Bleaching of Wool with Hydrogen Peroxide and a Silicate Stabiliser

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A modified factorial experimental design, a central composite rotatable plan, has been applied to a silicate–hydrogen peroxide system to determine the optimum bleaching conditions. In addition to high whiteness, the optimisation was limited by constraints on time and damage, as measured by alkali solubility. The predicted optimum obtained was verified by experiment and gave at least a 60% saving in time compared with phosphate–peroxide systems in commercial use.

INTRODUCTION

Cegarra et al. [1] have described the use of various stabilisers for the bleaching of wool with hydrogen peroxide. Their conclusions led them to optimise the conditions for a phosphate stabiliser, stabiliser C (Foret) [2], using a central composite rotatable design [3].

The use of a phosphate and a silicate stabiliser and the effects that may be achieved in sequential bleaching–shrink-resist treatments have been described [4]. Having shown the advantages of a silicate stabiliser in this respect, it was decided to optimise the silicate–hydrogen peroxide system using a central composite rotatable design.

The silicate formulation chosen is readily available and is the only addition required, apart from hydrogen peroxide. These are major considerations for obtaining a practical commercial recipe that is inherently robust in general use. It was recognised that the formulation chosen might be capable of further refinement and that alternative formulations may also be available.

MATERIALS

- A 100% wool tie lining fabric was chosen as the substrate for this study because of its well-documented characteristics (Table 1)

TABLE 1

100% Wool Worsted Martindale Abradant Fabric

Weight	190 g/m²	
Oil content	0.1–0.5%	
Alkali solubility	10.5%	
Whiteness index	46.4	
Yellowness index	32.3	
	Warp	*Weft*
Threads per cm	19	12
Yarn count (tex)	R49/2–R53/2	R67/2–R72/2
Singles twist (twists per metre)	350–450 'Z'	450–480 'Z'
Folding twist (twists per metre)	420–460 'S'	430–480 'S'
Mean fibre diameter (μm)	27.7–29.5	30.5–33.8

- Hydrogen peroxide, 27.5% wt/wt (100 vol.) laboratory-reagent grade
- Tubotex PC (CHT Tubingen) – a blend of sodium oxide, silica, alkalis, and sequestering and wetting agents.

MEASUREMENTS

Alkali solubility was estimated in accordance with IWTO Specification 4–60.

Reflectance measurements of yellowness and whiteness indices were made on a Zeiss RFC–3 spectrophotometer. ASTM yellowness index [5]:

$$YI = \frac{100\ (1.28X - 1.06Z)}{Y}$$

Jacquemart whiteness index [6]:

$$WI = [(100 - Y)^2 + 5.5\ (X - Z)^2]^{1/2}$$

where X, Y and Z are the tristimulus values.
Decreasing values of YI and WI indicate decreasing yellowness and increasing whiteness respectively.

EXPERIMENTAL

General

Four independent variables were studied, time (0.5–3.0 h), hydrogen peroxide concentration (1–4 vol.), temperature (30–70°C) and Tubotex PC concentration (measured in g/dm³).

The stabiliser system was regarded as a 'black box' for the purposes of this investigation. It was appreciated that changes in stabiliser concentration would also vary sequesterant and surfactant concentration as well as causing small changes in pH. It was felt that the addition of other chemicals to counter these fluctuations would defeat the object of the investigation and would also introduce more unknown variables between treatments.

The responses studied were alkali solubility (A/S), yellowness index (YI) and whiteness index (WI). Table 2 shows the experimental conditions, the observed responses and the predicted responses calculated from a fitted second-order polynomial.

The experimental work was carried out in a laboratory Dyemaster. The 31 experiments were grouped according to temperature and carried out in six batches. It will be shown later that this decision affected the estimation of measurement precision, so that the statistical analysis was not as satisfactory as it could have been.

Treatment Conditions

A liquor-to-goods ratio of 30:1 was chosen as being most representative of long-liquor treatments. The treatment pH was largely determined by the Tubotex PC concentration. Since this auxiliary has a buffering action, no attempt was made to adjust the pH to a constant value for each treatment. Aqueous solutions of Tubotex PC between 1.0 and 8.0 g/dm³ vary over the range pH 11.5–12.2. However, in the presence of wool, which also exerts a buffering action, the operating pH was in the range 9.75–10.25.

The volume of solution required for each treatment was calculated from the fabric weight, and the quantities of hydrogen peroxide and Tubotex PC determined accordingly. The Tubotex PC was dissolved in a small amount of

TABLE 2

Experimental Design and Response Data

Treatment No.	Variable: Time, $V(1)$ (h)	Variable: $[H_2O_2]$, $V(2)$ (vol.)	Variable: Temp., $V(3)$ (°C)	Variable: [Tubotex], $V(4)$ (g/dm^3)	Alkali solubility: Measured	Alkali solubility: Predicted	Whiteness index: Measured	Whiteness index: Predicted	Yellowness index: Measured	Yellowness index: Predicted
1	1.125	1.750	40.0	2.75	18.6	15.2	38.1	38.1	22.2	22.6
2	2.375	1.750	40.0	2.75	17.7	17.9	38.9	38.0	23.6	23.6
3	1.125	3.250	40.0	2.75	18.7	19.6	37.8	36.9	20.2	21.1
4	2.375	3.250	40.0	2.75	18.2	24.6	36.6	36.8	21.6	21.6
5	1.125	1.750	60.0	2.75	36.4	35.0	39.9	40.0	24.1	24.7
6	2.375	1.750	60.0	2.75	53.8	51.2	38.5	38.5	22.4	23.6
7	1.125	3.250	60.0	2.75	44.5	43.4	37.0	37.2	21.2	21.5
8	2.375	3.250	60.0	2.75	66.3	62.0	35.5	35.6	19.8	19.7
9	1.125	1.750	40.0	6.25	20.3	22.3	36.7	36.6	20.4	21.2
10	2.375	1.750	40.0	6.25	25.9	24.2	37.1	36.6	21.8	22.1
11	1.125	3.250	40.0	6.25	25.5	25.3	33.7	33.3	21.0	20.5
12	2.375	3.250	40.0	6.25	30.5	29.5	33.4	33.2	20.6	20.7
13	1.125	1.750	60.0	6.25	71.2	62.0	40.9	40.4	23.4	24.0
14	2.375	1.750	60.0	6.25	80.7	77.5	38.1	38.9	22.9	22.7
15	1.125	3.250	60.0	6.25	71.6	69.1	34.5	35.4	20.8	21.5
16	2.375	3.250	60.0	6.25	86.2	86.8	34.2	33.9	19.4	19.6
17	0.500	2.500	50.0	4.50	24.7	29.6	35.5	35.6	22.1	20.8
18	3.000	2.500	50.0	4.50	49.8	50.0	33.8	34.0	20.1	20.0
19	1.750	1.000	50.0	4.50	24.3	31.4	39.4	39.7	25.2	24.0
20	1.750	4.000	50.0	4.50	47.1	45.1	33.5	33.5	19.6	19.4
21	1.750	2.500	30.0	4.50	18.8	14.7	36.7	37.9	23.6	23.2
22	1.750	2.500	70.0	4.50	82.7	91.9	41.2	40.4	25.2	24.2
23	1.750	2.500	50.0	1.00	18.9	19.0	37.9	38.3	23.7	22.7
24	1.750	2.500	50.0	8.00	45.9	50.9	35.2	35.1	21.5	21.1
25	1.750	2.500	50.0	4.50	33.7	31.2	35.6	35.6	22.3	22.4
26	1.750	2.500	50.0	4.50	28.2	31.2	35.3	35.6	22.2	22.4
27	1.750	2.500	50.0	4.50	35.4	31.2	35.7	35.6	22.7	22.4
28	1.750	2.500	50.0	4.50	30.4	31.2	35.4	35.6	22.3	22.4
29	1.750	2.500	50.0	4.50	30.8	31.2	35.8	35.6	22.4	22.4
30	1.750	2.500	50.0	4.50	28.6	31.2	35.5	35.6	22.6	22.4
31	1.750	2.500	50.0	4.50	31.5	31.2	35.6	35.6	22.5	22.4
Untreated					10.5		46.4		32.3	

TABLE 3

Regression Coefficients of Responses[1,2]

Regression coefficient	Alkali solubility: Coded	Alkali solubility: Decoded	Whiteness index: Coded	Whiteness index: Decoded	Yellowness index: Coded	Yellowness index: Decoded
b_0	31.23	199.04	35.56	55.29	22.43	29.58
b_1	5.11	−40.44	−0.40	4.03	−0.22	9.50
b_2	3.44	−18.46	−1.55	0.35	−1.14	−2.95
b_3	19.30	−6.16	0.64	−0.91	0.24	−0.35
b_4	7.99	−10.97	−0.80	−1.59	−0.38	−0.62
b_{11}	2.15	5.50	−0.18	−0.46	−0.51	−1.31
b_{22}	1.76	2.97	0.27	0.46	−0.18	−0.30
b_{33}	5.25	0.06	0.89	0.01	0.32	0.083
b_{44}	(0.94)	(0.30)	0.29	0.09	−0.13	−0.04
b_{12}	(0.58)	(1.24)	(−0.02)	(−0.04)	−0.15	−0.32
b_{13}	3.38	0.54	−0.36	−0.06	−0.55	−0.09
b_{14}	(−0.19)	(−0.177)	(0.02)	(−0.02)	(−0.04)	(−0.03)
b_{23}	(1.01)	0.13	−0.43	−0.06	−0.44	0.06
b_{24}	(−0.34)	−0.26	−0.53	−0.40	0.18	0.14
b_{34}	4.98	0.28	0.46	0.03	0.18	0.01

1. Values within a column may be compared, but there is no relationship between coefficients for the different responses.
Figures in parentheses are not significant (see section on Results)
Response $= b_0 + b_1V(1) + b_2V(2) + b_3V(3) + b_4V(4) + b_{11}V(1)^2 + b_{22}V(2)^2 + b_{33}V(3)^2 + b_{44}V(4)^2 + b_{12}V(1)V(2) + b_{13}V(1)V(3) + b_{14}V(1)V(4) + b_{23}V(2)V(3) + b_{24}V(2)V(4) + b_{34}V(3)V(4)$ for decoded regression coefficients

2. The original coded coefficients were calculated to four decimal places; the rounded coded values were used to calculate the decoded values so that predictions will not be precise

warm water and added to the hydrogen peroxide, already diluted in three-quarters of the required volume of water, and contained in a suitable measuring cylinder. The solution was then made up to the required volume and used immediately.

The experiment was timed from the point at which the solution reached the required temperature, $V(3)$, (Table 2). The treatment temperature in each case was reached within 10–15 min from cold. This procedure approximates to the conditions prevailing in industry.

On completion of a treatment the sample was first rinsed in copious amounts of cold water, acid soured to pH 5 with formic acid, and then oven dried at 50°C for as short a time as possible. Analysis of samples was performed as described above.

RESULTS

General

Each response (A/S, YI and WI) was analysed according to the experimental design, and the predicted values are shown with the observed results in Table 2.

Regression coefficients (Table 3) give direct information as to the dependence of the response on a variable or interaction of variables. The integers refer to the variables, e.g. b_3 refers to the effect of temperature on the response, and b_{24} to the combined effect of hydrogen peroxide concentration and Tubotex PC concentration. The sign and magnitude of the coefficients for a given response may be used to rank the variables in order of importance, within the experimental range studied. For a regression coefficient to be significant at the 5% level it must be greater than about twice its standard error (critical values may be obtained from tables). Coefficients which fail to meet this condition are shown in parenthesis in Table 3.

An analysis of variance was performed on the results. The first- and second-order terms were evaluated in groups and the lack of fit of the experimental points to the curve was determined. The design incorporates a number of identical treatments, the statistical analysis of which allows an estimation of the repeatability of measurement in these results and thus forms the basis for estimation of the variation in the design as a whole. The significance of the first- and second-order terms and the lack of fit can be assessed by examining their F-ratios. First- and second-order terms were always significant. The results in Table 4 are for lack of fit. An F-ratio value of less than 4.06 for lack of fit in this experiment would indicate statistical confidence in the fit of the curve to the points. The apparent lack of fit for the responses is discussed below.

TABLE 4

Results for Lack of Fit

Response	F-ratio (error)
Alkali solubility	5.87
Whiteness index	24.19
Yellowness index	32.99

It is unlikely with three different responses such as A/S, WI and YI that a coincident, clear-cut optimum will materialise from the analysis. For example, alkali solubility may only be expected to increase as all the variables increase. The process therefore becomes a compromise, although we shall continue to refer to it as optimisation.

Plots of any two variables (two held constant) may be constructed to assist with the interpretation. The response is taken to be the Z-axis and the response surface is depicted as a contour diagram. If realistic constraints are applied and reference to the first-order regression coefficients is made, the large number of possible alternative recipes may be reduced to manageable proportions.

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Operating Constraints

Two constraints were placed on the system.

(a) Since wool may be degraded after bleaching and during finishing, we chose to optimise at 25% alkali solubility as representative of acceptable chemical damage. Clearly optimisation may be attempted for any response value within the range of data collected.

(b) Cegarra [7] has costed out the variables in bleaching, and concluded that time of treatment is the main economic consideration.

DISCUSSION AND TREATMENT OF RESULTS

Regression Coefficients

The regression coefficients (Table 3) are presented as coded and decoded values. The coded values may be compared with each other to indicate the relative importance of each effect. The decoded values may be used directly with the original variable values to calculate the response under any of the experimental conditions within the ranges chosen for the plan (polynomial at the foot of Table 3).

Alkali Solubility

The significant effects and interactions all had positive regression coefficients, so that any increase in the variables would lead to an increase in alkali solubility. The effects of temperature and stabiliser concentration had the greatest influence, whilst their interaction was nearly as great as the effect of time. Peroxide concentration had the smallest effect and made no contribution in combination with other variables. Temperature had the largest quadratic effect, indicating that its effect increased as it became higher.

Reflectance

Only temperature (b_3 positive) had an adverse effect on colour, and peroxide concentration (b_2 largest negative value) made the largest contribution to improving colour.

The regression coefficients clearly show that the temperature must be minimised since it both increases alkali solubility and reduces the improvement in colour. Whilst high peroxide and stabliliser concentrations are desirable, there will be an economic limitation on both. The constraint on time may be expected to moderate the adverse effect of stabiliser on alkali solubility.

Analysis of Variance

The F-ratios (error) indicate a highly significant lack of fit for whiteness and yellowness data and a significant lack of fit for alkali solubility. An enforced constraint on the use of laboratory equipment meant that the trials could not be carried out individually in a random fashion, but had to be batched according to temperature. The seven central

points (25–31, Table 2) together with trials 17–20 and 23 and 24 were perfomed at 50°C. The decision to batch 17–20, 23, 24 and 25 together with 26–31 in another batch was clearly in error. Perhaps a better choice would have been 17–19 with 25–27 and 20, 23 and 24 with 28–31 (maximum eight trials per batch).

The batch-to-batch differences appear to have introduced another source of variation, which may not be estimated from the available data.

Combination of lack-of-fit sum of squares and error sum of squares in an analysis of variance of first- and second-order effects showed that:

(a) For alkali solubility the first-order effects were significant as a group whereas the second-order effects were not significant; five of the ten second-order effects were not significant compared to their standard errors in Table 3

(b) For whiteness both first- and second-order groups were significant whereas for yellowness the first-order effects only were significant.

Optimisation

A plot of WI versus temperature for any given conditions resulted in a curve similar to that in Figure 1. There the chosen conditions were $V(1)=1.5$ h, $V(2)=2.5$ vol., $V(4)=5$ g/dm³. Clearly the region of interest was 40–50°C. For $V(3)$, set at 45°C, the same process was applied for WI versus H_2O_2, and Figure 2 was obtained. The likely range of interest for $V(2)$ was 2.5–3.0 vol. peroxide. Examination of regression coefficients had already indicated that time, $V(1)$, had only a small influence on the results, and for the following calculations it was held constant at 1.125 h.

With an estimated value for $V(1)$ and estimated ranges for $V(2)$ and $V(3)$ it was possible to compute a corresponding set of values for $V(4)$ (Tubotex PC concentration) to achieve

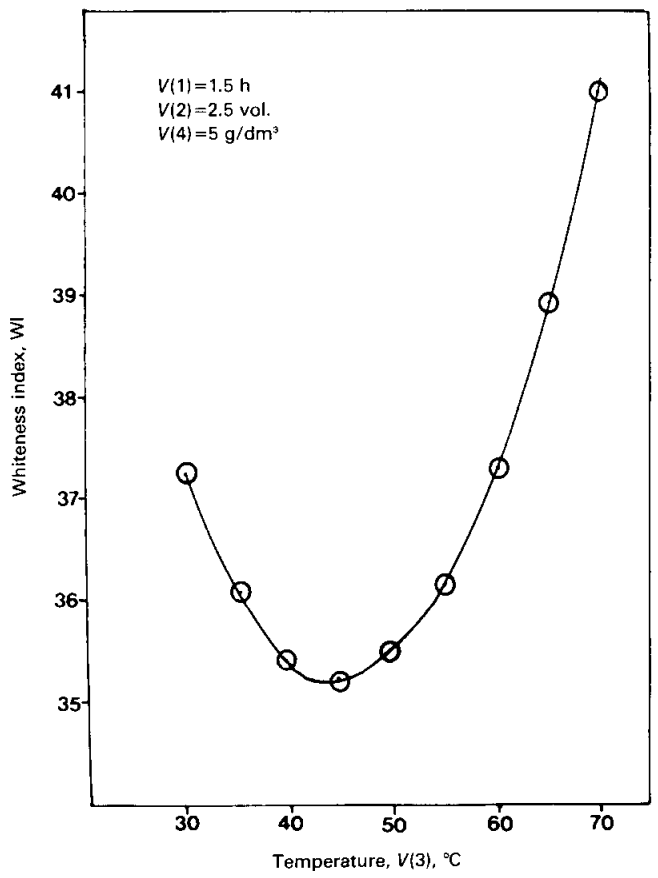

Figure 1 – Relationship between whiteness index and temperature for any given set of conditions

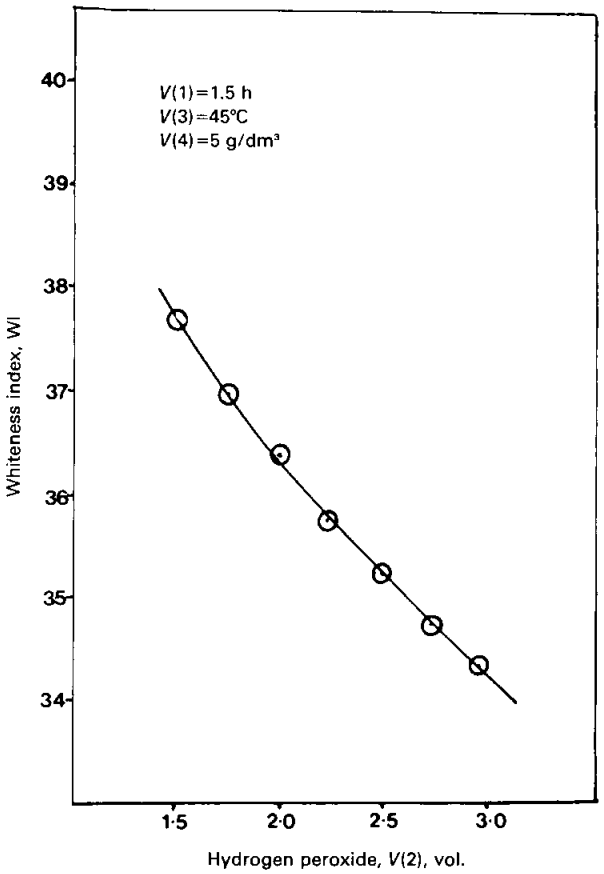

Figure 2 – Relationship between whiteness index and hydrogen peroxide concentration for any given set of conditions

25% alkali solubility. Having specifically determined values of $V(1)$, $V(2)$, $V(3)$ and $V(4)$ for this constraint, use of the appropriate WI equation allowed the calculation of the corresponding whiteness index. The results are shown graphically in Figure 3. The lowest WI value appears at 40°C for $H_2O_2=2.75$–3.0 vol. and Tubotex PC at 7.87 and 6.86 g/dm³. The trend of the plot suggested that at lower temperatures even better results for whiteness index might be obtained. However, the same calculations continued down to 30°C showed that WI increased below 40°C.

Table 3 shows the influence of temperature and stabiliser concentration (b_3, b_4, b_{34}) on alkali solubility. For the lowest WI values at 40°C, (i.e. 2.75 vol. peroxide, 7.87 g/dm³ stabiliser and 3.0 vol. peroxide, 6.86 g/dm³ stabiliser (1.125 h)) it may be calculated that +5% and +10% errors in temperature lead to alkali solubilities of 28.9, 33.6 and 28.3, 32.2% respectively, levels that are unacceptably higher than the 25% constraint. The risks to be taken at these conditions at 40°C are not justified by the predicted half unit improvement in whiteness index.

The next region of interest was at 42.5°C, again for $V(2)=2.75$ and 3.0 and for $V(4)=6.24$ and 5.53. The Tubotex PC concentrations are about 20% lower, and as such, are much more acceptable.

Recalculation of Figure 3 at 42.5°C and 1.125 h for $V(2)=2.5$–3.0 (in steps of 0.05) and calculated $V(4)$ values resulted in Figure 4. From this plot it was evident that the optimum conditions were $V(2)=2.8$, $V(3)=42.5$ and $V(4)=6.0$.

Recalculation of Figure 3 with time=1.0 and 1.5 h gave a change of no greater than ±0.1 unit of WI.

Hence the final conditions were chosen as shown in Table 5.

Useful information regarding the likely optimum condi-

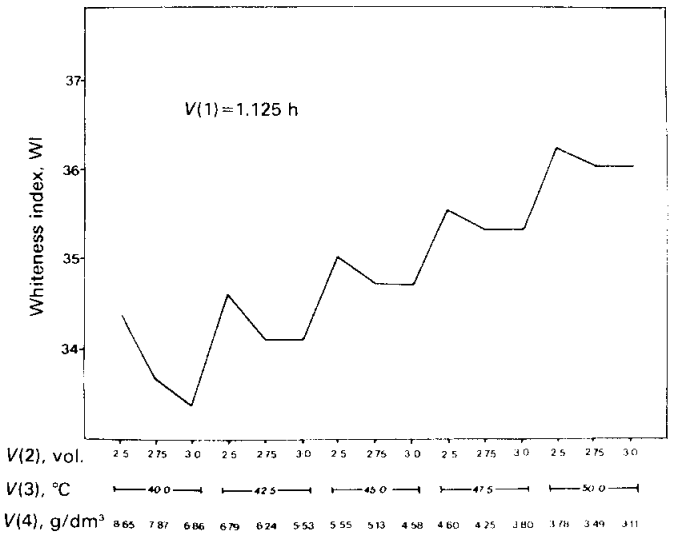

Figure 3 – Predicted whiteness index to conditions predicted to give 25% alkali solubility

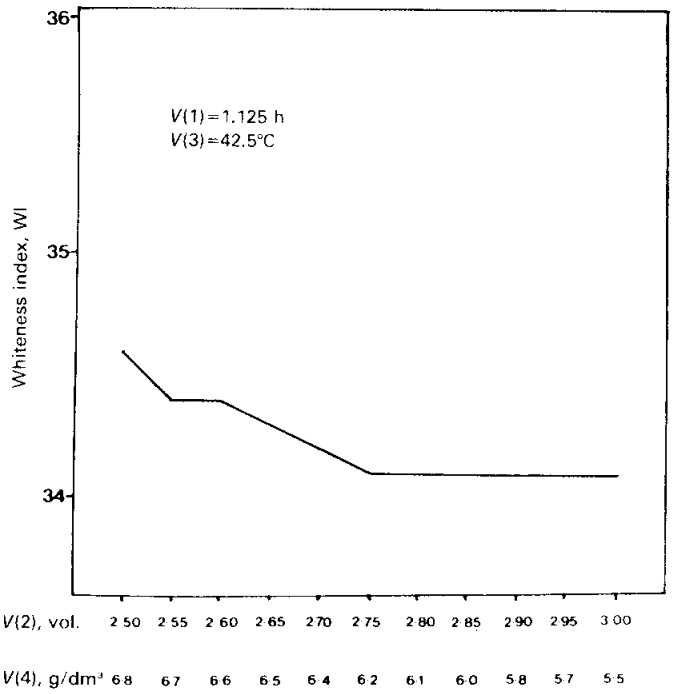

Figure 4 – Predicted whiteness index for conditions close to the optimum

TABLE 5

Optimum Bleaching Conditions

Variable	Optimum
Time, *V*(1)	1.125 h
H_2O_2, *V*(2)	2.8 vol.
Temperature, *V*(3)	42.5°C
Tubotex PC, *V*(4)	6.0 g/dm³

tions for a process may sometimes be obtained by partial differention of the fitted equation to obtain values of the variables at a stationary point in the response surface (e.g. maximum, minimum, point of inflection). Unfortunately, in this study this procedure predicted values at a stationary point for the responses well outside the range of the conditions chosen.

Stepwise regression analysis of trials 1–16 (i.e. full 2^4 factorial for alkali solubility and whiteness) was also performed. For alkali solubility the effects of temperature and stabiliser were confirmed as significant, whilst for whiteness index the significant effects were peroxide and stabiliser concentration.

Practical Test of the Recipe

Testing the recipe took the form of an examination of the robustness of the process, predicted results being compared with those observed.

Robustness

In this experiment all the variables were changed by ±10% from the optimum. In addition, two more runs were carried out with temperature varying by ±5%, but with the other variables at ±10%. These were included because of the system's high sensitivity to temperature variation. Data and results are presented in Table 6.

Clearly, the comparison between predicted and experimental results is quite good, in spite of earlier reservations about the quality of data for alkali solubility.

It is interesting to note the effect of extended time on the alkali solubility for *V*(2), *V*(3) and *V*(4) at their optimum values (Table 7). The first four rows suggest that alkali solubility passes through a shallow minimum, but this is unrealistic and a proper view would be that, over that part of the range, the alkali solubility will be insensitive to time. Clearly, process time can be doubled at optimum conditions before serious damage will occur to the wool.

TABLE 7

Effect of Time on Alkali Solubility

Time, *V*(1) (h)	Alkali solubility (%)
1.13	25.3
1.24	25.1
1.50	25.1
1.75	25.9
2.00	27.3
2.50	32.2
3.00	39.8

TABLE 6

Conditions, Predictions and Results for the Test of Robustness

	1		2		3		4		5	
Variables	Variables at −10%		As 1, but *V*(3) at −5%		Optimum		As 5, but *V*(3) at +5%		Variables at +10%	
Time, *V*(1), (h)	1.02		1.02		1.13		1.24		1.24	
Peroxide concn, *V*(2), (vol.)	2.54		2.54		2.82		3.10		3.10	
Temperature, *V*(3), (°C)	39.0		41.0		43.0		45.0		47.0	
Tubotex PC concn, *V*(4), (g/dm³)	5.40		5.40		6.0		6.60		6.60	
Response	*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*
Alkali solubility	19.2	17.2	21.3	18.8	25.3	22.9	32.7	29.8	36.0	37.9
Whiteness index	35.1	35.9	34.9	34.6	34.1	34.0	33.3	33.6	33.4	33.1
Yellowness index	21.6	23.2	21.6	22.3	21.3	21.6	20.9	20.7	20.9	20.6

General Comments

This experimental design has produced a recipe that has been verified in practice. It is most unlikely that another better optimisation exists outside the conditions chosen to represent industrial processing. It is equally unlikely that a better optimisation exists at a point much removed from that given here with the same constraints of time and damage. Examination of the robustness of the recipe, with respect to operator error, shows that temperature control is of paramount importance. Table 6 indicates that the working range should be from 41 to 43°C and must not exceed 45°C. This regime offers a saving in time of at least 60% over commercial recipes for phosphate stabilisers, which require 2.5–6.0 h (confidential survey).

Since the completion of this work, both pilot-plant and commercial trials have been carried out using the recipe. Pilot-plant trials on slubbing, yarn and cloth at liquor ratios, from 10:1 to 50:1 gave alkali solubilities very close to the predicted 25% with excellent values from reflectance measurements.

Commercial trials on slubbing and cloth, both at about 15:1 liquor ratio, achieved the predicted results. The bleached goods had excellent physical properties and gave no problems in subsequent processing.

* * *

The authors are indebted to Mr S N Myciunka for technical assistance.

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(The fact that chemicals with proprietary names are mentioned in this article in no way implies that there are no substitutes that may be of equal or better value.)