Development of brightness on handmade woolen carpets

R K Malik & K K Goswami
Indian Institute of Carpet Technology, Bhadohi 221 401, India

Received 29 March 2016; revised received and accepted 18 July 2016

A process for the achievement of brightness on handmade carpet made from coarse wool fibre considering chlorine based oxidation of wool has been developed. Box-Behnken design of experiment is adopted for three factors (sulphuric acid, sodium hypochlorite and sodium hydroxide concentrations) at three levels for computation of responses like whiteness index, brightness index, and wear and abrasion loss. The optimized conditions are determined by multiple regression analysis aided by computer generated ANOVA analysis of raw data and contour graphs corresponding to various response surface models. The optimum conditions for process parameters are found to be 10 g/L sulphuric acid, 4.5g/L sodium hypochlorite and 10g/L sodium hydroxide. The handle, softness, whiteness, lustre and the anti-shrinkage properties of treated wool fibre improve in comparison to those of original fibre.

Keywords: Abrasion properties, Brightness index, Carpet, Whiteness index, Wool

1 Introduction

Handmade carpets command an important place in the carpet sector as they provide a means of earnings to millions of people attached to the industry in various capacities. The carpet types in the handmade sector include hand knotted, hand tufted and rod aided hand knotted (Tibetan/ Indo-Nepali) carpets. In general, the handmade carpets are wool focused from material point of view, since wool possesses several advantageous properties. Various types of natural and synthetic fibres are also used as alternative raw materials to gain economic and other benefits. Although wool possesses many desirable properties, yet it is not free from faults. The most troublesome part originates from the frictional anisotropy shown by the fibre, which in turn, gives rise to a property called felting shrinkage. The scales on the surface of the wool fibres are all aligned in the same direction with their free ends pointing towards the tip resembling the appearance of the scales on fish skin. This structural arrangement results in a difference in the coefficient of friction when wool fibre is subjected to abrasion against adjacent fibres with scale and against scale directions. This is known as directional frictional effect (DFE) which is the root cause of felting shrinkage¹.

The strong entanglement between the filaments due to felting shrinkage poses many problems during processing of woolen carpets. The felting problem in woollen fabrics and garments is mitigated by shrink resist treatments with oxidizing agents, such as nascent chlorine (Hercosett process), dichloro isocyanuric acid, permonosulphuric acid, etc. followed by application of polymer coat. The oxidizing agents modify the morphology of the filaments by etching the surface and the polymer coat further reduces frictional difference. Other shrink resist treatments include use of enzymes and electrical discharge with plasma and UV²-⁶. However, no information on shrink resist treatments for woolen carpets is documented in the literature, although the carpet industry employs some esoteric techniques to address the problem.

A methodical research on chemical processing of carpets to develop so called bright cool wool technology for woolen handmade floor coverings has hardly been conducted till date². Handmade woolen carpet sector is age-old one and it mainly focuses on art and craft aspects without involving adequate supportive scientific information. The present research work has, therefore, been undertaken to fill up the gap between traditional practices and scientific reasoning in chemical processing of handmade woolen carpets.

The finishing of woolen carpet is generally carried out by mechanical as well as chemical treatments. The mechanical finishing comprises trimming of piles and hemming of edges which are generally carried out after chemical treatment. Traditionally, the chemical treatments are given by application of dilute solutions of sulphuric acid, bleaching powder and caustic soda in tandem to improve the functional properties of carpets,
such as sheen, glaze, or brightness. These treatments also improve properties like felting, handle, etc. but the reason for poor sheen/glaze/brightness is not clearly understood. Hence, optimization of the chemical process and a proper interpretation of the cause-effect relationships is the need of the hour. The present investigation is therefore aimed at establishing the effects of input chemical on output responses, like whiteness, brightness, and wear and abrasion loss, in order to narrow down the gap in understanding. A better understanding of wool and its chemical processing would improve unit value realization and benefit the sector immensely.

2 Materials and Methods
2.1 Carpet
Carpets (2 feet x 3 feet) used in this investigation, were prepared by a highly experienced artisan. All carpets were hand knotted made from 100% scoured but undyed wool yarns with a knot density of 54 knots/inch² and pile height of 12 mm. The wool selected for the investigation has an average diameter of 37.4 microns and a fibre length of 64.5 mm (Hauter). Wool was spun in woolen system to produce 3.9 Nm count yarns. Finishing treatment on carpets comprised mechanical trimming of piles and hemming of edges.

2.2 Chemicals
Unless stated otherwise all reagents, such as sodium hydroxide flakes (E. Merck) and sulphuric acid (98% w/w, sp. gravity 1.84; Qualigens,) conformed to AR grade. Sodium hypochlorite solution (Qualigens, av.Cl2 4% w/v) conformed to LR grade.

2.3 Methods
The following process sequence was followed for treatment of each sample:

Step I – Impregnation with aqueous sulphuric acid for 10 minutes at 30°C
Step II – Washing with fresh water with continuous scrapping
Step III – Impregnation with sodium hypochlorite solution for 10 minutes at 30°C
Step IV – Washing with fresh water with continuous scrapping
Step V – Impregnation with sodium hydroxide solution for 10 minutes at 30°C
Step VI – Washing with fresh water with continuous scrapping
Step VII – Neutralization with acetic acid, if necessary, and confirmation by checking pH
Step VIII – Drying

Knot density and pile height of carpets were determined according to IS specifications9. The average wool diameter was determined with the help of Sirolan Laser Scan and the average fibre length according to IWTO method, using WIRA Fibre Diagram Machine (WIRA Instrumentation, UK). Whiteness Index (HunterLab), and brightness data were recorded at 10° observer angle by using Minolta spectrophotometer, (model CM 2500d), equipped with Jaypak 4802 colour matching software. Illuminant D65 was used as light source and the test method ISO brightness R 457 was followed for estimation of optical properties10-12. Whiteness Index was measured using the following formula by spectrophotometer:

\[
WI = \frac{L}{100(Y)\frac{1}{2}} \quad \frac{b}{100(Y)\frac{1}{2}}
\]

\[
X' = \frac{X}{X_w} \\
Y' = \frac{Y}{Y_w} \\
Z' = \frac{Z}{Z_w}
\]

X, Y, Z are tri-stimulus values of sample, \(X_w, Y_w, Z_w\) are tri-stimulus values of MgO reference tile.

ISO brightness R 457 is defined as Intrinsic radiance (reflectance) factor measured with a reflectometer having characteristics described in ISO 2469, equipped with a filter or corresponding function having an effective wavelength of 457 nm and a half bandwidth of 44 nm, and adjusted so that the UV content of irradiation incident upon the test piece corresponds to that of the CIE illuminant C. It has been measured using Minolta spectrophotometer.

Carpet wear and abrasion loss was evaluated using carpet wear and abrasion tester (SDL International, U.K.) according to test method IWS TM 28314, by recording the weight loss in mg after subjecting the carpet to abrasion for 1000 cycles. In all experiments, the carpets were treated as per the process sequence summarized in Section 2.3. The dried carpets were conditioned at 20°C and 65 ± 2% RH and then subjected to evaluation.

2.4 Design of Experiment
Box-Behnken design of experiments (DOE) was adopted for quantitative estimation of the effect of different factors on various responses, especially on brightness of carpet. The independent variable and their levels were decided considering the findings of preliminary trials and on the basis of the feedback received from the industry regarding their average values used in traditional process. Sulphuric acid, sodium hypochlorite and sodium hydroxide were
taken as the independent variables and their levels are given in Table 1. Multiple regression analysis of experimental data was carried out by using statistical software DX7 as a statistical tool for computation of the empirical relation between various factors and their responses.

3 Results and Discussions

In the present study, the traditional process has been modified by replacing bleaching powder with sodium hypochlorite and attempts have been made to optimize the process parameters in quantitative terms. The brightness index (BI) of undyed silk carpet is found to be 36, whereas the same for undyed woollen carpet is found 31. Hence, BI of silk is set as the benchmark for the present study.

Three factors chosen for the studies are sulphuric acid ($X_1$, g/L), sodium hypochlorite ($X_2$, Av. Cl$_2$ in g/L) and sodium hydroxide ($X_3$, g/L) at three concentration levels (Table 2). The general form of the second degree polynomial equation has been generated by statistical package to estimate the responses of the input variables, as shown below:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 \ldots \ (1)$$

A three factor Box-Behnken experimental design involving a total number of 15 experiments including three replicates at the centre point is used (Table 2). Whiteness index (WI), BI, and carpet wear & abrasion loss (WAL) have been chosen as the dependent variables. The specimen obtained by treatments on carpet samples according to the DOE (Table 2) are subjected to testing for various responses. The experimental data vis-à-vis predicted values of responses are summarized in Table 3.
Multiple regression analysis on the experimental data furnished the following second order polynomial Eqs (2), (3) and (4), which are used to compute the predicted values of WI ($Y_1$), BI ($Y_2$) and WAL ($Y_3$) respectively, for a particular set of experimental conditions. The responses $Y_1$, $Y_2$ and $Y_3$ have been derived from the Tables 4-6. The polynomial equations are given below:

\[
Y_1 = 65.555 - 0.0964 X_1 - 1.045 X_2 - 0.150 X_3 + 0.00426 X_1 X_2 - 0.0766 X_2 X_3 - 0.00292 X_1^2 + 0.5722 X_2^2 + 0.00543 X_3^2 \quad \ldots (2)
\]

\[
Y_2 = 34.590 - 0.16638 X_1 - 0.7344 X_2 - 0.1429 X_3 + 0.00183 X_1 X_2 + 0.002433 X_1 X_3 - 0.09 X_2 X_3 - 0.000833 X_1^2 + 0.5485 X_2^2 + 0.007074 X_3^2 \quad \ldots (3)
\]

\[
Y_3 = 38.41 + 0.0389 X_1 + 0.2902 X_2 + 0.1073 X_3 - 0.0375 X_1 X_2 + 0.000866 X_1 X_3 + 0.03288 X_2 X_3 + 0.00391 X_1^2 + 0.00043884 X_2^2 + 0.005 X_3^2 \quad \ldots (4)
\]

### 3.1 Whiteness index

The multiple regression equation for whiteness index is given by the quadratic Eq. (2). The contour graph (Fig. 1) derived from the response surface obtained by plotting $X_1$ vs $X_3$ shows that the isometric lines of WI follow parabolic paths. The perpendicular drawn at a given point on $X_1$-axis intersects each isometric line at two points. The junction points approach each other with diminishing values of $X_1$ and eventually converge at a threshold value.
passes through a minimum with increase in alkali concentration \((X_3)\) at any given acid concentration. On the contrary, the WI decreases with increase in acid concentration in the domains 10:30 (Fig. 1). The predicted values closely match with the experimental values only when higher concentrations of NaOCl are used in the intermediate stage and alkali extraction is done at low alkali concentration (Table 3). This is understandable because at higher hypochlorite concentration the thioester linkage between lipid layer and protein, located on cuticle cells just beneath the surface, is ruptured more efficiently. Controlled alkali treatment dissolves the lipid, namely 18-MEA of wool but higher alkali concentrations cause yellowing of the fibre at the cost of WI. The highest value of WI is predicted at the point (10, 10).

### 3.2 Brightness Index

The same arguments hold good for the BI data which show that the BI increases with increase in both NaOCl and NaOH concentrations (Fig. 2). The lowest predicted value of BI lies at the central point \((X_1 = 3, X_2 = 25)\) and the highest value at the point \((4.5, 10)\) within the domain 1.50: 4.5 for NaOCl and 10:40 for NaOH. Starting from the point \((4.5, 10)\), the BI diminishes along the diagonal line, passes through a minimum at the central point \((3, 25)\) and again increases till the point \((1.5, 40)\) is reached. The multiple \(R^2\) value stands at 0.9235 which indicates that interactive effect of hypochlorite and alkali on BI is significant.

### 3.3 Wear and Abrasion Loss

Wear and abrasion loss (WAL) of carpet sample shows significant relation among all factors as
revealed by multiple R squared value which stands at 0.9683. The effect of H$_2$SO$_4$ and NaOCl on WAL is shown in Fig. 3 which indicates that the extent of weight loss due to wear and abrasion lies between 40.8mg/1000 cycles and 51.0 mg/1000 cycles within the given domains. The predicted weight loss is minimum at the origin (1.50,10) which continuously increases along either axes. The maximum weight loss is attained at the point (4.50, 30). The reactive species present in NaOCl solution is a function of pH$^{15}$; the concentration of elemental chlorine increases only at sufficiently low pH (<2). Thus, the higher the acid concentrationthe more is the liberation of chlorine which, as mentioned earlier, culminates with rupture of the lipid-protein bond on the cuticle surface. Such surface modification paves inroads for penetration of chemicals (alkali) into the inner layers of cuticle cells, resulting in loss of fibre strength and enhanced WAL.

Figure 4 shows the effect of NaOCl and NaOH on WAL of carpet. In this case, the weight loss is marginally affected due to increase in hypochlorite concentration alone. This is because hypochlorite disrupts the surface lipid layer and subsequent treatment with alkali at low concentration does not cause much damage to the exposed protein layer. However, the weight loss tends to increase with increase in alkali concentration, presumably due to susceptibility of wool to alkaline degradation. The shading or fibre loss due to abrasion is more pronounced when concentrations of both NaOCl and NaOH are high. The predicted weight loss is minimum at (3, 10) and maximum at (4.5, 40) within the given domain.

3.4 Statistical Analysis

The summary of results obtained by ANOVA analysis of various factors and WI as response is presented in Table 5. The analysis reveals that the factors $X_1$ (sulphuric acid), $X_2$ (sodium hypochlorite), interaction terms of $X_2X_3$ (product of factors sodium hypochlorite and sodium hydroxide), and quadratic terms $X_2^2$ (hypochlorite squared) and $X_3^2$ (sodium hydroxide squared) are also statistically significant. In general, the fitment of model represented by Eq. (2) is satisfactory since the multiple degree of determination ($R^2$ value) is 0.92.

The effect on WAL of carpet was examined by ANOVA analysis of various input variables and their responses (Table 6). The multiple regression Eq. (4) indicates that each factor has positive contribution towards WAL. The effect of factor ($X_3$) is statistically significant at 98% and that of factor ($X_2$) at almost 100% confidence levels. The contribution of remaining factors is not significant. The multiple degree of determination ($R^2$ value) is 0.97, indicating that the fitment of model represented by Eq. (4) is highly satisfactory in general.
The effect of sodium hypochlorite and sodium hydroxide on WAL of carpet is shown in Fig. 4. The wear and abrasion loss of carpet progressively increases with increase in concentration of each of the variables. The interactive action of the two input variables shows a synergistic effect. The predicted weight loss is minimum at (3, 10) and maximum at (3, 40). It is concluded that sodium hypochlorite and caustic soda have significant effect on shading or fibre loss due to abrasion of woolen carpet.

The fitment of models represented by Eqs (2)-(4) for WI, BI and WAL & respectively, having been established, attention has been paid on defining the optimum levels of all factors in their respective domains to achieve maximum (or minimum) output responses, as desired. The predicted values of $X_I$ and $X_2$ for highest WI lies at the point $X_I=10, X_2=10$ (Fig. 3). Substituting these values of $X_I$ and $X_2$ along with those of $X_2^{(max)}$ and $X_2^{(min)}$ in the domain 1.5:4.5 in Eq. (2), the predicted values of $W_{I_{\max}}$ and $W_{I_{\min}}$ stand at ~67.0 and 62.0 respectively. Substituting $X_2^{(max)}$ and $X_2^{(min)}$ for all possible combinations containing upper and lower extreme levels of $X_I$ and $X_2$ in Eqs (2), the predicted values indicate that the best possible combination for WI is $X_I=10, X_2=4.5$ and $X_2=10$, for which the predicted WI stands at 67. Similar exercise on BI data reveals that the predicted $B_{I_{\max}}$ lies at 36.2 with the same combination of $X_I, X_2$ and $X_2$. However, the predicted value of WAL under this set of conditions is marginally higher (41.6 mg/1000 cycles) than the $W_{AL_{\min}}$ of 40.8 mg/1000 cycles over the entire range. It is concluded that the optimum level of the factors is given by the combination $X_I=10, X_2=4.5$ and $X_2=10$. The experimental values obtained for WI, BI and WAL under these conditions are 68.04, 36.86 and 41.83 respectively, which are in good agreement with the forecasts.

3.5 Microscopic Studies

Viewed under scanning electron microscope, the scales on the surface of untreated wool fibre appear as flat plates with sharp edges; the free edges being slightly protruded above the surface (Fig. 5). Some clusters of particulate matter are seen randomly adhered to the surface, which account for low lustre of the fibre. This is because the light falling on the particles is scattered in all directions, resulting in an enhanced diffused reflectance of the reflected rays. The clusters grow in size upon treatment with acid which cannot be removed by subsequent treatments with hypochlorite and sodium hydroxide either in isolation or in tandem. These particles could be the deposits of inorganic salts, which, in all probability, are not the integral parts of the fibre. As expected, the fibre obtained by treatment with all the input chemicals under optimized conditions shows roughening of surface with vertical scratch marks, indicating removal of the lipid layer. The open ends of scale edges are rendered somewhat blunt. The cluster of particles persists to remain on the surface and their chemical identity still remains to be deciphered.

4 Conclusion

A 3-factor 3-level Box-Behnken DOE was employed to examine the effect of selected factors on the responses. Multiple regression analysis of experimental data using statistical software DX7 furnished three second degree polynomial equations for WI, BI and WAL. The forecast for responses computed according to these models is found to be in
good agreement with the experimental data. The forecast indicated that the optimum set of conditions is defined by $X_1=10$, $X_2=4.5$ and $X_3=10$ for both $W_{I_{\text{max}}}$ (67) and $B_{I_{\text{max}}}$ (36.2). The predicted value of WAL under these conditions is slightly higher (41.6 mg/1000 cycles) than the predicted minimum (40.8 mg/1000 cycles) over the entire range. These values are well within the acceptable limit of WAL (70 mg/1000 cycles) for commercial carpets according to international standards. Hence, the optimized process condition may be useful in commercial chemical finishing of woolen handmade carpets.

**References**