing agent which could otherwise contribute to colour development and result in incorrect values for cysteine content<sup>15</sup>.

#### *Iron analysis*

The iron contents of the treated samples were determined with the aid of an atomic absorption spectrophotometer equipped with a graphite furnace, following hydrolysis of the samples with concentrated nitric acid for 1 hour under reflux, and suitable dilution with de-ionised water.

#### *Whiteness measurements*

The bleached samples were assessed for whiteness on a Zeiss Elrepho Mat DFC 5 apparatus. The Y tristimulus value was taken as a measure of whiteness in accordance with a previous finding that this parameter was in good agreement with visual appraisals of bleached samples<sup>16</sup>.

An average of at least 8 readings along the length of the fabric was taken for each sample.

#### *Alkali solubility*

Alkali solubilities were determined according to IWTO test method 4-60(E).

#### *Cystic acid content*

Cystic acid analysis was performed according to IWTO test method 23-70 (D).

### *Abrasion resistance*

Abrasion resistances of the samples were assessed by measuring the number of cycles required on a Martindale apparatus to produce the first yarn break. The average resistance of three pieces of fabric was reported for each sample as the ratio  $r$ , defined as

$$r = \frac{\text{number of cycles to 1st yarn break in sample}}{\text{number of cycles to 1st yarn break in untreated control}}$$

## RESULTS AND DISCUSSION

### Effectiveness of reducing agents in stabilising ferrous sulphate solutions

The relative abilities of various reducing agents to stabilise ferrous sulphate solutions under conditions approximating those often employed in the first stage of the mordant bleaching process, are given in Table 1. The times taken until the first observable discolouration of the solutions were used as the basis for comparison.

It is clear that hypophosphorous acid is by far the most effective of the most commonly used reducing agents under the experimental conditions employed. Sodium disulphite and phosphorous acid, on the other hand, are the least effective.

**TABLE 1**  
**STABILITY OF FERROUS SULPHATE IN SOLUTIONS OF REDUCING AGENTS<sup>a</sup>**

REDUCING AGENT	RELATIVE STABILITY
Hypophosphorous acid, $\text{H}_3\text{PO}_2$	8,9
Phosphorous acid, $\text{H}_3\text{PO}_3$	1,0
Sodium sulphite, $\text{Na}_2\text{SO}_3$	3,3
Sodium hydrogen sulphite, $\text{NaHSO}_3$	4,7
Sodium disulphite, $\text{Na}_2\text{S}_2\text{O}_5$	1,0

a : 8g/l /  $\ell$   $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $2 \times 10^{-3}$  M reducing agent; pH 3; 80°C

### Ability to cleave disulphide bonds

Sulphur based reducing agents are known to cleave disulphides in a reversible reaction called sulphitolysis, to yield thiols and Bunte salt groups in equimolar amounts<sup>17</sup>. Both of these species form free cysteine residues upon acid hydrolysis.



The extent of sulphitolysis depends, *inter alia*, on the nature and concentration of the reducing agent, as well as on the solution pH and temperature. Furthermore, subsequent rinsing with water is known to reform up to 50% of the cleaved disulphide bonds<sup>18</sup>.

In Table 2 the extents of disulphide cleavage realised in white karakul by various reducing agents under conditions approximating those utilised in typical industrial mordant bleaching recipes, are compared. The extents of sulphitolysis were assessed before and after selective desorption by determining the cysteine content of acid hydrolysates of the samples. The cysteine content of an untreated control sample was 25  $\mu\text{mol/g}$ .

**TABLE 2**  
**DISULPHIDE BOND CLEAVAGE BY VARIOUS REDUCING AGENTS**  
**UNDER TYPICAL MORDANTING CONDITIONS\***

REDUCING AGENT	CYSTEIN BEFORE SEL. DESORPTION, $\mu\text{mol/g}$	CYSTEIN AFTER SEL. DESORPTION, $\mu\text{mol/g}$
$\text{H}_3\text{PO}_2$	25	26
$\text{H}_3\text{PO}_3$	26	24
$\text{NaHSO}_3$	93	70
$\text{Na}_2\text{SO}_3$	84	60
$\text{Na}_2\text{S}_2\text{O}_5$	127	74

\* $3 \times 10^{-3}$  M reducing agent ( $\sim 2\text{-}3\%$  on the mass of karakul in the case of the S based compounds); pH<sub>i</sub> (pH at the start of mordanting) = 3,0; 70°C for 90 minutes.

It can be seen that while phosphorous and hypophosphorous acid do not cleave disulphide bonds to any extent, under typical mordanting conditions the sulphur based reducing agents do promote sulphitolysis to a considerable degree. Although some recombination occurs during selective desorption with dilute acid, most of the disulphides cleaved during mordanting remain dissociated for the start of the bleaching step.

#### **Influence of reducing agent on the mordant bleaching process**

For this investigation, the use of hypophosphorous acid during mordanting was compared with that of sodium disulphite, the latter reducing agent being employed in concentrations up to 6% on the mass of karakul treated. Small amounts of white karakul were treated simultaneously with the pigmented karakul fabric and analysed for cysteine content prior to the bleaching stage. It

was assumed that similar extents of sulphitolysis occurred in the two karakul types.

Table 3 relates the type and concentration of reducing agent to the pH changes during mordanting, the amount of iron retained following mordanting and selective desorption, the extent of disulphide cleavage realised during these treatments and the bleaching results obtained in terms of whiteness achieved.

Surprisingly, the increase in the extent of disulphide bond cleavage (i.e. the increase in cysteine content) arising from increasing levels of sulphur-based reducing agent in the mordanting liquor was accompanied by a decrease in the amount of iron remaining on the karakul following a desorption rinse, in spite of the enhanced accessibility of the pigment granules that may be expected from the opening up of the fibre structure by sulphitolysis. pH and ionic effects were discounted as possible origins of this trend, as discussed below.

It can be seen from the initial and final pH's of the mordanting liquor in table 3 that the pH increase accompanying mordanting is greatest when hypophosphorous acid only is included. By performing a control experiment (sample 3) in which mordanting was accompanied by the dropwise addition of acid to contain the pH change to that which accompanies mordanting in the presence of sodium disulphite, it was shown that pH differences of the magnitude found here could not explain the observed differences in iron content following selective desorption. In a second control experiment (sample 4) the inclusion of sodium sulphate was also found to have no significant effect on either the iron content or the bleaching results obtained, indicating that an ionic effect played no significant role.

It is possible that the large excess of ferrous sulphate that is normally applied during mordanting (in the present investigation, a 25 fold excess over the iron eventually retained by the karakul) ensures that the concentration of metal reaching the sites of melanin granules is sufficiently great to achieve saturation of the reactive sites on the pigment without the aid of disulphide cleavage. Furthermore, in view of the relatively mild treatment conditions used for selective desorption, a more open, accessible fibre structure (brought about by sulphitolysis) may feasibly result in more iron-pigment interactions being disrupted during rinsing, i.e. lower levels of iron remaining after the rinsing step.

Whatever the reason(s), a decrease in the amount of metal catalyst present at the onset of bleaching not surprisingly results in lower levels of fabric whiteness.

### **Whiteness versus damage**

Any bleaching process has as its primary goal optimisation of the level of whiteness obtained while minimising the extent of fibre damage incurred. Bearing this basic fact in mind, the results presented in Figs. 1 and 2 clearly illustrate the advantages of using phosphorous based reducing agents during the first stage of mordant bleaching.



TABLE 3

**THE INFLUENCE OF REDUCING AGENT USED DURING MORDANTING ON SAMPLE WHITENESS FOLLOWING BLEACHING<sup>a</sup>**

Sample	Reducing agent	pH <sub>i</sub> <sup>c</sup>	pH <sub>f</sub> <sup>d</sup>	Fe <sup>e</sup> (mg/g)	Cysteine ( $\mu$ mol/g)	Whiteness ( $Y \pm s$ ) <sup>f</sup>
1.	Untreated control	—	—	—	25	5,2 $\pm$ 0,3
2.	1,2 ml/l H <sub>3</sub> PO <sub>2</sub>	3,0	3,6	3,0	26	17,2 $\pm$ 0,4
3.	1,2 ml/l H <sub>3</sub> PO <sub>2</sub> + acid	3,0	3,1	3,0	—	17,0 $\pm$ 0,7
4.	1,2 ml/l H <sub>3</sub> PO <sub>2</sub> + 6% Na <sub>2</sub> SO <sub>4</sub> b	3,0	3,1	3,1	—	17,5 $\pm$ 0,5
5.	1,5% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> b	3,0	3,1	2,6	45	16,7 $\pm$ 0,5
6.	3% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> b	3,0	3,1	2,5	74	14,4 $\pm$ 0,4
7.	6% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> b	3,0	3,1	2,5	87	13,6 $\pm$ 0,5

a: treatment conditions described in section 2.2

b: percentage concentrations on mass of sample treated

c: pH of liquor at start of mordanting

d: pH of liquor at end of mordanting

e: iron content of fabric after selective desorption

f: mean  $\pm$  standard deviation

For this investigation either hypophosphorous acid or sodium disulphite was employed as reducing agent in concentrations typically used in industrial processes, namely 1 ml/l and 3,5% (on mass of karakul), respectively.<sup>2,5</sup> Samples with varying levels of whiteness were obtained for each reducing agent by varying the concentration of ferrous sulphate during mordanting while keeping all other conditions of treatment constant. Fibre damage incurred was plotted against the whiteness obtained from the use of each reducing agent, fibre damage being assessed by alkali solubility (Fig. 1) and abrasion resistance (Fig. 2).

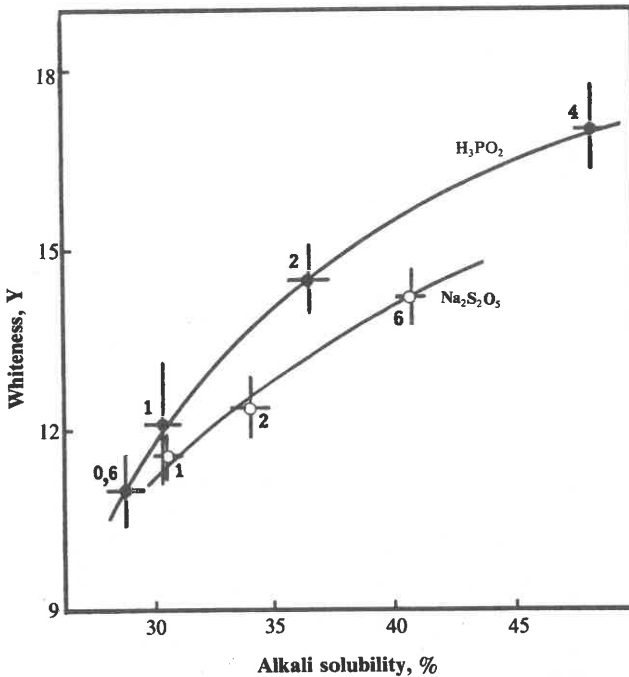


Fig. 1 – Relationship between whiteness and alkali solubility following the use of  $\text{H}_3\text{PO}_2$  and  $\text{Na}_2\text{S}_2\text{O}_5$  in mordant bleaching. The numbers alongside the curves represent the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  concentration (g/l) used during mordanting and the bars represent the standard deviations.

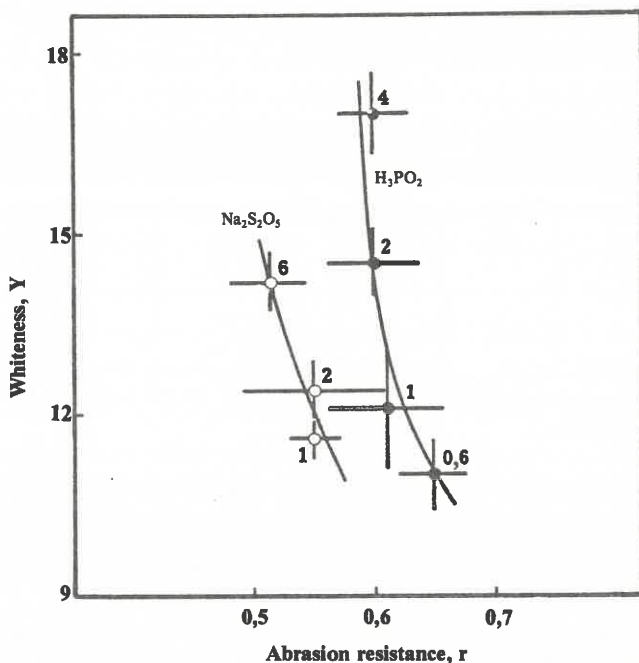


Fig. 2 – Relationship between whiteness and abrasion resistance following the use of  $H_3PO_2$  and  $Na_2S_2O_3$  in mordant bleaching. The numbers alongside the curves represent the  $FeSO_4 \cdot 7H_2O$  concentrations (g/l) during mordanting and the bars represent the standard deviations.

The relatively high standard deviations associated with the abrasion resistance values may be ascribed to variations in the strength of individual yarns within a bleached fabric sample. It is nevertheless clear from both Figs. 1 and 2 that by using hypophosphorous acid in the mordanting bath in place of sodium disulphite, significantly higher degrees of whiteness can be achieved for the same loss of fibre strength.

#### The use of phosphorous acid

The relatively high cost of hypophosphorous acid constitutes a disadvantage of using this reducing agent during mordanting. The bleaching results obtained following the use of the less expensive phosphorous acid were therefore investigated, and are given in Table 4. Two slightly different sets of mordanting conditions were used and yielded bleaching results, in terms of

whiteness and fibre damage, very similar to those obtained following the use of hypophosphorous acid (cf, Figure 1).

**TABLE 4**

**MORDANT BLEACHING RESULTS OBTAINED FOLLOWING THE USE OF PHOSPHOROUS ACID ( $H_3PO_3$ ) DURING MORDANTING<sup>a</sup>.**

Reducing Agent	pH <sub>i</sub>	pH <sub>f</sub>	Whiteness (Y ± s) <sup>b</sup>	Alkali Solubility (% ± s) <sup>b</sup>
0,55 g/ℓ $H_3PO_3$	3,0	3,7	15,5 ± 0,5	38,1 ± 0,4
0,40 g/ℓ $H_3PO_3$	3,3	4,0	16,0 ± 0,6	44,0 ± 0,4

a: treatment conditions as described in section 2.2, except that 4,0 g/ℓ  $FeSO_4 \cdot 7H_2O$  was used.

b: mean ± standard deviation.

It is clear therefore that the reducing strength of phosphorous acid, although significantly lower than that of hypophosphorous acid (Table 1) is nevertheless sufficiently great to ensure a stable mordanting bath and yield acceptable bleaching results in terms of whiteness and damage.

**The cause of the increased fibre damage resulting from the use of sulphur based compounds during mordanting.**

Some insight into the cause of the increased fibre damage resulting from mordant bleaching using sulphur based reducing agents may be obtained from Table 5 which provides additional information regarding the treatments described in Table 3. Here details of the reducing agent used during mordanting are related to the bleaching results obtained in terms of whiteness and damage.

Fibre damage was assessed by abrasion resistance and cysteic acid content, cysteic acid being the main oxidation product resulting from the attack of hydrogen peroxide on keratins<sup>17</sup>.

It is clear that when all other conditions of treatment are kept constant, increasing the concentration of sodium disulphite during mordanting results not only in reduced levels of whiteness but also in increased fibre damage following bleaching, reflected in slightly lowered abrasion resistances. This increased fibre damage cannot, however, be ascribed to a greater extent of oxidative attack on the fibre proteins during bleaching, since this would have resulted in raised levels of cysteic acid which were clearly not found.

It appears therefore that the excessive fibre damage resulting from the use of sulphur based reducing agents in the mordant bleaching process is simply an additive effect, with both the reductive damage incurred during mordanting via sulphytolysis and the oxidative damage incurred during bleaching, contributing to the extent of fibre damage present at the end of the process.

**TABLE 5**  
**RELATIONSHIP BETWEEN CHOICE OF REDUCING AGENT, WHITENESS AND FIBRE DAMAGE**

Sample <sup>a</sup>	Reducing agent	Whiteness (Y ± s) <sup>c</sup>	Abrasion resistance (r ± s) <sup>c</sup>	(Cysteic acid) (mass % ± s) <sup>c</sup>
1	Untreated control	5,2 ± 0,3	1,00	0,23 ± 0,04
4	1,2 ml / l H <sub>3</sub> PO <sub>2</sub>	17,5 ± 0,4	0,63 ± 0,05	0,88 ± 0,12
5	1,5% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> <sup>b</sup>	16,7 ± 0,5	0,54 ± 0,05	0,92 ± 0,03
6	3% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> <sup>b</sup>	14,4 ± 0,4	0,54 ± 0,06	0,85 ± 0,10
7	6% Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> <sup>b</sup>	13,6 ± 0,5	0,48 ± 0,03	0,73 ± 0,08

a: same samples as shown in Table 3

b: percentage concentrations on mass of sample treated

c: mean ± standard deviation

### SUMMARY AND CONCLUSIONS

The choice of reducing agent used to stabilise the ferrous sulphate solution during the first stage of mordant bleaching processes for pigmented keratin fibres can greatly influence the ultimate bleaching results obtained in terms of whiteness and fibre damage. In this respect, the use of phosphorous based reducing agents offers distinct advantages over sulphur based compounds.

The use of hypophosphorous and phosphorous acids during mordanting yields similar results indicating that the extremely high ability of the former compound to stabilise ferrous sulphate solutions offers little, if any, additional advantage to the process. The use of the less expensive phosphorous acid is therefore favoured from cost considerations.

The increased extent of fibre damage incurred during mordant bleaching using sulphur based reducing agents can be ascribed to reductive damage via sulphytolysis during the mordanting stage being augmented by oxidative damage during bleaching.

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## THE USE OF PROPRIETARY NAMES

The names of proprietary products where they appear in this report are mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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