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Flame retardant wool using zirconium oxychloride in various acidic media optimized by RSM

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ABSTRACT

The flame retardant wool was prepared using zirconium oxychloride with various acids. The thermal degradation of wool treated with the flame retardant synergistic system, zirconium oxychloride, citric acid and hydrochloric acid, was studied by thermal analysis, mass loss, limiting oxygen index (LOI) and vertical flame test. The fabric surfaces were also observed by SEM. The wool treated with the flame-retardant shows an increase in the decomposition temperature, residual mass and LOI. Also the wool treated with hydrochloric acid showed improved flame retardant properties compared to the use of formic acid. The response surface methodology (RSM) was also used for the experimental plan with four variables on the results of flame retardancy. The statistical analysis confirms the optimum conditions obtained by the experimental results.

1. Introduction

The flammable nature of fibrous products is one of the major problems of the present time. Fires from textiles are causing many deaths and injuries and considerable financial losses. Hazards from flammable fabrics have been recognized for many centuries, and repeated attempts have been made to control them [1].

Naturally occurring polyamide fibers, such as the sheep wool, display a high degree of natural flame retardancy [1]. Wool, a protein fiber, contains many kinds of α-amino acids such as cysteine, thiocarbamic acid, and cross-linking polypeptides with a helical structure [1].

The natural flame-resistant properties of the wool are connected with its relatively high nitrogen content (16%) [1], high moisture content (10–14%) [2], high ignition temperature (570–600 °C) [3], low heat of combustion, low flame temperature and high limiting oxygen index [4]. The performance of wool fabrics in the various test methods currently in use depends on the specified method and fabric construction. A horizontal method is much less severe than a 45° or a vertical test. Most wool fabrics will pass a horizontal test but may not pass some 45° or vertical tests. It follows that wool in some cases needs a flame-resist treatment in order to pass particular flammability specification and test method. Curtain and wall covering in public building, aircraft furnishings and blankets, furnishings and curtains in general transport, protective clothing and carpets of shag pile construction and low density are products which may require such treatment [5]. It has previously been proposed to apply titanium compounds to textile fibers as flame-retardant agents. Such compounds are not always suitable when wool fibers are used because they can cause yellowing. Moreover, although the process is satisfactory for many purposes, it is not entirely suitable for the manufacture of bleached wool.

Wool, when heated alone, pyrolyses by a complex series of reactions which yield a number of products at increasing temperatures. Initially at 230–240 °C rupture of the helical structure occurs and the major ordered part of the wool protein undergoes a solid to liquid phase change [6]. At 250–295 °C an endothermic reaction occurs associated with release of sulphur compounds due to the breaking of the cystine disulphide bonds and simultaneous release of hydrogen sulphide. Above 250 °C general pyrolytic decomposition occurs, including char-forming reaction with dehydration and loss of other volatiles. In the presence of air, formation of sulphur dioxide occurs between 270 °C and 320 °C [6]. Cleavage of the cystine disulphide bond is seen to play a very important role in the thermal degradation and combustion of keratin and it

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Table 1
Experimental for flame retardant wool based on CCD.

Run number	A: Zirconium oxychloride (%)	B: Temperature (°c)	C: Citric acid (%)	D: HCl (37%) (%)	Char length (cm)
1	10.60	95.00	12.80	5.65	1.3
2	5.60	77.00	12.80	5.65	1.4
3	8.10	70.86	9.55	8.00	1.35
4	8.10	86.00	9.55	8.00	1.05
5	8.10	86.00	9.55	4.05	1.25
6	10.60	77.00	6.30	10.35	1.3
7	8.10	86.00	9.55	8.00	1.1
8	8.10	86.00	9.55	8.00	1.0
9	8.10	101.14	9.55	8.00	1.0
10	8.10	86.00	9.55	8.00	1.05
11	8.10	86.00	9.55	8.00	1.0
12	12.30	86.00	9.55	8.00	1.5
13	5.60	95.00	6.30	10.35	1.65
14	5.60	95.00	12.80	10.35	1.45
15	3.90	86.00	9.55	8.00	1.85
16	8.10	86.00	15.02	8.00	1.45
17	8.10	86.00	4.08	8.00	1.15
18	10.60	77.00	12.80	10.35	1.3
19	5.60	7.00	6.30	5.65	2.0
20	10.60	95.00	6.30	5.65	1.5
21	8.10	86.00	9.55	11.95	1.1

has been suggested that the oxidation of cystine may be the initial exothermic reaction in the burning of wool [6]. Few reports have been published on the systematic study of the decomposition parameters of wool treated with flame retardant reagents [7,8].

The present study has optimized a process for improving the flame-resist properties of natural protein fibers which comprises depositing in the fibers a complexed zirconium compound and thermal degradation of treated wool and raw wool were investigated.

In recent years there have been a number of reports of treatments which enhance wool natural flame-resistant properties [9–13]. Benisek in the International Wool Secretariat Laboratories observed that mordanting treatments based on zirconium and titanium salts markedly improve wool flame resistance [9–11]. We have also reported the effect of zirconium oxychloride with formic acid on wool and showed an improvement in the flame retardant properties of wool fabrics [1].

Response surface methodology (RSM) may be used for an experimental plan with a number of variables on the results of flame retardancy. Response surface methodology is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. The most extensive applications of RSM are in the particular situations where several input variables potentially influence some performance measure or quality characteristics of the process. Thus a performance measure quality characteristic is called the response. The input variables are sometimes called independent variables, and they are subject to the control of the scientist or engineer. The field of response surface methodology consists of the experimental strategy for exploring the space of the process or independent variables. Empirical statistical modeling may then be used to develop an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response [14].

In the work reported in this paper, a vertical flame test and Differential Scanning Calorimetric (DSC) and Thermogravimetry (TG) were used to study the flame resistance and thermal behavior of wool fabric. Also scanning electron microscopy (SEM) and Energy Dispersive X-ray Microanalysis (EDXS) were used to study the surface morphology of the treated wools.

2. Experimental

2.1. Materials

The wool fabric with plain woven structure from 48/2 Nm yarns was supplied by Iran Merino. The fabric was scoured with 0.5% of a nonionic detergent at 50 °C for 30 min (L:G = 40:1) and then washed with tap water, and dried at room temperature. The zirconium oxychloride (35% ZrO_2) used in this study was supplied by Shanghai Yancui Co, China. hydrochloric acid and citric acid were obtained from Merck, Germany.

2.2. Preparation and application of flame retardant

Hydrochloric acid and citric acid were mixed with $ZrOCl_2$ according to Table 1, after which water was added until each solution achieved a liquor to wool ratio L:G = 20:1.

Hydrochloric acid was added to each of the above flame retardant solutions in order to maintain a pH = 2 during the exhaustion process. The wool treatment was started at 40 °C for 20 min and the temperature was raised for 30 min to the specified temperature and heated for 45 min. After being exhausted, the treated samples were rinsed with tap water and dried at room temperature. Finally, the modified wools were subjected to vertical flame testing.

2.3. Flammability test

The criterion for flame retardation in the present work is that the fabric must pass the rigorous test prescribed by the United States Federal Aviation Administration (F.A.A. test) [15]. Briefly, this test requires the burning of a vertically held fabric in a draft-free cabinet, in accordance with Federal Test Method Standard 191, Method 5903. A minimum of three specimens must be tested and the averages results reported. A flame 76 mm (3.2 in.) high is applied to the fabric, which is held 19 mm (3/4 in.) above the top edge of the burner. The flame is held in position for 12 s and then removed. For a sample to pass the test, the average burn length must not exceed 20 cm (8 in.), and the average flame time after removal of the flame source must not exceed 15 s.

2.4. Limiting oxygen index (LOI)

The LOI value is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support complete combustion of a

Table 2
Range of variables.

Variable	Lower limited	Upper limited
Temperature (°c)	77	95
Zirconium oxychloride (%)	5.60	10.60
Citric acid (%)	6.30	12.80
Hydrochloric acid (37%) (%)	5.65	10.35

vertically held sample that burns downward from the top. The higher the LOI value, the more efficient is the flame-retardant treatment. The LOI values were determined in accordance with ASTM D2863-06 by means of a General Model Stanton Redcroft FTA Flammability unit.

2.5. Thermogravimetry (TG)

Wool fabrics were performed in a TGA-PL thermogravimetric analyzer (Polymer Laboratories, UK) using a platinum crucible of 70 μL. The following analytical conditions were used, sample mass: 4.72 mg; initial temperature: 30 °C; final temperature: 600 °C; heating rate: 10 °C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

2.6. Differential scanning calorimetric (DSC)

Wool fabrics were tested in a DSC-Maia-200 F3 unit (Netzsch, Germany) with micropunched aluminum pans of 40 μL. The testing conditions were: sample mass: 13.43 mg; initial temperature: 20 °C; final temperature: 600 °C; heating rate: 10 °C min-1; purging gas: nitrogen 50 mL min^{-1}.

2.7. Scanning electron microscopy (SEM)

The wool fabrics morphology was observed by scanning electron microscopy (VEGA TESCAN, Czech Republic). The samples were fixed to SEM holders and coated with a thin layer of gold prior to SEM investigation with 15 and 20 kV beam voltages.

2.8. Experimental design

The central composite design used for experimental plan along with obtained response is shown in Table 1. Four variables including amounts of zirconium oxychloride, Hydrochloric acid and citric acid, and temperature were studied. The ranges of different variables are shown in Table 2. Also the influence of the variable on the results char length (C.L.) in centimeter is fitted in the following second order polynomial function (Eq. (A1)):

$$\text{C.L.} = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum c_i x_i^2 \qquad i \geq j \quad i = 1, 2, 3, 4 \tag{A1}$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i are regression coefficients that explain the influence of the variables in their linear form, b_{ij} are regression coefficients of the interaction terms between variables, and c_i are the coefficients of quadratic form of variables. The estimation equation regression coefficients b_i, b_{ij}, c_i along with determination coefficient R^2 are presented in Table 3.

3. Results and discussion

3.1. Thermal behavior

The thermal behaviors of the raw and wool treated with 8.96% $ZrOCl_2$, 9.85% citric acid, 9.01% hydrochloric acid at 95 °C obtained by TG and DSC curves are shown in Figs. 1 and 2. The thermal parameters can be obtained from DSC and TG curves as listed in Table 4. It can be seen from the figures that three separate processes take place during wool heating process. The first endothermic process, occurring from 30 °C to 160 °C and is accompanied by a decrease of 7% in wool fibers mass and is ascribed to the loss of water. It is considered that there are three different types of water within the fiber, i.e.: free water, loosely bonded water and chemically bonded water. As a consequence, the loss of water, as recorded by the thermogravimetric curve, is the result of the overlapping of three different processes in which the three types of water are lost.

Table 3
Regression coefficients and determination coefficient.

C.L. coefficient	Char length
b_0	14.45760
b_1	−0.67616
b_2	−0.15713
b_3	−0.41866
b_4	−0.28394
c_1	0.037199
c_2	6.87844E−004
c_3	9.45889E−003
c_4	0.010089
b_{12}	7.95766E−004
b_{13}	9.23077E−003
b_{14}	−0.015584
b_{23}	8.54701E−004
b_{24}	1.58129E−003
b_{34}	9.81997E−003
R^2	0.8949

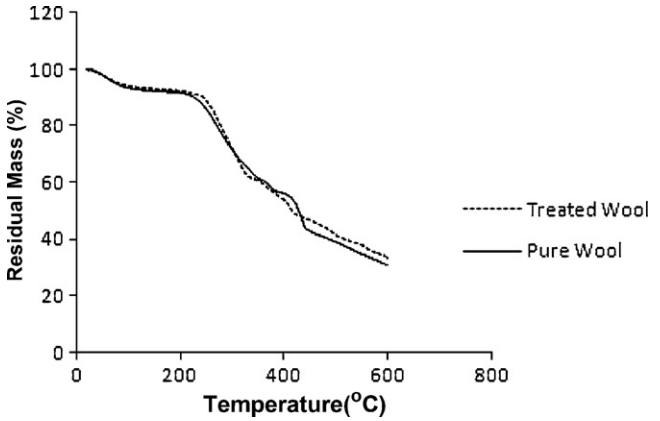

Fig. 1. Comparison of TG curve of raw wool and treated wool.

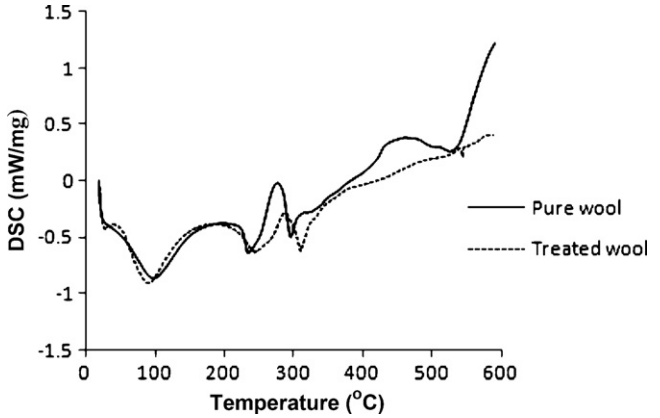

Fig. 2. Comparison of DSC curve of raw wool and treated wool.

Table 4
The thermal properties of second pyrolysis process of wool with and without flame-retardant treatment.

Sample	Temperature range (°C)	Mass loss (%)
Raw wool	190–330	38.16
Treated wool[a]	227–344	38.84

[a] Sample was obtained with 8.96% ZrOCl2, 9.85% citric acid, and 9.01% hydrochloric acid at 92 °C.

The second important endothermic process, occurring from 190 °C to 350 °C and accompanied by about 38% loss of wool fiber mass, is associated with the destruction of disulphide linkages and the elimination of H_2S, followed by the thermal pyrolysis of the chain linkages, peptide bridges and some other lateral chains, which finally leads to backbone degradation [16]. Consequently, this pyrolytic region includes several chemical reactions in which protein compounds are decomposed to smaller products and volatile compounds such as H_2S, CO_2, H_2O and HCN [16]. As presented in Fig. 1, TG curve of the treated sample shows a high decomposition temperature and an increased mass loss compared with raw wool (see Table 4). The wool treated with zirconium oxychloride and hydrochloric acid compared to wool treated with zirconium and formic acid (mass loss 46.05) [1] shows a decrease in mass loss during the second endothermic process. It is the fact that the presence of $ZrOCl_2$ and citric acid, which reacts in the condensed phase, could increases the number and extent of reactions forming volatile products. However application of hydrochloric acid instead of formic acid leads to decrease in the amount of volatile evolved products. These findings have been reported in the previous paper [1].

The third process is an exothermic reaction where the char oxidation reactions dominate. The presence of the flame retardants appears to have resulted in increased char (see Fig. 1) reported to be a cross-linked complex, which has a graphite-like structure, which has a higher than expected resistance to oxidation [16]. From Table 5, it is evident that the residual char and the LOI values for wool with flame-retardant treatment is more than that of the untreated wool. The data presented in the Table 5 show a little degree of charring effect of FR treated wool as compared with row wool. It is possible that Zirconium compounds promote the shielding effect of the complex char layer formed during combustion. These data suggest that the combustibility of the treated wool is reduced. Also DSC curves show a decrease in the enthalpies from 140.2 J g^{-1} for raw wool to 9.6 J g^{-1} for treated wool.

The wool treated with HCl compared to the wool treated with formic acid has been reported to show more residual chars and increased LOI which is caused by the increase in absorption of zirconium by the wool under acidic conditions [1]. This can be evaluated with EDXS analysis. The increase in zirconium absorption in wool treated with hydrochloric acid is probably caused by the increase in positive charge in wool (NH_3^+).

3.2. Statistical analysis

The analysis of variance (ANOVA) is given in Table 6. It can be concluded that all terms in this model are significant. According to the ANOVA results, the fitted model is (Eq. (A2)):

$$\begin{aligned}\text{C.L.} = {} & +(14.45760)+(-0.67616\times A)+(-0.15713\times B)\\ & +(-0.41866\times C)+(-0.28394\times D)\\ & +(7.95766E-004\times A\times B)+(9.23077E-003\times A\times C)\\ & +(-0.015584\times A\times D)+(8.54701E-004\times B\times C)\\ & +(1.58129E-003\times B\times D)+(9.81997E-003\times C\times D)\\ & +(0.037199\times A^2)+(6.87844E-004\times B^2)\\ & +(9.45889E-003\times C^2)+(0.010089\times D^2) \qquad \text{(A2)}\end{aligned}$$

In this equation, *A*, *B*, *C* and *D* are zirconium oxychloride (wt%), temperature (°C), citric acid (o.w.w. %) and hydrochloric acid (o.w.w. %), respectively.

The response surface of the model shows in Fig. 3. By using Design Expert Package software the optimum design point with total desirability of 100% is: 92.23 °C temperature, 8.96% zirconium oxychloride, 9.85% citric acid and 9.01% hydrochloric acid.

3.3. SEM

SEM was utilized in considering of the effect of zirconium compounds on the wool fiber and fabric surfaces. For the treated wool some particles of zirconium salt has been observed on the fiber surface (Fig. 4). The wool sample treated with 8.96 wt% zirconium oxychloride indicated an aggregation of zirconium on the edge of scales and scattering on the fiber surface randomly. Existence of zirconium element and other elements on the wool treated surfaces is investigated by EDXS analysis and is reported in Table 7 following the analysis of one of the particles observed in Fig. 4. The results of Table 7 shows that treated wool with hydrochloric acid are capable of adsorbing more salts compared to the wool treated with formic acid (4.97 wt%). These results are in accord with the results of thermal behavior part.

Table 5
The thermal properties of wool with and without flame-retardant treatment.

Sample	Temperature range (°C)	Residual mass (%)	LOI (%)	Enthalpy (J g^{-1})
Raw wool	391–597	30.80	25.4	140.2
Treated wool[a]	428–599	33.34	31.9	9.6

[a] Sample was obtained with 8.96% $ZrOCl_2$, 9.85% citric acid, and 9.01% hydrochloric acid at 92 °C.

Table 6
ANOVA for response surface quadratic model.

Source	Sum of squares	DF	Mean square	*F* value	*p*-Value Prob > *F*
Model	1.38	14	0.099	3.65	0.0600
A-$ZrOCl_2$	0.061	1	0.061	2.27	0.1829
B-Temp	0.061	1	0.061	2.27	0.1829
C-Citric acid	0.018	1	0.018	0.67	0.4459
D-HCl	0.011	1	0.011	0.42	0.5426
AB	1.062E−003	1	1.062E−003	0.039	0.8494
AC	0.045	1	0.045	1.67	0.2444
AD	0.028	1	0.028	1.03	0.3498
BC	5.000E−003	1	5.000E−003	0.19	0.6821
BD	3.706E−003	1	3.706E−003	0.14	0.7238
CD	0.045	1	0.045	1.67	0.2444
A2	0.81	1	0.81	29.89	0.0016
B2	0.046	1	0.046	1.72	0.2380
C2	0.15	1	0.15	5.52	0.0571
D2	0.046	1	0.046	1.72	0.2380
Residual	0.16	6	0.27		
Lack of fit	0.16	2	0.078	44.32	0.0019
Raw Error	7.000E−003	4	1.750E−003		
Cor. total	1.54	20			

Table 7
Elements analyzed of wool treated (normalized) (wt%).

Sample	Zr	S	Cl	Au	Total
Treated wool[a]	6.74	2.13	0.46	90.68	100

[a]Sample was obtained with $ZrOCl_2$ of 8.96%, citric acid of 9.85% and hydrochloric acid of 9.01% at 92 °C.

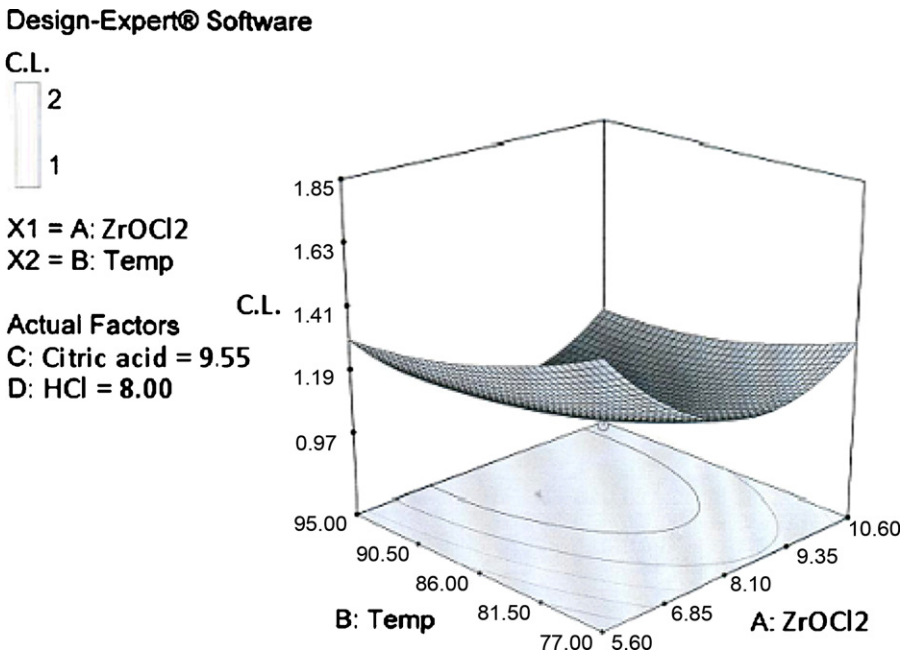

Fig. 3. 3D plot of A and B with their continue plot.

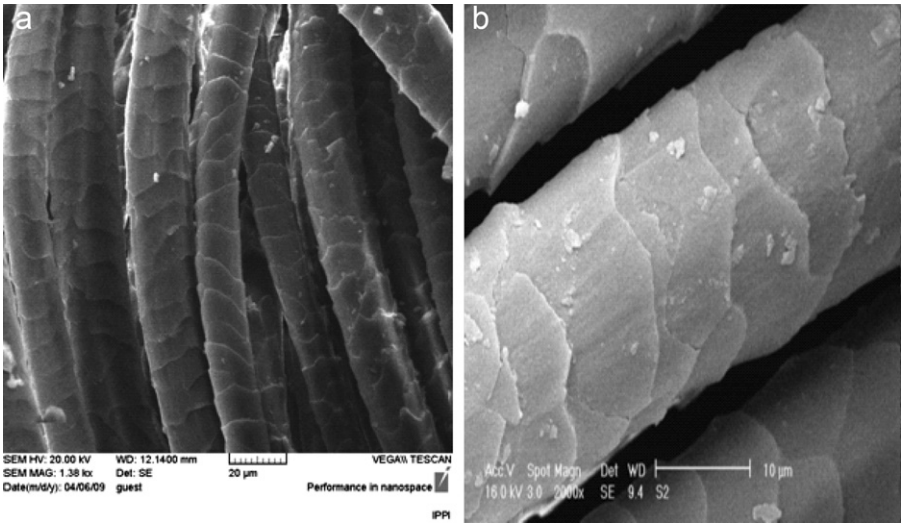

Fig. 4. SEM of (a) raw wool and (b) wool treated with 8.96% ZrOCl2, 9.85% citric acid, 9.01% hydrochloric acid at 92 C (L:R = 20:1).

4. Conclusions

The treatment of wool with $ZrOCl_2$ and citric acid accelerates the formation of non-combustible gases from the fiber. In comparison of untreated wool, the gases are decomposed at a temperature below the ignition temperature, therefore, the gases escape unburned. The TGA analysis of wool fiber revealed three major regions of weight loss. During the progress of thermal degradation, $ZrOCl_2$, citric acid and HCl may interfere with the pyrolysis reactions causing a higher onset decomposition temperature and higher mass loss in the second stage. The results of vertical flame test indicate that the treatment of wool with zirconium oxychloride increases the flame retardancy of wool to the great extent. Also the residual char for the $ZrOCl_2$ treated wool was increased comparing with untreated wool. This leads to formation of a layer on the fabric surface protecting the underlying polymer from the fire attack. The LOI value of the zirconium treated fabric was also increased to 31.9. The statistical analysis by DOE indicated that application of 8.96% $ZrOCl_2$, 9.85% citric acid and 9.01% hydrochloric acid at 92 °C on wool produces an optimum design point with desirability of 100%. In SEM images, particles of zirconium compounds on the edge of scales and the change of morphology in comparison with raw wool are observed.

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