# THE BLEACHING OF WOOL WITH HYDROGEN PEROXIDE IN THE PRESENCE OF A PHOSPHONIC ACID AS STABILISING AGENT

*by N. J. J. VAN RENSBURG*

## ABSTRACT

*Wool can be bleached successfully with hydrogen peroxide in the presence of an organic phosphonic acid derivative. This derivative compared favourably with conventional peroxide stabilising agents.*

## KEY WORDS

Bleaching – wool – phosphonic acid derivative – stabilising agent.

## INTRODUCTION

Hydrogen peroxide is one of the most widely used bleaching agents for wool and other protein fibres. The rate of decomposition of hydrogen peroxide in a bleaching bath depends on the pH of the solution and increases with an increase in pH[1, 2]. The decomposition of hydrogen peroxide is also affected by certain anions which can either act as a stabilising agent, e.g. sodium silicate, or accelerate the rate of decomposition of peroxide, e.g. copper and iron salts[3, 4].

An excess of alkali or oxidising agent may have a detrimental effect on the mechanical properties of wool[5] and most peroxide bleaching processes are therefore carried out in a weak alkaline medium in the presence of stabilising agents under conditions which permit efficient bleaching with minimum fibre damage[2,6,7]. Many stabilising agents are available for use in peroxide bleaching processes, different stabilisers being used under different conditions. Stabilising agents such as sodium silicate, tetra-sodium pyrophosphate, tri-sodium orthophosphate and Stabiliser C, which consists of a mixture of sodium oxalate and tetra-sodium pyrophosphate, are normally used under alkaline conditions[2, 8–10]. Stabilising agents, such as Lufibrol W, consist of organic compounds which are converted to peroxy-acids by hydrogen peroxide and are used under neutral conditions[11]. Protein-fatty acid condensation products,[12, 13] sequestering agents,[14–16] and acylated phosphonic acid derivatives[17, 18] could also be employed in peroxide bleaching baths. Since very little information is available on the application of phosphonic acid derivatives as stabilising agents for peroxide bleaching, the effect of a phosphonic acid derivative on the bleaching of wool by hydrogen peroxide was investigated.

## EXPERIMENTAL

An undyed, chemically untreated 3-step 2-twill worsted fabric of density 268 g/m$^2$, was used in this investigation. All the chemicals used were of laboratory grade. Hydrogen peroxide (100 vols) was used as the bleaching agent while Stabiliser C (Laporte Chemicals), Lufibrol W (B.A.S.F.) and Dequest 2010* (Monsanto) were used as stabilising agents. The concentration of hydrogen peroxide was determined by titration with a standard potassium permanganate solution according to the method described by Vogel[19].

The alkali solubility of the samples was determined within one day after treatment according to the method laid down by the International Wool Textile Organization[20]. The degree of whiteness of the samples was determined with a Zeiss Elrepho apparatus using the formula suggested by Berger[21]. The breaking strength and abrasion resistance of the samples were determined according to the method of the South African Bureau of Standards[22] and on a Stoll Abrasion Tester, respectively.

### FACTORS INVESTIGATED:

(a) The influence of the variation of pH on the bleaching of wool by hydrogen peroxide in the presence of HEDP as a stabilising agent was the first factor investigated. Wool fabrics were bleached with different concentrations of hydrogen peroxide employing HEDP (2 ml/l) as the stabilising agent. The wool was bleached for 2 hours at 65°C at a wool to liquor ratio of 1:40. Tergitol TMN (1 ml/l) was used as a wetting agent. The pH of the solution was adjusted to the required value with $Na_2HPO_4$. The degree of whiteness of the fabrics bleached at pH values ranging from pH 3 to 9, is given in Table I.

(b) The influence of the concentration of HEDP on the bleaching of wool by hydrogen peroxide was also investigated. The results obtained by bleaching wool with a specific concentration of hydrogen peroxide (5 ml/l) in the presence of varying amounts of HEDP in acidic and alkaline media, appear in Table II.

(c) In order to investigate the effect of HEDP on the degree of whiteness of wool in the absence of hydrogen peroxide, wool was treated for 2 hours at 65°C with aqueous solutions of HEDP as well as with other stabilising agents and the degree of whiteness of the fabrics subsequently determined. The treatment was carried out at a wool to liquor ratio of 1:40 in the presence of Tergitol TMN (1 ml/l). The results obtained are given in Table III.

(d) A comparison of the effects of HEDP and some conventional stabilising agents on the degree of whiteness of wool treated with peroxide was carried out. Wool

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*Dequest 2010 is the registered trademark for 1-hydroxyethylidene 1,1-diphosphonic acid (HEDP).

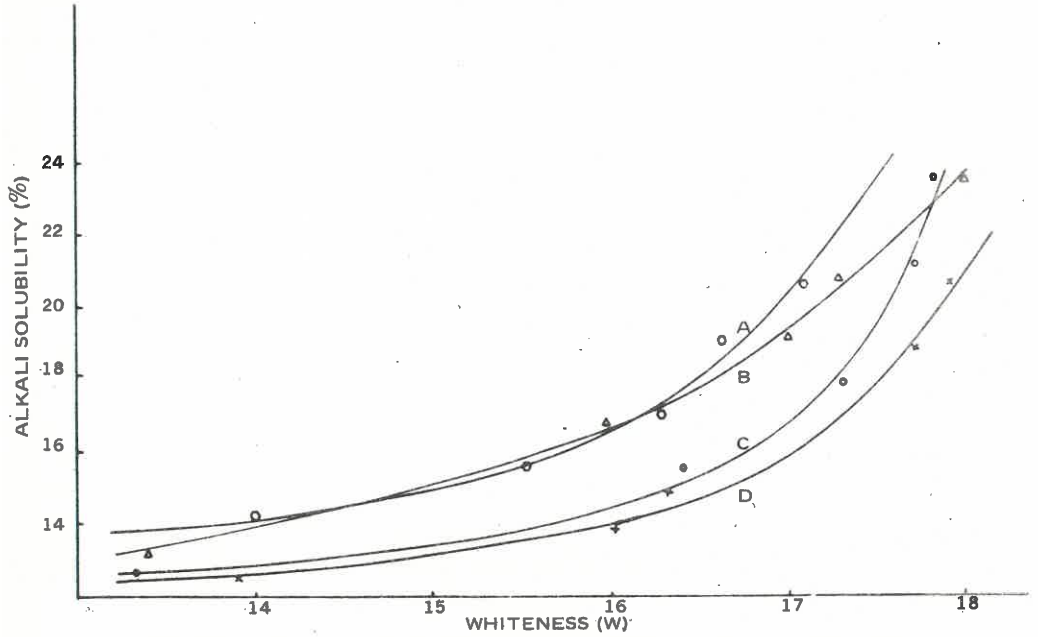


**FIGURE I**

**The degrees of whiteness and the alkali solubilities of wool bleached with hydrogen peroxide in the presence of various stabilising agents**

A = HEDP, pH 2,3
B = Stabiliser C
C = HEDP, pH 9,0
D = Lufibrol W

fabrics were bleached for 2 hours at 65°C with various concentrations of hydrogen peroxide (0, 2, 5, 10 and 15 ml/l) in the presence of a number of stabilising agents (2 g/l) and the degree of whiteness and alkali solubilities of the specimens subsequently determined. The results obtained are represented graphically in Figure I.

(e) The influence of various stabilising agents on the mechanical properties of wool bleached with hydrogen peroxide was investigated. Fabrics were treated for 2 hours at 65°C at a wool to liquor ratio of 1:40 in the presence of Tergitol TMN (1,0 ml/l). The peroxide concentration was 10 ml/l while 2 g/l of each stabilising agent were used. Stabiliser C was used at pH 9,0, Lufibrol W at pH 5,6 and HEDP at pH 2,3. The breaking strength and abrasion resistance of the fabrics were determined after treatment. The results obtained appear in Table IV.

(f) Finally, the effects of different stabilising agents on the rate of decomposition of hydrogen peroxide were compared. Freshly prepared solutions of aqueous hydrogen peroxide (10 ml $H_2O_2$/l) containing various stabilisers (2,0 g/l) were

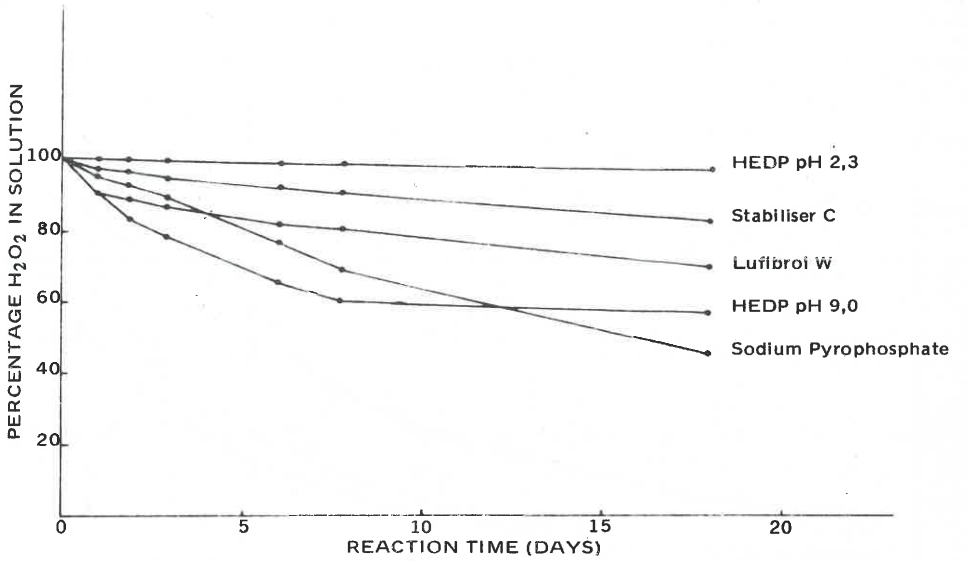


**FIGURE II**

**The effect of various stabilising agents on the stability of hydrogen peroxide solutions**

inserted in a thermostat at 50°C and the peroxide content of the solutions was determined at regular intervals by titration with standard potassium permanganate solutions. The concentration of the hydrogen peroxide was then calculated, after allowance had been made for permanganate consumption by the various stabilising agents. The results obtained are represented graphically in Figure II.

## RESULTS AND DISCUSSION

(a) From Table I it is apparent that at low concentrations of hydrogen peroxide the pH had no significant effect on the degree of whiteness of the fabrics whereas at high concentrations of hydrogen peroxide an increase in the pH increased the degree of whiteness of the fabrics.

It is evident from Table I that wool can be bleached with hydrogen peroxide in the presence of HEDP as stabilising agent at all pH values investigated. Table I also contains the results obtained when the fabrics were bleached with peroxide using HEDP as stabilising agent without adjustment of the pH of the bleaching liquor and it can be seen that, even in this case, an effective bleach was obtained. An aqueous solution of HEDP (2,0 ml/l) has a pH of 2,3 and if bleaching is carried out at this pH, additional chemicals required for the buffering of the bleaching liquor are unnecessary, and bleaching costs are reduced. The majority of the

## TABLE I

### THE INFLUENCE OF pH ON THE DEGREE OF WHITENESS OF WOOL BLEACHED WITH HYDROGEN PEROXIDE IN THE PRESENCE OF HEDP (2,0 ml/l)

| Concentration of $H_2O_2$ (ml/l) | WHITENESS* | | | | |
|---|---|---|---|---|---|
| | pH 3,0 | pH 5,0 | pH 7,0 | pH 9,0 | pH not adjusted (pH 2,3) |
| 1,0 | 14,3 | 14,7 | 14,7 | 14,5 | 14,5 |
| 2,5 | 15,2 | 15,0 | 15,2 | 15,2 | 15,0 |
| 5,0 | 15,5 | 15,7 | 15,8 | 16,0 | 15,1 |
| 10,0 | 16,1 | 16,3 | 16,5 | 17,0 | 15,6 |
| Control** | 13,1 | | | | |

*The degree of whiteness of a fabric increases with increased numerical value.
**The control was treated in water in the absence of hydrogen peroxide and HEDP.

## TABLE II

### THE INFLUENCE OF THE CONCENTRATION OF HEDP ON THE DEGREE OF WHITENESS OF WOOL BLEACHED BY HYDROGEN PEROXIDE*

| Concentration of HEDP (ml/l) | WHITENESS | |
|---|---|---|
| | pH 3,0 | pH 9,0 |
| 10,0 | 16,0 | 17,3 |
| 5,0 | 16,0 | 16,8 |
| 2,0 | 16,2 | 16,6 |
| 0,5 | 15,8 | 16,5 |
| 0,1 | 15,9 | 16,0 |
| 0,02 | 15,9 | 16,4 |
| 0,005 | 16,0 | 15,8 |
| 0,001 | 15,5 | 15,6 |
| 0 | 15,6 | 15,5 |

*The experimental conditions were the same as for Table I.

stabilising agents currently employed for peroxide bleaching can be used only in acidic or alkaline media. HEDP, on the other hand, can be used in acidic as well as in alkaline bleaching baths and in this respect it offers an advantage over other stabilising agents.

(b) The results obtained by bleaching wool with hydrogen peroxide in the presence of varying amounts of HEDP, as given in Table II, show that at pH 3,0 the concentration of HEDP used during the bleaching treatment did not significantly affect the degree of whiteness of the fabrics. The results show furthermore, that at this pH the degree of whiteness of the bleached fabrics was the same when bleached in the presence of HEDP, as it was when bleached in the absence of HEDP. Under alkaline conditions, however, the degree of whiteness of the fabrics was increased significantly with the use of more concentrated solutions of HEDP. This shows that in an alkaline medium HEDP, like other conventional stabilising agents, improves the bleaching of wool by hydrogen peroxide.

(c)

**TABLE III**

**THE INFLUENCE OF HEDP, STABILISER C AND LUFIBROL W ON THE WHITENESS OF WOOL IN THE ABSENCE OF HYDROGEN PEROXIDE**

| Concentration of stabilising agent (g/l) | WHITENESS | | | | |
|---|---|---|---|---|---|
| | STABILISER C, pH 9,0 | LUFIBROL W, pH 5,6 | HEDP pH not adjusted* | HEDP pH 3,0 | HEDP pH 9,0 |
| 10,0 | 11,1 | 13,7 | 14,8 (2,0) | 15,2 | 12,3 |
| 5,0 | 12,3 | 13,7 | 14,5 (2,1) | 14,5 | 13,0 |
| 2,0 | 12,9 | 13,8 | 14,3 (2,3) | 14,0 | 13,7 |
| 0,5 | 13,4 | 13,4 | 14,2 (2,8) | 14,3 | 13,9 |
| 0,1 | 13,2 | 13,4 | 13,8 (3,3) | 13,8 | 13,9 |
| 0,02 | 13,6 | 13,6 | 14,0 (4,0) | 14,1 | 14,0 |
| 0,005 | 13,5 | 13,3 | 14,0 (4,0) | 14,0 | 13,4 |
| 0,001 | 13,3 | 13,5 | 14,0 ( – ) | 13,8 | 12,9 |
| Control | 13,4 | 13,7 | 13,8 ( – ) | 13,7 | 13,5 |

*The pH of the solution is given in parenthesis

Table III shows that HEDP acted as a bleaching agent in an acid medium. The degree of whiteness of the fabrics was increased by increasing the concentration of the HEDP. Hardly any bleaching effect was obtained with less than 0,5 g/l HEDP. In an alkaline medium, on the other hand, no bleaching effect was obtained with the HEDP. At higher concentrations of HEDP, a yellowing of the wool was in fact observed. Furthermore, it is interesting to note that the wool was not discoloured

by Lufibrol at pH 5,6; whereas higher concentrations of Stabiliser C at pH 9,0 caused some yellowing.

(d) Figure I shows the alkali solubilities and degrees of whiteness of wool bleached with various concentrations of hydrogen peroxide in the presence of different stabilising agents. A comparison of the alkali solubilities obtained by bleaching wool in the presence of different stabilising agents shows that Lufibrol W gave the lowest alkali solubilities, followed by HEDP (pH 9,0), Stabiliser C and HEDP (pH 2,3). However, in the case of fabrics with a high degree of whiteness, Stabiliser C gave lower alkali solubilities than HEDP (pH 9,0). A comparison of the degrees of whiteness shows that Stabiliser C and Lufibrol W gave the whitest fabrics, followed by HEDP (pH 9,0) and HEDP (pH 2,3), the latter having given the lowest degrees of whiteness of all the stabilising agents studied.

(e) The influence of the various stabilising agents on the mechanical properties of wool bleached with hydrogen peroxide is shown in Table IV.

**TABLE IV**

**ABRASION RESISTANCE AND BREAKING STRENGTH OF WOOL FABRICS BLEACHED WITH HYDROGEN PEROXIDE IN THE PRESENCE OF VARIOUS STABILISING AGENTS**

| Treatment | Abrasion Resistance (Cycles to end point) | WARP | | WEFT | |
|---|---|---|---|---|---|
| | | Breaking Strength (Kg) | Extension (%) | Breaking Strength (Kg) | Extension (%) |
| Water | 505 | 48,2 | 48,5 | 32,3 | 26,5 |
| Hydrogen peroxide | 432 | 57,3 | 48,0 | 32,2 | 32,0 |
| HEDP | 510 | 50,0 | 50,0 | 35,0 | 28,0 |
| HEDP + Hydrogen peroxide | 485 | 51,4 | 52,0 | 32,3 | 21,0 |
| Stabiliser C + Hydrogen peroxide | 505 | 50,8 | 50,0 | 34,1 | 31,0 |
| Lufibrol W + Hydrogen peroxide | 445 | 51,8 | 49,0 | 31,8 | 26,0 |
| Untreated | 497 | 51,8 | 47,0 | 32,7 | 29,0 |

The results show that the presence of a stabilising agent in the bleaching bath did not affect the mechanical properties of the wool fabrics significantly. Treatment of wool with HEDP in the presence of hydrogen peroxide, as well as with HEDP alone, did not differ significantly from normal bleaching treatments using conventional stabilising agents. HEDP may therefore be used as a stabilising agent in bleaching baths without impairing the mechanical properties of wool.

(f) The results represented by the graphs in Figure II, show that, of the stabilising agents studied, sodium pyrophosphate and HEDP at pH 9,0 had the smallest stabilising effect on the rate of decomposition of hydrogen peroxide. Lufibrol W gave a slightly better stabilising effect, followed by Stabiliser C. The greatest stabilising effect was, however, obtained by HEDP at pH 2,3. This stabilising effect is probably due to the fact that HEDP functions as a sequestering agent. It has, in fact, been claimed that HEDP is a much more efficient sequestering agent than EDTA or tripolyphosphonic acid[2,3].

## CONCLUSIONS

Wool can be bleached successfully with hydrogen peroxide with an organic phosphonic acid (HEDP) as a stabilising agent. Bleaching with peroxide in the presence of the phosphonic acid does not impair the mechanical properties of wool. The organic phosphonic acid derivative used, compares favourably with the conventional stabilising agents and can be used in acid as well as alkaline bleaching baths. A higher degree of whiteness is, however, obtained under alkaline than under acidic conditions. HEDP also bleached the wool slightly in the absence of hydrogen peroxide in an acidic medium.

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## THE USE OF PROPRIETARY NAMES

The fact that chemicals with proprietary names have been used in this investigation in no way implies that they are recommended by SAWTRI or that there are not others which are as good or even better.

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