

# Novel Technique Treatment of Cotton with Laccase Aqueous Solution for the Prevention of Metal Allergy Symptoms

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**Abstract:** A novel fibre treatment technique was studied for preventing metal allergy symptoms. Treated cotton fabrics with laccase (LA) aqueous solution by the technique showed the functions of capturing and detecting hapten metal ions. The treatment consists of two steps. Namely, the treatment with LA aqueous solution and the dry heat treatment. It was found that the LA-treated cotton fabrics adsorbed nickel ions and showed colour change from pale orange to purple by immersed in nickel chloride aqueous solution. The colour change was clear enough to be perceived by the naked eye. The changed colour and colour difference of the LA-treated cotton fabric depended upon the concentration of the nickel solution. The fabric has sufficient adsorption capacity to capture  $\text{Ni}^{2+}$ . The LA-treated fabric adsorbing  $\text{Ni}^{2+}$  and colour-changed was able to regenerate repeatedly by washing with citric acid aqueous solution.

**Keywords:** metal allergy, fibre treatment, capturing and detecting hapten metal ions, laccase acid.

## Experimental



Cotton fabrics were dipped into LA aqueous solution with or without  $\text{NaH}_2\text{PO}_4$  and shaken at 40 °C under normal pressure or treated at 132 °C under 0.3 MPa. The fabrics taken out were dried at 80 °C and heated between stainless steel plate heaters at 150 - 200 °C. The treated fabrics were washed with Marseille soap aqueous solution, rinsed four times and air-dried at room temperature. Each of the LA-treated cotton fabrics was immersed into  $\text{NiCl}_2$  aqueous solution with a given concentration. The colour of the cotton fabric samples were measured by a spectrophotometer (Konica Minolta, CM-26d). The colour measurements were made employing CIE standard illuminant D<sub>65</sub>, 10°-view angle and SCI (specular component included) mode, in which all the reflected lights from a sample including the regular reflection are integrated. The resulting colours were expressed in  $L^*a^*b^*$  standard colourimetric system (CIE 1976). The colour difference  $\Delta E^*$  of the samples before and after colour change by  $\text{Ni}^{2+}$  was also calculated. The amount of  $\text{Ni}^{2+}$  adsorbed on the LA-treated cotton fabric was determined from the difference in the  $\text{Ni}^{2+}$  concentration before and after the nickel solution in which it was immersed. The  $\text{Ni}^{2+}$  concentration was calculated from the absorbance of a colour indicator Nitroso-PSAP. The LA-treated cotton fabric immersed into the  $\text{NiCl}_2$  aqueous solution and dried was immersed into citric acid aqueous solution (pH = 2.5), rinsed by distilled water and dried. The series of the procedures were repeated and the colour of the dried fabric was measured after each process by the spectrophotometer.

## Results and Discussion

The colour of the cotton fabric treated with LA and  $\text{NaH}_2\text{PO}_4$  was pale orange and turned purple when it was immersed into  $\text{NiCl}_2$  aqueous solution as shown as photographs in Table 1. The colour change is clearly visible to the naked eye. The Table also summarises colourimetric values. The values obtained show that the hue and lightness have changed significantly. The  $\Delta E^*$  for the change in the colour was 22.8. The results show that LA-treated cotton fabric undergoes a distinct colour change in response to nickel, indicating that it detects the metal.

The amount of nickel adsorbed per unit mass of the dried LA-treated cotton fabric was  $v_{\text{Ni}} = 1.4 \times 10^{-5} \text{ mol g}^{-1}$ , whereas  $v_{\text{Ni}}$  of untreated cotton fabric was  $0.45 \times 10^{-5} \text{ mol g}^{-1}$ . It can be said that the LA-treated cotton fabric has sufficient adsorption capacity to capture nickel ions in order to avoid triggering the allergic symptoms because the amount of adsorbed nickel is much greater than the amount of nickel that has been leached out by soaking nickel silver in artificial sweat under a standard condition. The regenerative properties of the LA-treated fabric are also reported.

**Table 1** Photographs and colourimetric values of the LA-treated fabric before and after immersion into  $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ NiCl}_2$  aqueous solution, and amounts of  $\text{Ni}^{2+}$  adsorbed on per unit mass of it  $v_{\text{Ni}}$ .

Sample	LA-treated cotton before immersion in $\text{NiCl}_2$ sol.	LA-treated cotton after immersion in $\text{NiCl}_2$ sol.
Photograph		
$L^*$	69.2	60.3
$a^*$	27.3	23.9
$b^*$	18.8	-1.90
$h / ^\circ$	34.6	355
$\Delta E^*$	22.8	
$v_{\text{Ni}} / 10^{-5} \text{ mol g}^{-1}$	0	1.4

## References

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