Application of the Method of the Experimental Design to the Study of a Processing of Unshrinkableness of Wool Fibers

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ABSTRACT: The objective of this study was to optimize the character of the unshrinkableness of wool fibers. A study of the processing of fibers of wool by an oxidative processing by performic acid was carried out by a complete factorial design to determine the most influential parameters of this study and then to optimize this process by the method of simplex. In parallel, a new ozone treatment was applied and a central composite design adapted to this protocol made it possible to identify the most influential parameters. This last type of processing has the advantage of being less polluting.
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Key words: enzymes; fibers; calculations

INTRODUCTION

A variety of shrinkproof finishes for textiles has been developed to prevent or to minimize their shrinkage during use and particularly during laundering.[1] Shrinkage of wool due to felting is the primary type of shrinkage for which such finishes are applied. There are essentially three general approaches that have been used to shrinkproof woolen textiles: These are pretreatment with oxiding agents, reducing agents, or solvents, treatment with oligomers or polymers, and combinations of the first two methods. Approaches using oxiding agents are the oldest methods and are commonly used for rendering wool shrink-resistant, which include dry and wet chlorine, dichlorocyanuric acid, potassium permanganate, peroxymonosulfuric acid, and ozone.[2–14] Sodium sulfite is the most commonly used reducing agent. Polar organic solvents or organic solvents mixtures are also employed as pretreatments. Earlier approaches for imparting shrink resistance to woolen fabrics with polymers used various crosslinking agents. More recent commercial approaches have improved the shrinkproofing processes by first pretreating the fiber (preferably par oxidative chlorination), followed by subsequent reduction to form reactive sites. Currently, the unshrinkable processing of wool fibers in industry is carried out in 90% of the cases according to a continuous process of preoxidation by a chlorinated solution followed of the deposit of a polymer of polyamide–epichlorhydrine (Hercosett 57®). However, the use of this kind of substance on an industrial scale is subjected to environmental restrictions, limiting the rejection of the organochlorinated compounds in the effluents. As these processes are being condemned, an activity of research has been developed to substitute chlorine by more neutral agents of oxidation on the environmental level. The use of enzymes, in particular proteases, on fibers made up of 95% protein content constitutes an interesting way but imposes, nevertheless, a preprocessing oxidizing of the surface, making it possible to prepare enzymatic hydrolysis.[15] Two satisfactory oxidants on the ecological level were planned to carry out this stage of preoxidation: acid performic and ozone. These two techniques are proving to be very promising; an optimization by the method of experimental design was thus undertaken.

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EXPERIMENTAL

Oxidation by performic acid

One volume of H_2O_2 (30% v/v) is introduced into 4 vol of HCO_2H (80% aqueous solution). After 2 h incubation at 25°C, the solution (eventually diluted in distilled water) is used extemporarily on wool fibers by respecting a report/ratio of bath of 1% (g of fiber/mL of oxidizing solution). After a variable time of application, the wool is rinsed abundantly with tap water and then with distilled water. The fiber samples are rinsed with distilled water and spun dry at 25

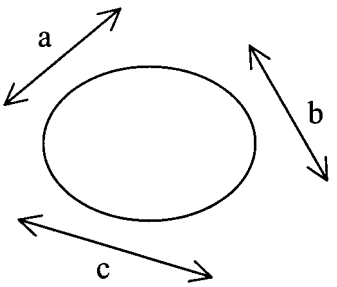

Figure 1 The felt ball does not form a perfect sphere. The average diameter of the felt ball is obtained by the calculation of the arithmetic mean of three measurements: a, b and c.

kg/cm^2 by a scarf ERNST BENZ Textilmaschinen Rünlang–Zürich and are dried 24 h at ambient temperature.

Oxidation by ozone

Ozone is generated by an ozonizer, an Ozat-1A® (Ozonia), starting from pure oxygen of more than 99%. The nominal production of the apparatus to a flow of 1 Nm^3/h of approximately 86 g O_3 h^{-1} is an output of the production of 6% (g/g). The exact concentration of ozone in oxygen is measured by UV photometry at 254 nm by an analyzer in line, a BMT 963 (Ozonia).

Dried wool fibers (10.05 ± 0.05 g) are immersed in 1 L of distilled water, which may contain hydrogen peroxide and/or NaOH. After drying, the fibers are placed in a closed enclosure through which an ozone flow circulates.

Measure whiteness and degree of yellow measurements

Measure whiteness and degree of yellow of wool fibers measurements were carried out by the company Prouvost Lefevbre according to standard IWTO 35-87(E): Wool (2.0 g) is equilibrated at 20 ± 2°C and at 65 ± 2% of relative humidity. The trichromatic parameters, green (X), yellow (Y), and amber (Z), of wool fibers are measured by a colorimeter HERE DIGITAL colorimeter. This apparatus is calibrated beforehand by a white sample or quasi-white, a black body, and a brilliant ceramics cream recommended by the manufacturer. The results are expressed by the calculation of the degree of white *W* (size without unit) in excellent agreement with the visual judgment of whiteness:

$$W = \sqrt{(100 - 0.94Y)^2 + (2.84X - 2.35Z)^2}$$

Whiteness is expressed in a unit of size which must be the weakest possible to approach absolute white. On the market, the maximum variations of this parameter oscillate between 52 for the least-white fibers and 42 for whitest. In a general way, the degree of yellow varies in a field of values ranging between 11 for the least-yellow fibers and 15 for the most yellow.

Measure diameter and percentage of fibers of diameter measurements (fineness)

Measure diameter and percentage of fibers of diameter higher than 30 μm measurements were carried out by the company Prouvost Lefevbre according to standard IWTO 12-95: The samples of wool cut in fragments of 1.8 × 2.0 mm are conditioned 24 h at 20 ± 2°C in an atmosphere whose relative humidity is fixed at 65 ± 2%. The fiber fragments are dispersed in a solution of 2-propanol that is 8% (v/v) in water. The suspension is transferred through a measuring cell positioned in the way of a laser ray of light. The reduction of the intensity of the laser beam caused by the passage of a fiber fragment insulated is measured by a detector. The signal is analyzed by a computer by comparison with the tables of calibrations. The average diameter (smoothness) and the percentage of fibers whose diameter is higher than 30 μm (percent $>$ 30 μm) are then directly calculated. This last parameter is a good indicator of the general state of the wool samples. Indeed, only the burst fibers have a diameter greater than 30 μm. This percentage must thus be the weakest possible to guarantee the integrity of the wool fiber samples.

Measure resistance or tenacity of wool fibers

This operation was carried out by the Institut Textile de France at Villeneuve d' Ascq (France) according to standard IWTO 32-82(E). Tenacity provides a measurement of the physical properties of wool fibers. This method is used in the textile industry to determine quantitatively the possible modifications and damage that might appear during the processing of

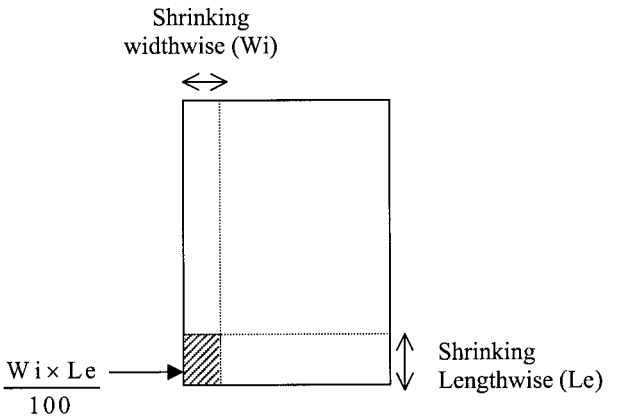

Figure 2 Diagrammatic representation of the dimensional modifications of wool knitting. The corrective factor (*Lo* × *La*/100) makes it possible to account only once for the withdrawal of the grayed surface localized in a surface of withdrawal common to *Lo* and *La*.

TABLE I
Experimental Domain and Coding of the Variables

Variables	Factors	Levels −1	Levels +1
X_1	U_1, Oxidation duration	5 min	15 min
X_2	U_2, Temperature of enzymatic treatment	35°C	55°C
X_3	U_3, HCO_3H concentration	0.083*M*	0.83*M*
X_4	U_4, Oxidation temperature	10°C	33°C

bleaching, dyeing, or resistance to the contracting. The fiber samples to be tested are conditioned 24 h in a standardized atmosphere: 20 ± 2°C and 65 ± 2% of relative humidity. The paralleled fibers are placed in a mobile system of a grip, applying a uniform pretensioning to the entire sample. During the test, the spacing of the grips involves the rupture of the package of fibers. Tenacity is defined as the ratio of the breaking strength to the linear density of the sample:

$$\text{Linear density (tex)} = \frac{\text{sample weight (mg)}}{\text{sample length (mm)}} \times 10^3$$

$$\text{Tenacity (cN/tex)} = \frac{\text{breaking strength (cN)}}{\text{linear density (tex)}}$$

The normal tenacity of a fiber of 21-μm diameter varies from 8.5 with 10cN/Tex.

Measure aptitude for felting

This method meets the standard IWTO: 20-69(F): A preequilibrated fiber (1.000 ± 0.005 g, 24 h at 20 ± 2°C, and 65 ± 2% of relative humidity) is introduced into 50 mL of phosphate buffer (50 m*M* adjusted at pH 7) and placed in an apparatus carrying out a three-dimensional rotary movement at a rate of 80 rotations per minute (Aachner Filzertest, ROSIK). Agitation is maintained for 60–90 minutes until a felt ball is obtained whose diameter does not evolve any more. After drying with the drying oven (50°C, 5 h), the average diameter (d_m) of the ball is calculated starting from three measurements carried out using a slide caliper as shown in Figure 1.

Felting moves in the ranges of values of 0.200–0.130 g/cm^3 for intense feltings, 0.130–0.100 g/cm^3 for average feltings, and 0.100–0.05 g/cm^3 for weak feltings. The densities lower or equal to 0.05 g/cm^3 are obtained only in the case of fibers perfectly unshrinkable; they remain not easily measurable.

Measure resistance to the contracting during machine washing

This operation was carried out by the Institut Textile de France of Villeneuve d' Ascq according to standard IWS TM31: The small quantities of fibers treated by the laboratory during this study do not make it possible to obtain fabric parts whose dimensions are sufficient to carry out the normally test IWS TM31. The aptitude for the contracting (or withdrawal) appreciated on knitting of only 100 cm^2 can thus be analyzed only by way of an estimate. The dimensional changes of the samples were measured after a cycle of washing 7A (stage of relieving of knitting) followed by of five drying cycles of washing 5A (stage of felting) and flat drying. The result is expressed by calculation of the percentage of the change of the surface of the wool knitting:

$$\%\text{ of surface change} = Le + Wi - \left(\frac{Wi \times Le}{100}\right)$$

with *Le* the percentage of change of length of knitting and *Wi* the percentage of change of the width of

TABLE II
Matrix and Responses (Whiteness, Degree of Yellow, Fineness, Tenacity, and Felting Density)

Run	X_1	X_2	X_3	X_4	U_1 (min)	U_2 (°C)	U_3 (*M*)	U_4 (°C)	Whiteness (*W*)	Yellow	Fineness (μm)	% > 30 μm %	Tenacity (cN/tex)	Felting density (g/cm^3)
1	−	−	−	−	5	35	0.083	10	41.9–42.1	10.8–10.6	21.15–21.25	4.3–4.4	8.33–8.63	0.179–0.184
2	+	−	−	−	15	35	0.083	10	40.7–40.9	10–10.2	21.30–21.4	5–4.9	8.24–8.54	0.17–0.175
3	−	+	−	−	5	55	0.083	10	41.7–41.5	10.4–10.2	21.20–21.3	4.7–4.8	7.78–7.48	0.168–0.163
4	+	+	−	−	15	55	0.083	10	40.3–40.5	10.2–10.4	21.15–21.25	4.5–4.4	8.21–8.41	0.17–0.167
5	−	−	+	−	5	35	0.83	10	41.9–42.1	11.5–11.3	21.45–21.35	4.8–4.7	8.52–8.82	0.214–0.21
6	+	−	+	−	15	35	0.83	10	45–44.8	14–14.2	21.40–21.3	4.8–4.8	7.81–7.51	0.211–0.216
7	−	+	+	−	5	55	0.83	10	47.1–47.3	13.7–13.9	21.1–21.2	4.2–4.3	7.69–7.39	0.184–0.18
8	+	+	+	−	15	55	0.83	10	46–46.2	12.1–12.3	21.20–21	4.6–4.6	6.55–6.85	0.120–0.125
9	−	−	−	+	5	35	0.083	33	40.9–40.7	10.6–10.4	21.15–21.25	4.1–4.1	8.28–8.58	0.190–0.185
10	+	−	−	+	15	35	0.083	33	40.3–40.5	10.6–10.4	21.45–21.35	4.3–4.4	8.34–8.55	0.192–0.19
11	−	+	−	+	5	55	0.083	33	40.7–40.9	10–10.2	21.20–21.3	4.3–4.4	8.32–8.22	0.168–0.163
12	+	+	−	+	15	55	0.083	33	40.4–40.2	10.5–10.3	21–21.1	3.9–3.8	8.24–8.47	0.174–0.17
13	−	−	+	+	5	35	0.83	33	46–46.2	14.3–14.1	21.5–21.6	4.9–7.8	7.54–7.87	0.199–0.195
14	+	−	+	+	15	35	0.83	33	47.3–47.5	14.8–14.6	21.6–21.5	5.7–5.8	5.09–5.3	0.098–0.093
15	−	+	+	+	5	55	0.83	33	48.3–48.1	15.8–15.9	21.25–21.35	5.1–5	5.27–5.6	0.069–0.064
16	+	+	+	+	15	55	0.83	33	51.5–51.3	17.1–17	21.9–21.8	7.3–7.2	2.75–2.98	0.09–0.095

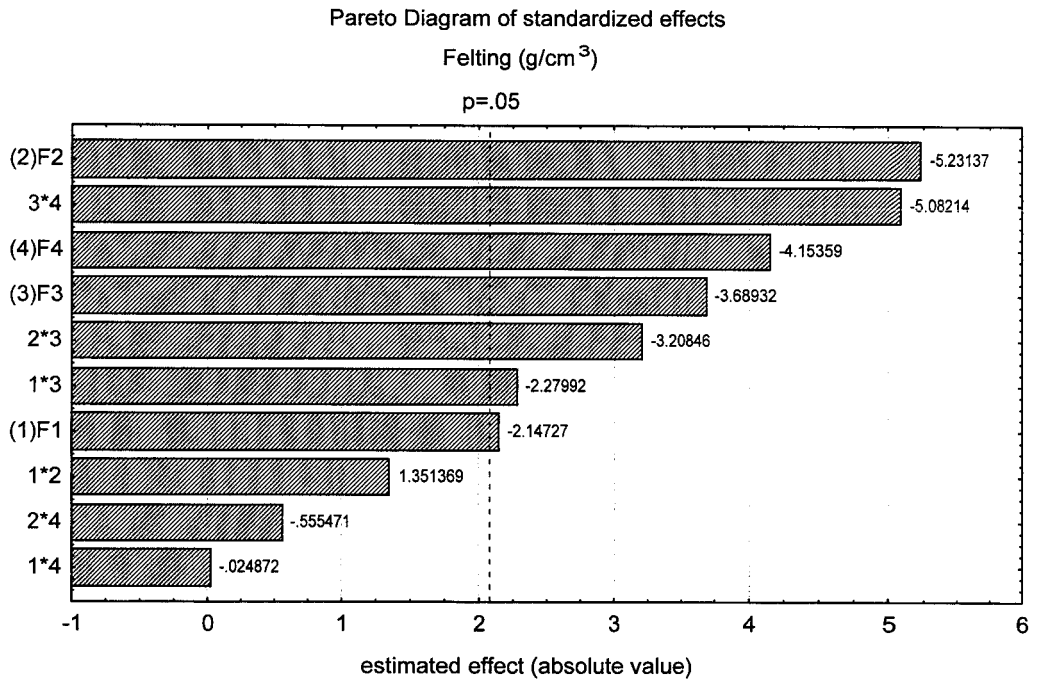

Figure 3 Pareto diagram of standardized effects for felting response according to Table III.

knitting. *Le* and *Wi* can take a positive or negative value according to the nature of the changes observed (+: relieving; −: withdrawal). The term ($Wi \times Le/100$) corresponds to a corrective factor shown in Figure 2, with *Lo* the percentage of change length of knitting and *La* the percentage of change of the width of knitting. *Lo* and *La* can take a positive or negative value according to the nature of the changes observed (+: relieving; −: withdrawal). The term ($Le \times Wi$)/100 corresponds to a corrective factor shown in Figure 2.

Within the framework of the European Standards, the maximum limits of withdrawal that are most drastic are applied to the fitting of the textile articles. In this case, the percentage of change of the surface at the end of cycle 7A followed by five cycles of 5A should not exceed −8%. This value of withdrawal thus corresponds to a lower limit not to be exceeded.

RESULTS AND DISCUSSION

Unshrinkable processing by preoxidation with performic acid and enzymatic hydrolysis by subtilisines

Methods

In this study, a complete experimental design factorial 2^4 (2 blocks)[16,17] was undertaken to study the influence of the following factors on the unshrinkable processing. The various factors as to their levels of variation are gathered in Table I. The factors measured on

TABLE III
Estimated Effects for Felting Density with Effect Value, Coefficient Value, Student Test, and *p(F)* Value as It Appeared in Pareto Diagram

Variable	Effect	Err-type	*t*(21)	*p*	−95.% Conf. lim.	+95.% Conf. lim.	Coefficient	Err-type Coefficient	−95.% Conf. lim.	+95.% Conf. lim.
Mean	0.161594	0.003769	42.87072	6.2E-22	0.153755	0.169432	0.162	0.00377	0.153755	0.1694325
(1)F1	−0.01619	0.007539	−2.14727	**0.0436**	−0.031865	−0.00051	**−0.008**	0.00377	−0.01593	−0.000255
(2)F2	−0.03944	0.007539	−5.23137	**3.5E-05**	−0.055115	−0.02376	**−0.02**	0.00377	−0.02756	−0.01188
(3)F3	−0.02781	0.007539	−3.68932	**0.00136**	−0.04349	−0.012135	**−0.014**	0.00377	−0.02174	−0.006068
(4)F4	−0.03131	0.007539	−4.15359	**0.00045**	−0.04699	−0.015635	**−0.016**	0.00377	−0.02349	−0.007818
1 * 2	0.010188	0.007539	1.351369	0.19096	−0.00549	0.025865	0.005	0.00377	−0.00274	0.0129325
1 * 3	−0.01719	0.007539	−2.27992	**0.03317**	−0.032865	−0.00151	**−0.009**	0.00377	−0.01643	−0.000755
1 * 4	−0.00019	0.007539	−0.02487	0.98039	−0.015865	0.01549	−9E-05	0.00377	−0.00793	0.007745
2 * 3	−0.02419	0.007539	−3.20846	**0.00422**	−0.039865	−0.00851	**−0.012**	0.00377	−0.01993	−0.004255
2 * 4	−0.00419	0.007539	−0.55547	0.58444	−0.019865	0.01149	−0.002	0.00377	−0.00993	0.005745
3 * 4	−0.03831	0.007539	−5.08214	**4.9E-05**	−0.05399	−0.022635	**−0.019**	0.00377	−0.02699	−0.011318

Estimated effects of variables: felting density G/CM3; R^2 = 0.83,503; Adj.: 75,648; 2**(4-0) plan; mean square = 0.0004547. Dependent variable: felting density G/CM3. Conf. lim., confidence limit.

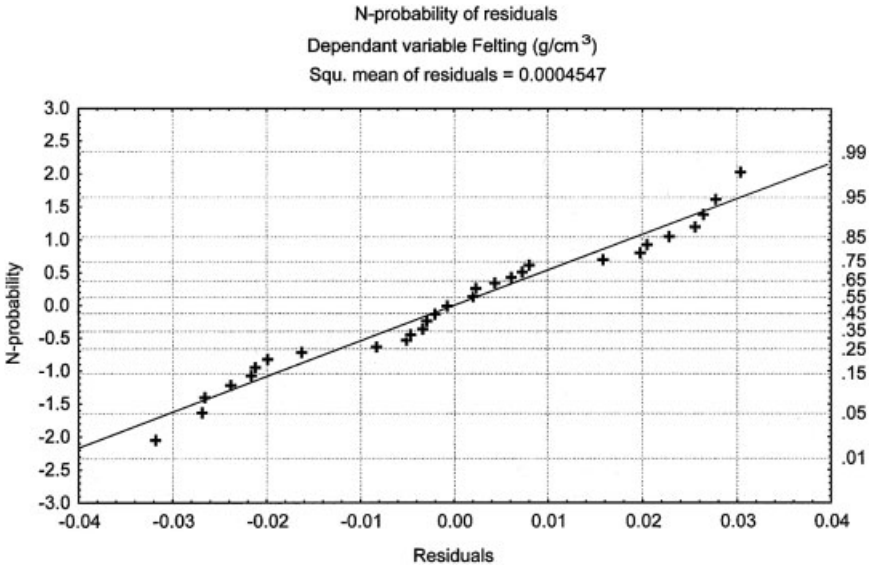

Figure 4 *N*-probability of residuals for the Felting response.

the treated fibers are the tenacity (resistance to the stretching in cN/tex) and the density of felting (g/cm^3), in which the reduction directly conditions the unshrinkable character of the fibers. Felting and tenacity are closely related to the structure of the wool; it thus acts as significant measurement. If a poor answer is obtained on these points, it encourages the abandonment of the processing.

Modde, Minitab 3.1, and Statistica[18–20] were used for the study and to generate results. Due to the numerous responses, only the general approach was developed and some of the tables afforded by the software were described as examples for all the responses. First, the responses were gathered in the design table (Table II). Second, we fit a full model by multiple linear regression and examine the model terms for significance. Then, we modify the model, if necessary, to improve the prediction by pooling nonsignificant model terms into error. ANOVA tables and *p*-values are useful for determining which terms can be removed from the model. The final model should maintain a hierarchical structure.

Then, we check the final model by examining studentized residuals and diagnostic plots. Finally, we generate contour and 3D plots to determine the region where a predicted optimum process outcome occurs.[21–25] Then, we use the predicted model and confidence intervals to narrow the settings of the factors. By changing one factor while holding the rest constant, we obtain a plot that can be useful to decide which axes to use on a contour or 3D plot. Then, we pick the factors that have the most complex behavior (most curved or steepest change rate) and use them as

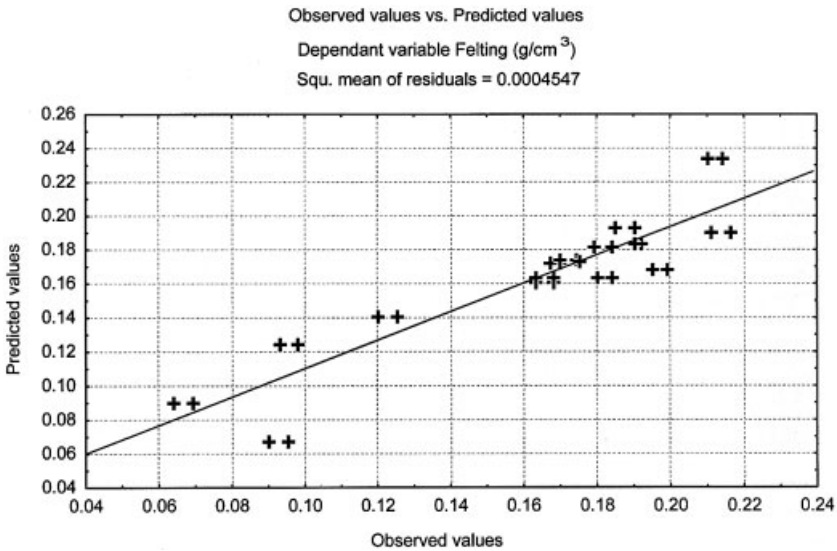

Figure 5 Observed values versus predicted values for the Felting response.

TABLE IV
Coefficients of the Factors and Interactions on the Whole Responses

	Whiteness (*W*)		Yellow		Fineness (μm)		% >30 μm (%)		Tenacity (cN/tex)		Felting density (g/cm^3)	
b	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient
Mean (b_0)	0	**43.8**	3E-29	**12.26**	0	**21.322**	2E-25	**4.78**	1.6E-30	**7.38**	6E-22	**0.1616**
b_1	0.136	0.19	0.2337	0.156	0.2154	0.0344	0.0075	**0.22**	8.6E-06	**−0.39**	0.0436	**−0.008**
b_2	6E-06	**0.73**	0.0764	0.238	0.0616	−0.053	0.5935	0.04	3.1E-07	**−0.4919**	3E-05	**−0.02**
b_3	1E-16	**2.89**	1E-12	**1.9**	0.005	**0.0844**	4E-05	**0.38**	7.1E-12	**−0.9088**	0.0014	**−0.014**
b_4	2E-05	**0.65**	5E-05	**0.65**	0.0143	**0.0719**	0.0383	**0.17**	6.6E-08	**−0.5425**	0.0005	**−0.016**
b_{12}	0.2684	−0.1	0.1996	−0.17	0.9086	−0.003	0.9671	0	0.38455	0.05937	0.191	0.0051
b_{13}	7E-05	**0.6**	0.1433	0.194	0.4254	0.0219	0.009	**0.22**	5E-07	**−0.4763**	0.0332	−0.009
b_{14}	0.0416	0.26	0.47	0.094	0.2154	0.0344	0.0874	0.13	0.00225	**−0.2325**	0.9804	−9E-05
b_{23}	8E-07	**0.84**	0.0186	**0.325**	0.9086	−0.003	0.2729	0.08	4.2E-05	**−0.3444**	0.0042	**−0.012**
b_{24}	0.8382	0.02	0.1314	0.2	0.4254	0.0219	0.0746	0.14	0.10186	−0.1144	0.5844	−0.002
b_{34}	9E-08	**0.96**	6E-05	**0.638**	0.005	**0.0844**	3E-05	**0.4**	5.6E-09	**−0.6288**	5E-05	**−0.019**

axes on the other plots. This will put the simplest (least interesting) dimensions off the graph.

The statistical analysis of the model was performed in the form of analysis of variance (ANOVA). This analysis included the Fisher's *F*-test (overall model significance), its associated probability $p(F)$, correlation coefficient *R*, and determination coefficient *R*2, which measures the goodness of fit of the regression model. It also includes the Student's *t* value for the estimated coefficients and the associated probabilities $p(t)$. ANOVA showed that the regression model was significant: As an example, if $p = 6.62$ *e*-09, then $P < 0.05$ when it is significant with good values of the coefficient of determination *R*2 (0.835).

This value represents the percent of variation in the data that can be *explained* by the fitted model. As an estimator, it usually overestimates how well the model fits the data because there is no penalty for adding additional terms to the model. The overall model fit is significant as evidenced by a *p* value of <0.05.

The mathematical equation which models the studied system is in the form of a polynomial of general formula:

$$Yi = b0 + \sum_i biXi + \sum_{i,j} bijXiXj + \varepsilon$$

where *Yi* is the predicted response; *xi, xj*, input variables which influence the response variable *Y*; *b*0, the offset term; *b*, the *i*th linear coefficient; *bi*, the *ij*th interaction coefficient, and ε, the experimental error.

Results and discussion

As example for felting, the Pareto diagram (Fig. 3) shows the $t(21)$ values for each coefficient. For the felting density, all the studied factors were significant (in bold in Table III) as it appeared in the ANOVA table of estimated effects (Table III), in the following order: *F*2 (−0.02), *F*4 (−0.016), *F*3 (−0.014), and *F*1 (−0.008). The significant interactions were the following: *F*3*F*4 (−.019), *F*2*F*3 (−0.012), and *F*1*F*3 (−0.009). The other interactions were nonsignificant.

Normal probability plots of the residuals (Fig. 4) are useful in examining the model and its assumptions. A studentized residual is the sample residual divided by the square root of its estimated variance. If the studentized residuals were the result of random noise (roughly normal), then they should plot along a straight line. When data falls far off this line, the model should be examined. In Figure 4, the points on this plot lie fairly close to the straight line, so the model seems appropriate.

Figure 5 shows the correlation between the experimental and the predicted data points for the felting response. For the same reason, when data fall far off the line, the model should be examined. In Figure 5, the points lie fairly close to the straight line so the model seems to be appropriate. The calculated effects are gathered in Table IV.

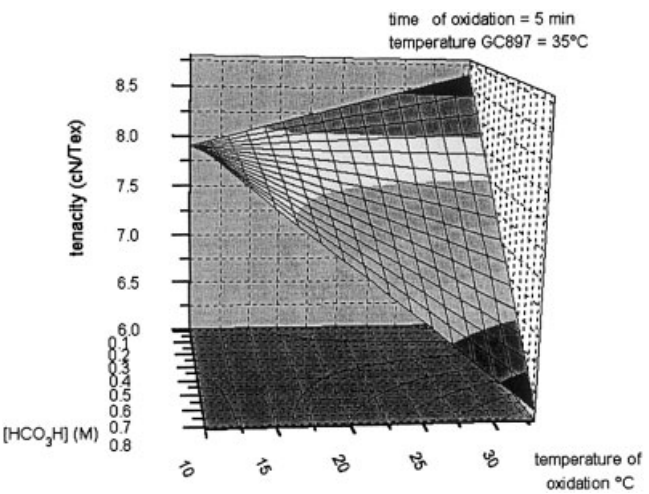

Figure 6 Surface response of tenacity according to the temperature of oxidation and the performic acid concentration.

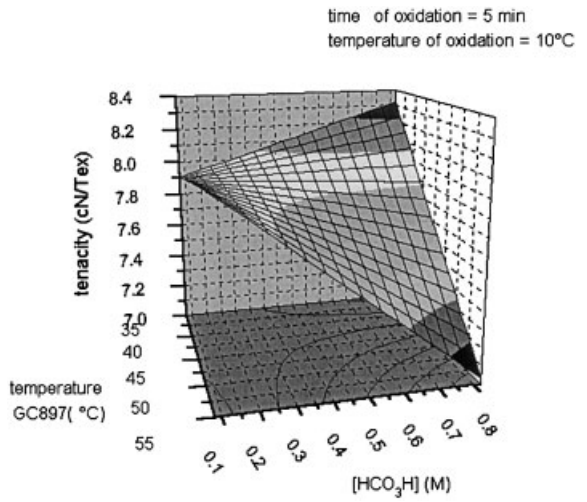

Figure 7 Surface response of tenacity according to the temperature of the enzymatic hydrolysis and the performic acid concentration.

The density of felting is one of the most significant parameters at the origin of this work. This density must be the weakest possible because it is partly responsible for the contracting to the washing of the fabric parts; we will also examine first the role of the various factors studied for this answer. It is noted that all the factors significantly improve the resistance of wool fibers to felting (and thus the contracting): The temperature of the enzyme treatment ($b2 = -0.02$), the concentration of the performic acid solution ($b3 = -0.014$), the temperature of the enzyme solution ($b4 = -0.016$), and, as a smaller influential value, the oxidation duration ($b2 = -0.008$). Unfortunately, a significant decrease of the tenacity of the fibers is also noted for these same factors (respectively, $b2 = -0.49$, $b3 = -0.3$, $b4 = -0.54$, and $b1 = -0.39$). Let us note

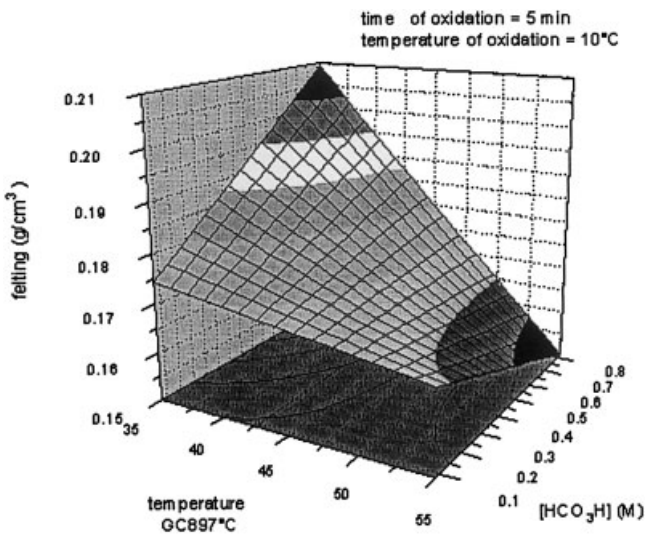

Figure 8 Surface response of the aptitude for felting according to the temperature of the enzymatic hydrolysis and the performic acid concentration.

TABLE V
Factors Studied by the Simplex Method

Variables		U_i^0	ΔU_i^0
X_3	Quantity of performic acid	10 mL	15 mL
X_4	Temperature of the enzymatic treatment	15°C	5°C

that there are two interactions between these factors ($b23$ and $b34$). The ideally largest possible tenacity is strongly decreased by the performic acid concentration ($X3$), the temperature of oxidation ($X4$), the temperature of the solution of proteases ($X2$), and, more modestly, by oxidation duration ($X1$). The interaction $b34$ is thus a significant interaction. These results corroborate those obtained with the percentage of the fibers whose diameter is higher than 30 μm and show that any processing by the acid performic will, unfortunately, involve the deterioration of the resistance of the fibers.

The mathematical equation which models the studied system is in the form of a polynomial of general formula:

$$Y = b0 + \sum biXi + \sum bijXiXj$$

Applied to tenacity, this expression becomes

$$Y = b0 + b1X1 + b2X2 + b3X3 + b4X4 + b13X1X3 + b14X1X4 + b23X2X3 + b34X3X4$$

with $b0 = 7.38$, $b1 = -0.39$, $b2 = -0.4919$, $b3 = -0.9088$, $b4 = -0.5425$, $b13 = -0.4763$, $b14 = -0.2325$, $b23 = -0.3444$, and $b34 = -0.6288$.

Applied to felting, the expression becomes

$$Y = b0 + b1X1 + b2X2 + b3X3 + b4X4 + b13X1X3 + b23X2X3 + b34X3X4$$

with $b0 = 0.162$, $b1 = -0.008$, $b2 = -0.02$, $b3 = -0.014$, $b4 = -0.016$, $b13 = -0.009$, $b23 = -0.012$, and $b34 = -0.019$. From these mathematical expressions, one has access to the surfaces of the answers (Figs. 6–8).

These curves illustrate perfectly the positive influence of the increase of the performic acid concentra-

TABLE VI
Construction of Simplex in Coded Variables

Run no.	X_1	X_2	X_3	⋯	X_{k-1}	X_k
1	0	0	0	⋯	0	0
2	A	B	B	⋯	B	B
3	B	A	B	⋯	B	B
4	B	B	A	⋯	B	B
⋯	⋯	⋯	⋯	⋯	⋯	⋯
k	B	B	B	⋯	A	B
$k+1$	B	B	B	⋯	B	A

TABLE VII
Experimental Conditions of Simplex

Experiment no. (u)	U_3 (mL)	U_4 (°C)	Simplex (exp. no.)	Felting (g/cm^3)	Tenacity (cN/tex)
Exp.1	10	15	Exp. 1, exp. 2, exp. 3 (I)	0.181	9.22
Exp.2	24.5	16.5		0.172	8.88
Exp.3	13.9	20		0.170	8.25
Exp.4	28.4	21.1	Exp. 2, exp. 3, exp. 4 (II)	0.191	8.64
Exp.5	40.0	17.6	Exp. 2, exp. 4, exp. 5 (III)	0.158	7.62
Exp.6	31.1	12.8	Exp. 2, exp. 5, exp. 6 (IV)	0.196	7.74
Exp.7	49.6	14.1	Exp. 5, exp. 6, exp. 7 (V)	0.189	7.21
Exp.8	53.5	18.9	Exp. 5, exp. 7, exp. 8 (VI)	0.148	6.73
Exp.9	42.9	22.4	Exp. 5, exp. 8, exp. 9 (VII)	0.111	6.25

tion and of the temperature of the enzymatic stage of hydrolysis on the reduction of the felting aptitude for the fibers. Unfortunately, these same factors to which the temperature of the oxidizing solution is added decrease the resistance (or tenacity) of the fibers. There is not, thus, a simple formulation making it possible to obtain unshrinkable processing while maintaining a sufficient tenacity.

With regard to the other answers of the experimental design, the percentage of fibers whose diameter is higher than 30 μm is an indicator of the physical state of the fibers. A significant value of this percentage can be the sign of the degradation of fibers by bursting. Table IV shows that the performic acid concentration $X3$ ($b3 = 0.38$), the oxidation duration $X1$ ($b1 = 0.22$), and the temperature of oxidation $X4$ ($b4 = 0.17$) were significant. This factor interacts also positively with the temperature of oxidation $X4$ ($b34 = 0.4$) and the oxidation duration $X1$ ($b13 = 0.22$). The yellowing of wool fibers is detrimental; it must be the weakest possible. The analysis of the effects (Table IV) shows that concentration of the agent of oxidation ($X3$) and the temperature of oxidation ($X4$) increases yellowing in a significant way ($b3 = 1.9$ and $b4 = 0.65$). The strong interaction $b34$ ($b34 = 0.638$) between these two factors is thus normal. Whiteness is a significant parameter being able to affect the commercial value of wool. Let us recall that its measurement is expressed in a unit of size which must be ideally the weakest possible to approach the absolute white. The three factors influencing this parameter are, by order of importance, the performic acid concentration ($X3$, $b3 = 2.89$), the temperature of the enzymatic processing ($X2$, $b2 = 0.73$), and the temperature of oxidation ($X4$, $b4 = 0.65$). Their respective effects, $b3$, $b2$, and $b4$, are positive sizes, which thus affect the whiteness negatively. The impact of the performic concentration in acid is such that significant interactions logically appeared with the factors $X2$ and $X4$ ($b23 = 0.84$ and $b34 = 0.96$). In the same direction, an interaction of $X3$ with the duration of oxidation $X1$ is also observable in spite of the weak influence of this last factor ($b13 = 0.6$). In the experimental field studied, any significant effect ($b0 = 21.32$ was largely superior to the significant effects as $b3$, $b4$, or $b34 = 0.08$) does not seem to influence the smoothness of wool fibers. Thus, this answer cannot be the subject of a mathematical modeling.

Optimization of the performic acid process by the simplex method

Optimization was continued on the two most influential factors of the preceding study by the method of simplex[26–29] to decrease the density of felting of fibers while imposing a minimal tenacity of 7.5 cN/tex. The levels are represented in Table V.

The simplex of the type I was chosen and its method of construction is described in Table VI with the following considerations:

$$A = \pm \frac{1}{(k\sqrt{2})}(\sqrt{k+1} + k - 1)$$

$$B = \pm \frac{1}{(k\sqrt{2})}(\sqrt{k+1} - 1)$$

where k is the number of optimized factors. The unfolding of simplex in natural variables and its progression are shown in Table VII.

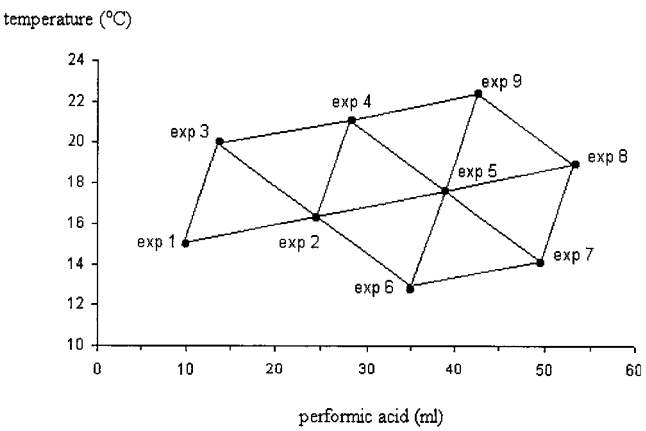

Figure 9 Progression of simplex with rotation around the optimal point corresponding to the experiment 5.

TABLE VIII
Factors Studied for the Ozone Treatment

Variables	Factors	Abbreviation	Levels	
			−1	+1
X_1	U_1 NaOH concentration	[NaOH]	0 m*M*	4 m*M*
X_2	U_2 proteases concentration for the hydrolysis solution	[GC 897]	0 μL/L	180 μL/L
X_3	U_3 hydrogen peroxide concentration	$[H_2O_2]$	0 m*M*	250 m*M*
X_4	U_4 ozone concentration	$[O_3]$	30 g O_3 m^{-3}	100 g O_3 m^{-3}

With the output of the 7th simplex (Table VII), we finish the study because the new point calculated by axial symmetry of the point of experiment 9 compared to the center of gravity of experiments 5 and 8 refers us to the operating conditions of experiment 7. As Figure 9 shows, the best compromise is obtained during experimentation 5. In this case (40 mL of performic acid solution and temperature enzymatic solution at 17.6°C), tenacity is equal to 7.62 cN/tex, which remains reasonable and allows a good spinning mill. The aptitude for felting is 0.158 g/cm^3, which corresponds to a profit of 12.7% compared to an untreated reference sample. A new processing of wool was examined by using ozone followed by enzymatic hydrolysis.

Unshrinkable processing by preoxidation with ozone and enzymatic hydrolysis by subtilisines

Methods

The use of ozone in the stage of preoxidation presents multiple advantages. This molecule does not produce undesired toxic products during its decomposition or during its reaction with proteins of wool. It can be used in the presence of various initiators as hydrogen

TABLE IX
Experimental Matrix of the Composite Experimental Design

Run no.	Factors (X_i)				Answer (Y)				
	X_1	X_2	X_3	X_4	Whiteness (W)	Yellow	Smoothness (μm)	% > 30 μm (%)	Felting (g/cm^3)
1	−1	−1	−1	−1	44.4	13.7	21.6	5.8	0.150
2	1	−1	−1	−1	43.8	11.4	21.6	5	0.142
3	−1	1	−1	−1	44.5	13.3	21.4	4.7	0.123
4	1	1	−1	−1	43.7	12.2	21.5	4.6	0.131
5	−1	−1	1	−1	40.2	11.7	21.5	5.6	0.126
6	1	−1	1	−1	41.2	11.75	21.6	4.9	0.118
7	−1	1	1	−1	41.2	11.1	21.4	4.8	0.096
8	1	1	1	−1	40.7	10.2	21.5	5.6	0.094
9	−1	−1	−1	1	44.7	12.3	21.5	4.6	0.050
10	1	−1	−1	1	43.4	12.3	21.2	4.7	0.050
11	−1	1	−1	1	42.6	13.2	21.0	4.5	0.050
12	1	1	−1	1	41.8	11.8	20.4	4.2	0.050
13	−1	−1	1	1	42.0	13.0	21.4	5.2	0.050
14	1	−1	1	1	42.7	12.6	21.0	4	0.050
15	−1	1	1	1	38.3	10.8	20.7	4.5	0.050
16	1	1	1	1	39.5	10.7	20.5	4.2	0.050
17	−1	0	0	0	41.2	11.9	21.0	4.6	0.050
18	1	0	0	0	41.4	11.8	20.7	4.1	0.050
19	0	−1	0	0	43.4	13.5	21.4	4.7	0.056
20	0	1	0	0	41.9	12.2	20.9	4.7	0.050
21	0	0	−1	0	44.3	13.5	21.1	4.7	0.050
22	0	0	1	0	40.7	11.7	21.6	5.6	0.050
23	0	0	0	−1	40.9	11.2	21.4	4.9	0.075
24	0	0	0	1	39.8	10.6	20.0	3.2	0.050
25	0	0	0	0	42.6	12.7	21.1	4.6	0.052
26	0	0	0	0	42.4	12.7	21.0	4.5	0.050
27	0	0	0	0	42.5	12.9	21.1	4.6	0.051
28	0	0	0	0	42.6	12.8	21.2	4.5	0.054
29	0	0	0	0	42.6	12.6	21.2	4.6	0.048
30	0	0	0	0	42.5	12.5	21.1	4.6	0.050

TABLE X
Estimated Effects for the Response Percent of Fibers >30 μm with Effect Value, Coefficient Value, Student Test, and *p*(*F*) Value as It Appeared in Pareto Diagram

Variable	Effect	Type-err	*t*(15)	*p*	−95.% Conf. lim.	+95.% Conf. lim.	Coefficient	Type-Err. Coefficient	−95.% Conf. lim.	+95.% Conf. lim.
Mean	4.5307	0.12702	35.67	**6E-16**	4.25997	4.801429	**4.5307**	0.12702	4.25997	4.801429
(1)*X*4 (*L*)	−0.62222	0.19276	−3.228	**0.0056**	−1.03307	−0.21137	**−0.311**	0.09638	−0.51654	−0.105687
*X*4 (*Q*)	−0.28947	0.50806	−0.57	0.5773	−1.37238	0.793436	−0.145	0.25403	−0.68619	0.396718
(2)*X*3 (*L*)	0.07778	0.19276	0.4035	0.6923	−0.33307	0.488627	0.0389	0.09638	−0.16654	0.244313
*X*3 (*Q*)	0.41053	0.50806	0.808	0.4317	−0.67238	1.493436	0.2053	0.25403	−0.33619	0.746718
(3)*X*2 (*L*)	−0.2	0.19276	−1.038	0.3159	−0.61085	0.210849	−0.1	0.09638	−0.30542	0.105425
X2 (*Q*)	1.31053	0.50806	2.5795	**0.0209**	0.22762	2.393436	**0.6553**	0.25403	0.11381	1.196718
(4)*X*1 (*L*)	−0.46667	0.19276	−2.421	**0.0286**	−0.87752	−0.05582	**−0.233**	0.09638	−0.43876	−0.027909
*X*1 (Q)	−0.88947	0.50806	−1.751	0.1004	−1.97238	0.193436	−0.445	0.25403	−0.98619	0.096718
1*L* * 2*L*	−0.1125	0.20445	−0.55	0.5902	−0.54827	0.323271	−0.056	0.10222	−0.27414	0.161636
1*L* * 3*L*	0.0625	0.20445	0.3057	0.764	−0.37327	0.498271	0.0313	0.10222	−0.18664	0.249136
1*L* * 4*L*	−0.1125	0.20445	−0.55	0.5902	−0.54827	0.323271	−0.056	0.10222	−0.27414	0.161636
2*L* * 3*L*	0.1875	0.20445	0.9171	0.3736	−0.24827	0.623271	0.0937	0.10222	−0.12414	0.311636
2*L* * 4*L*	−0.0375	0.20445	−0.183	0.8569	−0.47327	0.398271	−0.019	0.10222	−0.23664	0.199136
3*L* * 4*L*	0.3375	0.20445	1.6508	0.1196	−0.09827	0.773271	0.1688	0.10222	−0.04914	0.386636

Estimated effects of dependent variables: % of fiber >30 μm; $R^2 = 0.68{,}329$; adj.: 38,769; 4 Fact.; 1 Block; 30 obs.; square mean of residuals = 0.1671964. Conf. lim., confidence limit.

peroxide, as the hydroxide ions to produce radical species (OH in particular) are very reactive. We thus considered the use of this molecule within the framework of unshrinkable processing. A central composite experimental design was carried out to seek an optimum.[16–25] We studied the influence of the factors gathered in Table VIII.

No notable reduction in the resistance of fibers was noted in a preliminary feasibility study; the only measured answers are the average diameter of fibers and their aptitude for felting. The experiment matrix of the composite plan and the results are indicated in Table IX.

A central composite experimental design was established in three parts: a factorial design in two levels such as we have defined and used in the previous paragraphs, the experimental point placed in the center of the experimental domain, and, finally, the axial points. These last experimental points were placed on the axes of each factor and more remote from these to encircle the experimental domain.

These answered a particular criterion of optimization: The error of forecast of answers is the same for all the points of a sphere (or a hypersphere) centered at the origin of the experimental domain. It is the criterion of rotatibility. Distance α of the experimental points to the center of the domain is given, for a design without replicas by the formula $\alpha = [nc]^{1/4}$; *nc* is the number of the summits of the study domain. Here, *nc* was equal to 16 (2^4); the previous formula gives us $\alpha\ [nc]^{1/4} = 2$.

TABLE XI
Values of the Effects Calculated Starting from the Software

	Whiteness (*W*)		Yellow		Smoothness (μm)		% > 30 μm (%)		Felting (g/cm^3)	
b	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient	*p*	Coefficient
Mean b_0	2E-26	**42.126**	1E-21	**12.452**	5E-28	**21.041**	6E-16	**4.531**	1E-08	**0.048**
b_4 (*L*)	0.1764	−0.25	0.54	0.0694	0.0018	**−0.2611**	0.006	**−0.311**	7E-08	**−0.032**
b_4 (*Q*)	0.3996	−0.403	0.289	−0.3211	0.5346	−0.1158	0.577	−0.145	0.529	0.0056
b_3 (*L*)	1E-06	**−1.367**	2E-04	**−0.5361**	0.3905	−0.0611	0.692	0.039	0.0648	−0.007
b_3 (*Q*)	0.0594	0.9474	0.034	**0.6789**	0.328	0.1842	0.432	0.205	0.3376	0.0086
b_2 (*L*)	0.0006	**−0.761**	0.002	**−0.4028**	0.0628	−0.1389	0.316	−0.1	0.1411	−0.005
b_2 (*Q*)	0.1066	0.7974	0.162	0.4289	0.0522	0.3842	0.021	**0.655**	0.529	0.0056
b_1 (*L*)	0.4985	−0.122	0.004	**−0.375**	0.0541	−0.1444	0.029	**−0.233**	0.5632	−0.002
b_1 (*Q*)	0.0107	**−1.353**	6E-04	**−1.2711**	0.1652	−0.2658	0.1	−0.445	0.0545	0.0181
b_{12}	0.3163	0.1937	0.095	0.2094	0.7378	−0.025	0.59	−0.056	0.0632	0.007
b_{13}	0.0021	**−0.694**	0.316	−0.1219	0.1088	−0.125	0.764	0.031	0.1201	0.0058
b_{14}	0.8181	0.0437	0.23	0.1469	0.1457	−0.1125	0.59	−0.056	0.8602	0.0006
b_{23}	0.3808	−0.169	0.002	**−0.4406**	0.8669	0.0125	0.374	0.094	0.7783	−0.001
b_{24}	0.0672	0.3688	0.086	0.2156	0.7378	0.025	0.857	−0.019	0.8602	−6E-04
b_{34}	0.8181	−0.044	0.658	−0.0531	1	0	0.12	0.169	0.6991	0.0014

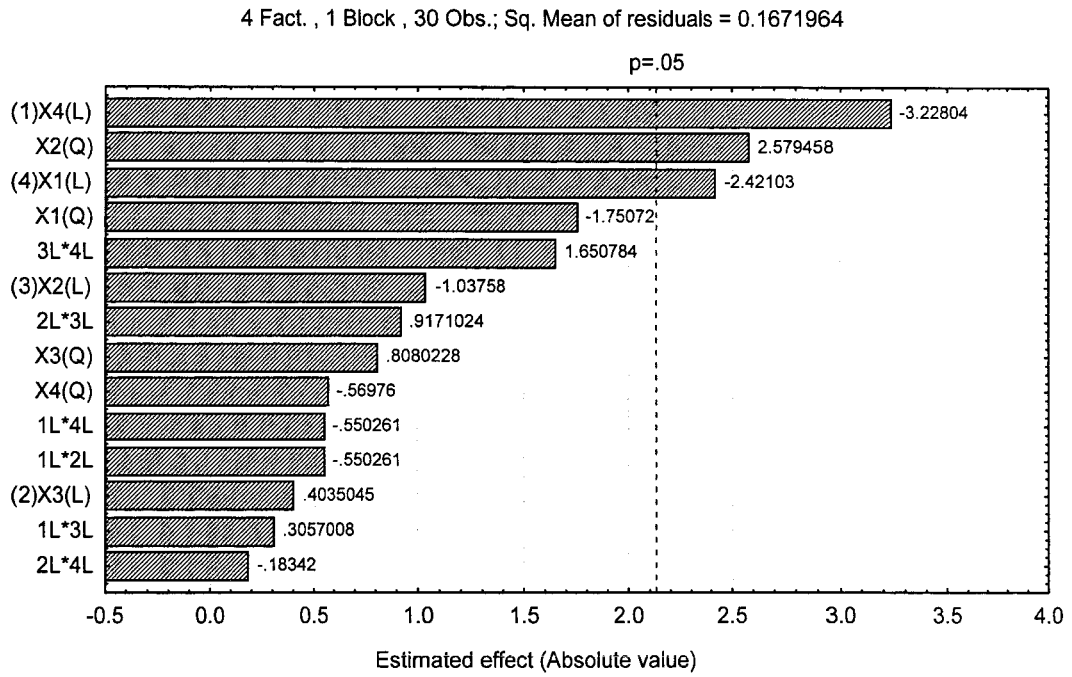

Figure 10 Paretodiagram of standardized effects for the response percent of fibers >30 μm according to Table X.

For reasons of experimental constraints, we did not take the value of $\alpha = 2$ but $\alpha = 1$, while respecting a symmetry of the matrix. The values of the effects relating to each factor are determined by matrix algebra according to the relation

$$b = (X^t X)^{-1} X^t Y$$

with X the experiment matrix, X^t the transposed experiment matrix, Y the matrix of the answers, and $(X^t X)^{-1}$ the reverse of the matrix of the matrix product of X^t by X.

Results and discussion

The effects and their significance relating to the factors and the effects of interactions between these factors were calculated using the software and are gathered in Table X (example of ANOVA table of estimated effects for the % of fibers >30 μm as an example) and Table XI (effect values accompanied by their errors for all the factors and their significance for all the responses). The significant effects appear in bold in Table XI. A Pareto diagram for only one response as an example was plotted and appears in Figure 10.

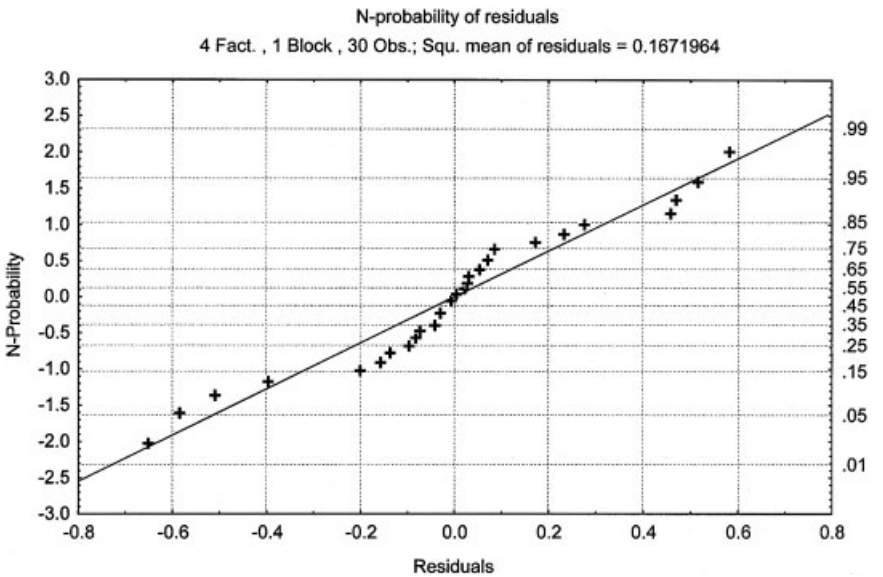

Figure 11 *N*-probability of residuals for the response percent of fibers >30 μm.

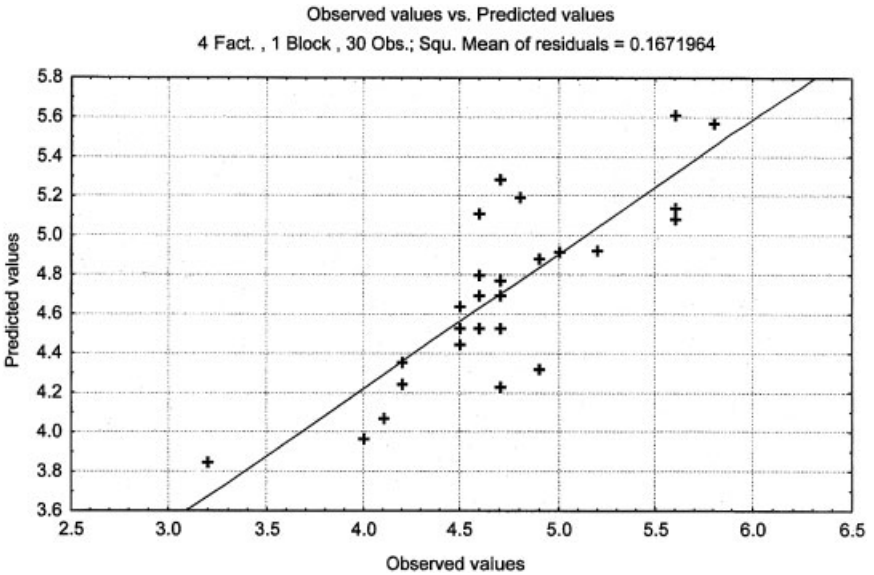

Figure 12 Observed values versus predicted values for the response percent of fiber >30 μm.

Normal probability plots of the residuals (Fig. 11) were obtained as for the preceding experimental design. As an example, for the *N*-probability plot of residuals for the response percent of fiber >30 μm, we observed that the points on this plot lie fairly close to the straight line, so the model seems appropriate.

Figure 12 shows the correlation between the experimental and the predicted data points for this response. The points lie fairly close to the straight line, so the model seems to be appropriate.

The central composite experimental design is represented by a polynomial of the second degree compared to each coded variable taken independently. This model is used to plot responses curves shown in Figures 13 and 14:

$$Yi = b0 + \sum_i biXi + \sum_i biiX_i^2 + \sum_{i,j} bijXiXj + \varepsilon$$

Coefficients of the effects were *bi* reported as *bi* (*L*) and *bii* reported as *bi* (*Q*) in the results and discussion (*L* represents linear coefficients and *Q* represents quadratic coefficients).

The observation of the curves shows a significant reduction in the aptitude for felting under the influence of the increase of the ozone concentration [effect *b*4 (*L*) = −0.032]. This tendency was confirmed by the realization of a test of withdrawal to the washing of a wool fabric made starting from a sample treated by the ozone and hydrolyzed by the proteases of GC 897. In addition, we noted a clear reduction in the average

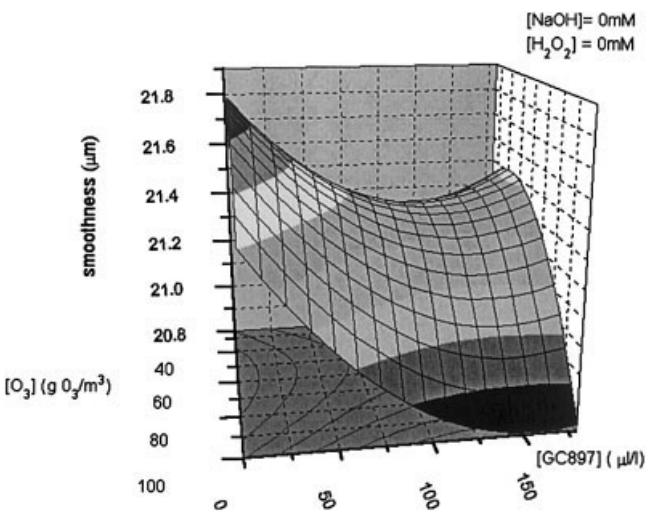

Figure 13 Response curve relative to the evolution of the smoothness (average diameter) according to the most influential factors.

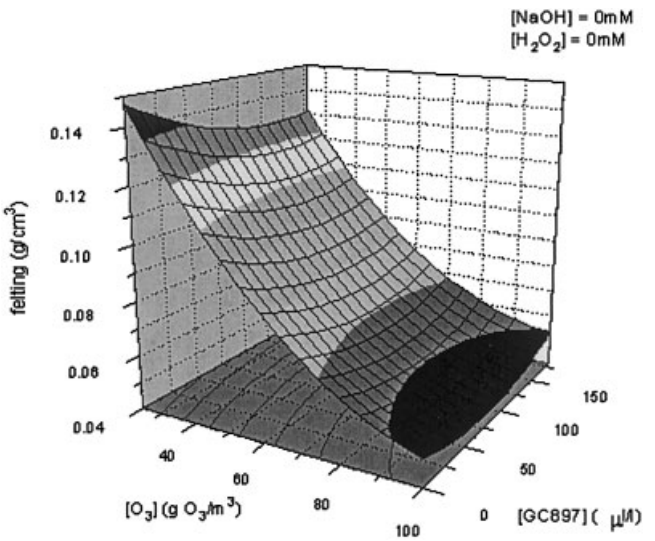

Figure 14 Response curve relative to the evolution of the felting according to the most influential factors.

diameter of wool fibers under the influence of the ozone concentration [effect $b4$ (L) = −0.311] and of the NaOH concentration [effect $b1$ (L) = −0.233 and $b1$ (Q) = 0.655]. This evolution shows well that part of the attack was directed toward the surface of the fiber. Let us note that if a substantial matter loss can be considered by this processing no deterioration of the resistance of the fibers was observed.

CONCLUSIONS AND PERSPECTIVES

With the output of these various studies, ozonation seems more interesting than that based on performic acid.[30] It indeed has several advantages:

- It makes it possible to generate very reactive species as radicals with respect to fibers, which makes it possible to consider a shorter processing run (≤10 min).
- Contrary to the processing based on performic acid, it thus limits the aptitude for felting to the contracting without affecting the resistance of the fibers.
- It is completely ecological after thermal destruction of the ozone.
- The very useful bleaching of wool fibers in the wool industry can be awaited.

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