Development of protective clothing for pesticide industry: Part II — An ecofriendly approach in selection of resin

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Two low formaldehyde-based resins along with one normal resin based on DMDHEU have been applied separately as well as along with fluorocarbon finish on 100% cotton and 70/30 polyester-cotton blended fabrics in varying concentration and their effects on add-on, durability in terms of water and oil repellency and tensile strength studied to make the finishing process more ecofriendly and suitable for its use in protective clothing for pesticide industry. The resins have also been evaluated in terms of their influence on water vapour permeability, creasing behaviour, stiffness and free formaldehyde content of the finished fabrics. It is observed that the type of resin and its concentration affect the durability of fluorocarbon finish to laundering. Glyoxal-based resin exhibits minimum free formaldehyde content, minimum loss in strength and better durability to laundering even at lower concentration. The optimized recipe consists of the fluorocarbon finish, glyoxal-based resin, magnesium chloride as a catalyst and a softener applied in acidic conditions, and could be used to prepare the dress materials suitable for the persons working in pesticide industry.

Keywords: Cotton, Fluorocarbons, Polyester-cotton fabric, Protective clothing, Water vapour permeability

I Introduction

Pesticide contamination through skin is the most common cause of poisoning during mixing, loading, application and equipment maintenance in pesticide industry1. Liquid pesticides, which are either water soluble or emulsifiable concentrates, offer the greatest risk. Fluorocarbon finishes make the fabric water and oil repellent, thereby reducing the risk of pesticide penetration2-4 during the accidental spillage. The use of resin along with the fluorocarbon finishes is recommended to improve the durability of finish to repeated launderings5. Resins like urea formaldehyde, melamine formaldehyde, preparations based on cyclic ethylene urea, triazines and epoxy resins have been developed. Among these, the dimethylol dihydroxyethylene urea (DMDHEU) is widely used due to its good wrinkle recovery with minimum effect on other useful properties. However, the subsequent formaldehyde release from DMDHEU treated fabrics is of considerable concern, particularly at elevated temperatures and high relative humidity6.

Formaldehyde is a toxic chemical and is found to be carcinogenic to some animals7. Germany has laid down strict ecostandards for textiles exported to it. The maximum limit of free formaldehyde for apparels, which are worn next to skin, is 75ppm (ref. 8). In Indian context, though the ecostandards are not that strict, there is still a need to find ecofriendly substitutes. The clothings worn by persons in pesticide manufacturing units need to have the least amount of free formaldehyde as they work in hot and humid conditions.

Keeping this in mind, a comparative evaluation of the effect of selected low formaldehyde- and DMDHEU-based resins on the durability of fluorocarbon finish on cotton and polyester-cotton blended fabric has been made. The application was done under acidic conditions in the presence of a catalyst. The treated fabrics were evaluated for add-on, durability of fluorocarbon in terms of water and oil repellency and properties like tensile strength, crease recovery, bending length, whiteness index and water vapour permeability. The finished fabrics were also tested for the free formaldehyde content.
2 Materials and Methods

2.1 Materials

2.1.1 Fabrics

100% cotton and 70/30 polyester-cotton blended fabrics, having the following specifications, were used:

<table>
<thead>
<tr>
<th>Weave</th>
<th>Cotton</th>
<th>Polyester-cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/1 Twill</td>
<td>132</td>
<td>65</td>
</tr>
<tr>
<td>Ends/inch</td>
<td>30°</td>
<td>30°</td>
</tr>
<tr>
<td>Picks/inch</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>Weight, g/m²</td>
<td>154</td>
<td>178</td>
</tr>
<tr>
<td>Warp count</td>
<td>30°</td>
<td>30°</td>
</tr>
<tr>
<td>Weft count</td>
<td>15°</td>
<td>13°</td>
</tr>
</tbody>
</table>

The study was carried out on bleached, undyed and unfinished fabrics.

2.1.2 Chemicals

DMDHEU-based resin KVSNI (Clariant), glyoxal-based resin Allenlink WFR (L.N. Chemicals), cyclic ethylene urea precondensate resin Creasex (Fibrolite), PE-based commercial softener (Ultrason HDP), fluorocarbon finish NUVA-CSF (Clariant), catalyst (magnesium chloride), acetic acid, isopropyl alcohol, ammonium acetate and acetyl acetone (laboratory reagents) were used for the study.

2.2 Methods

2.2.1 Fluorocarbon Finish and Resin Treatment

The unfinished and bleached fabrics were padded separately with different concentrations of selected resins using the following recipes:

- **Cotton**
  - NUVA CSF: 60gpl
  - Resin: 40gpl, 80gpl
  - MgCl₂: 10gpl
  - Softener: 30gpl
  - Isopropyl alcohol: Nil
  - CH₃COOH: 2ml (pH 4-5)

- **Polyester-cotton**
  - NUVA CSF: 60gpl
  - Resin: 40gpl, 80gpl
  - MgCl₂: 10gpl
  - Softener: 30gpl
  - Isopropyl alcohol: 15gpl
  - CH₃COOH: 2ml

The fabrics were padded with liquor (2 dips 2 nips method) at an expression of 70%, dried at 100°C for 10 min and then cured at 180°C for 45 s in Mathis laboratory dryer.

To have a better understanding of the effect of resins, the experiments were also carried out using only resin without the fluorocarbon finish.

The fabrics were coded as shown below:

- \( C_0 \) — Cotton untreated.
- \( C_{40}, C_{80} \) — Cotton treated with DMDHEU-based resin at 40gpl and 80gpl respectively.
- \( C_{40}^{\text{glyoxal}}, C_{80}^{\text{glyoxal}} \) — Cotton treated with glyoxal resin at 40gpl and 80gpl respectively.
- \( C_{40}^{\text{urea}}, C_{80}^{\text{urea}} \) — Cotton treated with ethylene urea-based resin at 40gpl and 80gpl respectively.
- \( P_0 \) — Polyester-cotton blend untreated.
- \( P_{40} \) — Polyester-cotton blend treated with DMDHEU-based resin at 40gpl.
- \( P_{40}^{\text{glyoxal}} \) — Polyester-cotton blend treated with glyoxal-based resin at 40gpl.
- \( P_{40}^{\text{urea}} \) — Polyester-cotton blend treated with ethylene urea-based resin at 40gpl.

2.2.2 Determination of Add-on

Add-on (%) of each sample was obtained by weighing the unit area of dry and conditioned untreated and treated samples.

2.2.3 Determination of Durability of Fluorocarbon Finish to Laundering

The durability of finish to laundering was determined by subjecting the samples to predetermined number (0, 1, 5, 10, 15, 20 and 25) of laundry cycles using the ISO 6330-1984(E) test method with flat drying to simulate home laundering. The laundering was done in 5gpl soap solution at a material-to-liquor ratio of 1:50 for 10 min at 40°C. The laundered samples were then evaluated for water and oil repellency.

2.2.3.1 Determination of Water Repellency

Water repellency was determined using spray test, in qualitative terms, in accordance with IS: 390-1975 test method. The repellency was assessed on the basis of the area of specimen wetted by the spray of water on a six-point photographic test rating.

2.2.3.2 Determination of Oil Repellency

The oil repellency was determined using the test method D6506-96 (HES Quality Test Standard). A drop of machine oil was dropped from a height of 20mm with a micropipette (0.05ml) and left for 15 min. The oil repellent property was then rated on a five-point rating scale.

2.2.4 Determination of Tensile Strength

The tensile strength and elongation of yarns were determined on an Instron as per the IS: 1969-1985 test method.
2.2.5 Determination of Crease Recovery

The creasing behaviour was studied as per the IS: 4681-1981 test method.

2.2.6 Determination of Bending Length

The stiffness of the fabric samples was determined in terms of bending length in accordance with ASTM D 1388-96 test method.

2.2.7 Measurement of Whiteness Index

The whiteness indices of fabrics were measured as per the Hunter’s Lab scale using an ACS spectrophotometer II spectrophotometer interfaced with computer colour matching system. The illuminant used was D65 with 10° observer.

2.2.8 Measurement of Water Vapour Permeability Index

The water vapour permeability indices of the treated fabrics were measured as per the BS 7209 and BS 3424 standards using Shirley’s water vapour permeability tester M-261.

2.2.9 Determination of Free Formaldehyde Content of Treated Fabrics

For the determination of free formaldehyde content, ISO/DIS-14184-1 test method was used where 2g of fabric sample was treated with 100ml of distilled water at 40°C for 1 h. The extract was filtered through glass filter and to 5ml of this solution, about 5ml of acetyl acetone solution was added. The content was heated in a water bath at 40°C for 30 min and then kept at room temperature for another 30 min. The optical density of this coloured solution was measured at 412nm and the formaldehyde content was found from the pre-calibrated curve generated by using the standard solution of known formaldehyde content. Acetyl acetone solution was made by mixing 15g of ammonium acetate, 0.3 ml of glacial acetic acid and 0.2 ml of acetyl acetone with 80ml of distilled water.

3 Results and Discussion

The comparative assessment of various resins in terms of their effectiveness and other properties has been made. The reaction of resin with substrate is important to understand the anchoring and crosslinking behaviour.

3.1 Reaction Mechanism

The reaction mechanism of DMDHEU crosslinking with cellulosic substrate is shown in Scheme 1.

Scheme 1—Reaction mechanism of DMDHEU crosslinking with cellulosic substrate

Glyoxal, a dialdehyde, can form four linkages with cellulose and may be regarded as a tetrafunctional crosslinking agent unlike formaldehyde which is difunctional. The reaction mechanism of glyoxal crosslinking with cellulosic substrate is given below:

\[
\text{O} - \text{HC} = \text{CHO} + 3 \text{Cell} - \text{OH} \rightarrow \text{O} - \text{HC} = \text{CH} = \text{O} - \text{Cell} + \text{H}
\]

or

\[
\text{O} - \text{HC} = \text{CH} = \text{O} - \text{Cell} + 2 \text{Cell} - \text{OH} \rightarrow \text{Cell} - \text{O} - \text{HC} = \text{CH} = \text{O} - \text{Cell} + \text{H}
\]

The reaction between resin and cellulose is extremely complicated and depends on the several factors like molecular structure of cellulose, activity of the reagent, nature of linkages (both chemical and physical) between reagent and cellulose, length and structure of crosslinks formed, and finally the resistance of these links to acid and alkaline hydrolysis.

3.2 Effect of Type and Concentration of Resin on Various Properties

3.2.1 Add-on

In both the fabrics, the weight gain increases on increasing the resin concentration. This is attributed to the higher amount of attachment of finishes with
3.2.2 Durability of Fluorocarbon Finish to Laundering

The fluorocarbon finish (NUVA-CSF) was applied to make the fabrics protective against the pesticides. Resin was added to the finish to improve its durability to laundering. The effectiveness of resin was, therefore, evaluated in terms of the durability of the fluorocarbon finish. It was studied by subjecting the samples to a predetermined number of laundry cycles and measuring the water and oil repellency (Table 1).

3.2.2.1 Water Repellency

Cotton fabric, in an untreated state, shows a spray rating of 0, indicating the complete wetting of the sample, and the application of fluorocarbon finish results in a marked improvement, whereby a rating of 100 is observed in all the cases. But on subsequent laundering, the effect of fluorocarbon finish decreases to varying extent, depending upon the type and concentration of resin used. In case of resin I (DMDHEU-based) at 40gpl, a rating of 70 is obtained after 10 launderings, which further reduces to 50 after 15 launderings. Resin I at 80gpl gives better durability than at 40gpl. But resins II (glyoxal-based) and III (ethylene uria-based) give better results at both the concentrations with a rating of 70 even after 25 launderings (Table 1).

In polyester-cotton blend, the rating of 50 is witnessed in an unfinished state, probably due to the hydrophobic character of polyester in the blend. On application of fluorocarbon finish followed by laundering, the order of effectiveness of resins is: resin II > resin III > resin I (Table 1). In general, the polyester-cotton blend shows better water repellency than cottons, indicating a combined effect of hydrophobic character of polyester along with the presence of resin. Resin III at 40gpl for cotton and resin II at 40gpl for both the fabrics show good results. The effectiveness of resin II at 40gpl could be attributed to the fact that the glyoxal is a tetrafunctional crosslinking agent unlike formaldehyde which is difunctional, thereby being more effective even at lower concentration.

3.2.2.2 Oil Repellency

Application of fluorocarbon finish also makes the fabrics oil repellent, reinforcing the dual role of these finishes as being water and oil repellent. On a scale of 1-5, both the fabrics in an untreated state show a rating of 1, indicating the complete absorption of the oil droplet, but the application of fluorocarbon finish results in a marked improvement in oil repellency (Table 1). For cotton, initially the resin II gives better results, but after 25 launderings all the resins show a comparable rating of 3. Resins I and III at 80 gpl give better results than at 40gpl but the trend is opposite in resin II. In polyester-cotton blend also, the resin II

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Add-on</th>
<th>Water repellency</th>
<th>Oil repellency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Durability to laundering</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>OL 1L 5L 10L 15L 20L 25L</td>
<td>OL 1L 5L 10L 20L 25L</td>
</tr>
<tr>
<td>C-0</td>
<td>5.00</td>
<td>00 00 00 00 00 50 50</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-I 40</td>
<td>100</td>
<td>100 100 100 100 100 100</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-I 80</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-I 100</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-II 40</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-II 80</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-II 100</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-III 40</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>C-III 80</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>PC-0</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>PC-I</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
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<td>PC-II</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>PC-III</td>
<td>0.07</td>
<td>00 00 00 00 00 00 00</td>
<td>1 1 1 1 1 1 1</td>
</tr>
</tbody>
</table>

L. — Number of laundry cycles
gives better results than the resins I and III. In general, the trend for oil repellency is similar to that for water repellency.

3.2.3 Tensile Strength

The application of resin on cotton fabrics results in 20-30% strength loss in warp direction and 40-50% strength loss in weft direction. This could be attributed to the asymmetric distribution of load in the crosslinked cotton compared to one which is not crosslinked. Table 2 shows that in case of cotton the increase in resin concentration results in the higher loss in strength in both the directions for all the resins. In comparison to resin I, the strength losses are higher in resins II and III at the corresponding concentrations. In polyester-cotton blend, the strength loss is much lower than that in 100% cotton. Also, the initial tensile strength in polyester-cotton blend is fairly high and therefore the final strength of the finished fabric is also high.

The experiments were also done with only resin and with combined recipe of resin and fluorocarbon finish to get the better understanding of the role of resin (Table 2). It is observed that the increase in concentration of all the resins results in higher strength loss with both the recipes, but it is found to be comparatively higher in the recipe containing only resins without the fluorocarbon finish. This indicates that the loss in strength is primarily due to the addition of resin in both 100% cotton and polyester-cotton blend, though the loss is more for cotton fabrics. But, the entrapment of fluorocarbons leads to incomplete crosslinking of resin, resulting in a marginal improvement in tensile strength of samples.

On studying the effect of resin on durability of fluorocarbon finish to laundering in conjunction with strength loss (Tables I and 2), the resins II and III at 40gpl are found to be the optimum choice because even after 25 launderings they give a rating of 70 for water repellency with minimum strength loss of about 30%.

3.2.4 Crease Recovery

It is observed that the samples finished with only resin show higher crease recovery (Table 2) and the increase in concentration of all the resins results in an improvement in crease recovery. The presence of fluorocarbon finish in the recipe results in a reduction in crease recovery angles in almost all the cases, indicating that though the entrapment of fluorocarbon finish is resulting in better strength it is rendering the fabric more prone to creasing. The increase in resin concentration from 40gpl to 80gpl results in an improvement in crease recovery for resins II and III in cotton fabric (Table 2). In case of resin I, there is not much difference in crease recovery angle at 40gpl and 80gpl concentrations. For resin II, both the concentrations show similar crease recovery angles, indicating that the lower concentration of resin II can give the required crease recovery properties.

In case of polyester-cotton blend, it is observed that the presence of only resin does not affect the crease recovery angle to a large extent (Table 2), rather in some cases it decreases probably, indicating that the inherent property of polyester to recover from crease is not affected by the presence of resin. Also, in case

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Breaking load, kgf</th>
<th>Crease recovery, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With resin</td>
<td>With resin and fluorocarbon</td>
</tr>
<tr>
<td></td>
<td>Warp  Weft</td>
<td>Warp  Weft</td>
</tr>
<tr>
<td>C-0</td>
<td>70.52 37.16</td>
<td>70.52 37.16</td>
</tr>
<tr>
<td>C-I 40</td>
<td>43.16 36.25</td>
<td>52.53 31.99</td>
</tr>
<tr>
<td>C-II 80</td>
<td>37.11 22.35</td>
<td>48.45 13.99</td>
</tr>
<tr>
<td>C-II 40</td>
<td>40.23 26.13</td>
<td>47.19 22.39</td>
</tr>
<tr>
<td>C-II 80</td>
<td>35.71 21.12</td>
<td>36.95 13.82</td>
</tr>
<tr>
<td>C-III 40</td>
<td>45.33 25.15</td>
<td>49.74 19.01</td>
</tr>
<tr>
<td>C-III 80</td>
<td>49.99 25.23</td>
<td>43.10 13.34</td>
</tr>
<tr>
<td>PC-0</td>
<td>93.71 76.18</td>
<td>93.71 76.18</td>
</tr>
<tr>
<td>PC-I</td>
<td>89.16 63.76</td>
<td>77.51 71.84</td>
</tr>
<tr>
<td>PC-II</td>
<td>75.80 68.05</td>
<td>75.45 68.28</td>
</tr>
<tr>
<td>PC-III</td>
<td>83.77 66.64</td>
<td>106.10 53.85</td>
</tr>
</tbody>
</table>
of polyester-cotton blend the crease recovery angle of unfinished fabric is very high (261°) and the further application of resin does not bring about any significant change in crease recovery property.

3.2.5 Bending Length

As the concentration of resin on cotton increases, the bending length also increases (Table 3). Crosslinking improves the dimensional stability and affects the softness of material negatively. This ultimately results in increased bending length, irrespective of the type of resin used. Of the three resins, the resin II at 40gpl shows the least change in the properties of cotton.

In polyester-cotton blend, there is more change in bending length, resulting in a stiffer fabric but it is of similar magnitude in all the three resins.

3.2.6 Whiteness Index

To study the effect on whiteness during the application of resin, the fabrics were cured at 180°C for 45 s. As is evident from Table 3, the resin application does not show any significant yellowing both on cotton and polyester-cotton fabrics.

3.2.7 Water Vapour Permeability

Water vapour permeability is an indicator of comfort of fabric during its use. Since the fabrics under study are going to be used for protective clothing, to be worn in hot and humid conditions, it is imperative to study this property. It is observed that the application of resin along with fluorocarbon finish results in some change in water vapour permeability.

The untreated cotton fabric shows a water vapour permeability index of 98% (Table 3) but the application of finish results in some reduction. Resin I at 80gpl reduces it to 95.3% but for resin III, it remains more or less the same. The untreated polyester-cotton blend gives a water vapour permeability index of 100% due to the openness of the weave, but the application of finish causes 8% reduction in case of resin I, 4.7% in resin II and 2.6% in resin III.

In general, the water vapour permeability index of finished fabric is high enough to ensure comfort during wear.

3.2.8 Free Formaldehyde Content

While comparing the free formaldehyde contents of samples finished with selected resins, it is found that, in general, the resin II gives minimum free formaldehyde at both the concentrations (Table 3). Resin I at 80gpl gives maximum free formaldehyde, rendering it unfit for use due to the ecological considerations. Thus, the glyoxal-based resin could be used as a substitute of normal resins.

4 Conclusions

The type of resin and its concentration affect the durability of fluorocarbon finish to launderings. The DMDHEU based resin gives good water and oil repellency at 80gpl, even after 25 laundry cycles, but the strength loss in cotton is very high. Resins II and III give better results in terms of water and oil repellency though the strength losses are slightly higher than those in case of resin I at the corresponding concentrations.

Resins II and III at 40gpl give an optimum combination of durability of fluorocarbon finishes to laundering and fabric strength. Other properties, like bending length, crease recovery, whiteness index and water vapour permeability, are also found to be satisfactory. The glyoxal-based resin II gives the minimum free formaldehyde content which is within the permissible limits, making it eco-friendly. Thus, the DMDHEU-based resin could be substituted by glyoxal-based resin for use with fluorocarbon finishes to produce protective clothing.

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