Soiling and Soil Removal Behaviour of Textiles: Part I—Crosslinked Cotton Fabrics*†

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Received 20 March 1978; accepted 10 November 1978

Soiling and cleaning of cotton garments and household textiles were never considered a major problem before the advent of wash-wear and durable-press fabrics. The problem of removing soils from a fabric came into picture when cotton fabrics began to be treated with nitrogenous crosslinking agents to produce durable-press fabrics. When cotton is blended with synthetic hydrophobic fibres and reacted with crosslinking agents to produce durable-press goods, the resulting products show additional properties which encourage soiling and make cleaning more difficult.

From studies on the soiling and soil release behaviour of crosslinked cotton different conclusions have emerged, making the complex phenomena of soiling and soil removal even more complex. The results so far reported in literature can be summarized as follows: (1) The soiling behaviour remains unaltered upon crosslinking. (2) The crosslinked cotton shows greater resistance to soiling. (3) Soiling is greater in the case of crosslinked fabrics.

These contradictory conclusions emphasize the need for a systematic study. In view of the above, an extensive research programme on soiling and soil release has been initiated at this institute with a view to understanding different fundamental parameters—zeta potential, contact angle, surface energy and location of soil—which influence soiling and soil removal. Parameters like the nature of the soil, weave, construction and morphology of the fabric, detergent formulation, etc., have also been included in the research programme. On the basis of the information collected during these studies, it is hoped that new soil release agents will be synthesized.

Materials and Methods

Fabric—Scoured, bleached and mercerized cotton poplin 112/72 ends/picks, 36s x 30s counts was used.

Crosslinking agents—Dimethyloldihydroxyethyleneurea (DMDHEU), dimethyldihydroxyethylcarbamate (DMDHEC), trimethylolmelamine (TMM), hexamethyloleamine (HMM), and dimethylolethyleneurea (DMEU), all of laboratory grade were used.

Additives—Polyvinylacetate dispersion (Fixotex CHV), silicone emulsion (Katarang SIH), polyethylene emulsion (Vasarang PE) and wax emulsion (Lust PA
II) obtained from Hico Products Pvt. Ltd, Bombay were used. The compounds are usually used as softeners, except the first one, which is used as a stiffening agent.

Soils—The following soils were used:

(1) Oily soil: Lubricating oil (used), a composite mixture of density 0.9 g/cm³ and viscosity 275.2 cp.

(2) Particulate soils: (a) Ferric oxide with particle size 0.5 - 1.6 μ, (b) carbon particles with particle size 2 - 4 μ and (c) Bandy black clay with particle size 7.5 - 3 μ.

Bandy black clay is a mixture of several inorganic oxides.

(3) Synthetic sebum: It was prepared by dissolving 30 g glyceryltristearate, 30 g stearic acid, 20 g octadecanol and 20 g octadecane in 500 ml carbon tetrachloride.

(4) Wet soils: Aqueous dispersions of ferric oxide and carbon particles.

Surfactant—Sodium dodecylsulphate (SDS), obtained from Koch Light Laboratories Ltd, UK, was used.

Treatment with crosslinking agents—The fabric was impregnated with a solution containing the required quantity of the crosslinking agent, catalyst and softener (optional) keeping material to liquor ratio 1:10. The concentration of the crosslinking agents was varied over the range 100-300 g/litre. The catalyst (MgCl₂, 6H₂O) concentration was always 25% of the crosslinker concentration. The concentration of the softener was 50 g/litre. The impregnated fabric was padded with 75% wet pick up, dried at 110°C for 50 sec and cured at 150°C for 4 min in a stenter. The treated fabric was washed, dried and stored in a conditioned room.

Soiling with lubricating oil—A 6 x 6 in fabric sample mounted on an embroidery hoop was soiled with 0.2 ml lubricating oil by means of "Agla" micrometer syringe. The oil was allowed to wick completely for 15 hr.

Soiling with particulate soils—Soiling with ferric oxide, carbon particles and Bandy black clay was carried out using "FIRA soiling tester" based upon the dynamic adsorption tester (AATCC Standard Test 70B 1964). Felt cubes (40) to be soiled were taken in a cylinder along with the soil and tumbled for 60 min. The excess soil was removed and the soiled cubes were retumbled for another 60 min for ensuring uniform distribution of soil among the cubes. Two fabric samples were mounted on two ends of the cylinder and the soiled cubes impinged on the samples. The cylinders were rotated and the test was continued till the reflectance of the white fabric was reduced by 75%. It was found that 12 cycles of 100 min each are adequate to reduce the reflectance to the desired level.

Soiling with synthetic sebum—The fabric sample was padded with a solution of synthetic sebum of concentration in the range 5 - 50%. The padded fabric was dried followed by soiling with particulate soils using FIRA soiling tester.

Wet soiling or soiling from aqueous dispersion—In the first set of experiments, the optimum quantity of each particulate soil in the dispersion was determined by varying the quantity of soil in the soiling bath. The optimum quantity of soil was that which reduced the reflectance of white fabric by 40 - 50%. The optimum value was found to be 60 mg in the case of carbon particles and 90 mg in the case of ferric oxide in 200 ml solution. To see the effect of carboxymethylcellulose (CMC), varying quantities of CMC were taken in the soiling bath along with the particulate soil. The optimum quantity of CMC was found to be 100 mg in 200 ml washing solution. The aqueous dispersion contained 0.1 g/litre SDS, particulate soil and CMC (optional). The fabric sample was soiled in the dispersion at 30 rpm for 30 min in Tergotometer. The sample was rinsed and dried and the reflectance was measured.

Washing of soiled samples—The soiled samples were washed in 1 g/litre SDS, keeping material to liquor ratio 1:65, at 50°C and 50 rpm for 10 min using Tergotometer. After the washing, the samples were rinsed thoroughly and dried.

Evaluation of soiled fabrics—Reflectance measurements of the soiled area of the sample were carried out on Beckman DU spectrophotometer at the wavelength of maximum absorption. In the case of sample soiled with lubricating oil, four reflectance readings on each side of the sample were taken at different places of the soiled area. For particulate soils, reflectance measurement was possible only on one side of the sample. In all cases, an average reading was taken to calculate the degree of soiling. The same procedure was followed after washing the sample and the percentage soil retention was calculated from the Kubelka-Munk values.

\[
\text{Soil retained, } \% = \frac{\Delta (K/S) \text{ after wash} - \Delta (K/S) \text{ before wash}}{\Delta (K/S) \text{ before wash}} \times 100
\]

where \(K/S = \frac{(1 - R)^2}{2R}\); \(R\) is the reflectance; and \(K/S\) is the ratio of the absorbed light to scattered light.

Repeated washing and boiling-washing cycles—The retention of soil after repeated washing cycles and accumulation of soil after repeated soiling-washing cycles were measured following the methods described above. Assessment of soil retained was made after each cycle.

Properties of crosslinked fabrics—The fabrics treated with the crosslinking agents were tested for dry
Results and Discussion

Soil retention behaviour of DMDHEU treated cotton fabric—Data on the retention of oily soil after repeated washing cycles presented in Fig. 1 show that (a) crosslinked fabrics retain soil to a higher degree than the untreated one, and (b) the retention of soil increases with increase in the concentration of the crosslinking agent on the fabric.

Accumulation of soil on the fabric can be judged by giving repeated soiling-washing cycles (Figs 2 and 3), utilising lubricating oil as soil. It is evident from Figs 2 and 3 that (a) up to 12% DMDHEU concentration,
the difference in the accumulation of soil among crosslinked fabrics at various concentrations is marginal, and (b) above 12%, the accumulation of soil increases markedly with increase in crosslinker concentration on the fabric.

A plausible explanation for this behaviour can be obtained from the examination of Fig. 4, which shows a correlation between the properties imparted to the crosslinked fabrics and the concentration of the crosslinking agent. The maximum crease recovery angle is obtained at 1.5% of bound nitrogen, which corresponds to 12% DMDHEU (owf); the crease recovery angle ceases to increase with further increase in the concentration of the crosslinking agent on the fabric. In other words, a concentration of the crosslinking agent beyond 12% is not utilized in imparting the easy-care properties, but is consumed in some other reaction on the fabric surface. It may be concluded that (a) the presence of the crosslinking agent on the surface of the fabric leads to a faster rate of soiling, (b) excess crosslinker which is not utilized in crosslinking of cellulose chains remains on the surface of the fabric in some other form and is not washed away during repeated soiling-washing cycles, and (c) the crosslinking agent which is utilized in the formation of crosslinks promotes gradual soil accumulation.

Similar conclusions can be drawn with other soils also (Fig. 5). It may be inferred from the shape of curves depicted in Fig. 5 that the forces responsible for soiling with different soils, the retention of soil on washing and the sites for soil retention are of the same type, irrespective of the nature of the soil. Most of the curves
follow the same pattern, except in the case of fabrics crosslinked with 4 and 8% DMDHEU and soiled with Bandy black. The gradual loss of accumulated soil on subjecting the fabric to repeated soiling-washing cycles, as seen in Fig. 5, may be due to the fact that saturation of Bandy black on the surface of the fabric occurs during the second soiling-washing cycle and after that it is washed away gradually from the surface.

Higher concentrations of crosslinkers used in the present study are of academic interest only. The crosslinking bath in practice never contains excess crosslinker beyond 8-10%. It should be noted here that household usage of textile goods undergoes more than five soiling-washing cycles. At the initial stage of usage, the crosslinked fabric will differ only marginally from the untreated fabric in its soiling and soil removal behaviour. However, the build-up of soil on long usage will grow at a faster rate in the case of crosslinked fabrics even at the lower levels of crosslinker concentration and ultimately the accumulated soil will become a part of the fabric structure.

It is evident from Fig. 6 that retention of the particulate soil is less on the fabric soiled first with synthetic sebum and then with particulate soil compared to the samples directly soiled with particulate soil.

This result is exactly opposite to the experience in everyday life, because the soil retention on cuffs and collars is always more than on other parts of the garment. This is due to embedding of particulate soils in natural sebum as a consequence of continuous rubbing during use. The soiling medium for synthetic sebum employed in the present study is carbon tetrachloride, which is a non-swelling medium for cellulosic fibre in contrast to the aqueous medium of soiling in the case of natural sebum. Obviously, synthetic sebum cannot penetrate the surface of the fabric and will be deposited only on the surface. Although the particulate soil was bombarded on the sebum-treated fabric surface by “FIRA soiling tester”, the force is not sufficient to allow particulate soil to diffuse through the sebum layer and get attached to the fabric surface. As a result of this, most of the particulate soil will be deposited only on the surface of synthetic sebum. By increasing the sebum deposition on the surface of the fabric, the retention of particulate soil on the fabric can be reduced, as is evident from the results presented in Table 1. During washing, the particulate soil will go into aqueous solution more easily in the case of sebum treated fabric, because the particulate soil is held very loosely on synthetic sebum surface.

The retention of particulate soil on synthetic sebum treated fabric depends on the retention of synthetic sebum on the fabric surface. If synthetic sebum is retained more on the fabric surface after washing, particulate soil retention will be less.

To get further confirmation of this, fabric samples were soiled first with the individual components of the synthetic sebum followed by soiling with particulate soils. The results given in Table 2 indicate that the particulate soil retention was in the order: octadecyl alcohol > octadecane > stearic acid > glyceryl tristearate.

The retention of individual sebum components determined gravimetrically was in the order: glyceryl tristearate > stearic acid > octadecane > octadecyl alcohol.

<p>| Table 1—Effect of Concentration of Sebum on the Retention of Particulate Soil |</p>
<table>
<thead>
<tr>
<th>Fabric</th>
<th>5% Sebum</th>
<th>20% Sebum</th>
<th>50% Sebum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>7.23</td>
<td>6.00</td>
<td>5.70</td>
</tr>
<tr>
<td>16% DMDHEU treated</td>
<td>16.15</td>
<td>14.74</td>
<td>10.00</td>
</tr>
</tbody>
</table>

<p>| Table 2—Effect of Constituents of Sebum on the Retention of Particulate Soil |</p>
<table>
<thead>
<tr>
<th>Fabric</th>
<th>Octadecyl alcohol</th>
<th>Octadecane</th>
<th>Stearic acid</th>
<th>Glyceryl tristearate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>43.50</td>
<td>11.47</td>
<td>10.21</td>
<td>2.00</td>
</tr>
<tr>
<td>16% DMDHEU treated</td>
<td>12.65</td>
<td>27.51</td>
<td>19.17</td>
<td>10.80</td>
</tr>
</tbody>
</table>
alcohol. This means that when the synthetic sebum component (glyceryl tristearate) is retained more on the fabric surface, the particulate soil retention is less.

The following conclusions emerge from the above observations: (a) Retention of particulate soil on synthetic sebum treated fabric is inversely proportional to the retention of synthetic sebum after washing. (b) This conclusion is limited to this particular method of soiling. (c) Retention of particulate soil on sebum treated fabric is independent of the nature of the particulate soil. (d) Retention of synthetic sebum depends upon the individual components of sebum. (e) Retention of individual components of synthetic sebum on fabric cannot be explained on the basis of the hydrophobic-hydrophilic nature of the components, but may depend on the washing temperature and naturally on the melting point of the individual component.

Fabric treated with different crosslinking agents—Similar studies on soiling and soil removal were carried out employing other crosslinking agents, namely TMM, HMM, DMEU, DMDHEC, etc. In some cases, a mixture of crosslinking agents was employed. The total quantity of the crosslinking agent was kept constant (4% owf) in all cases. The results presented in Fig. 7 indicate that the retention of soil by the fabric treated with different crosslinking agents falls in a narrow range; however, it is always higher than that in the untreated control.

DMDHEU treated fabric with additives—Along with the crosslinking agent, other chemicals, such as electrolytes, softeners, handbuilders, wetting agents, are usually present in commercial finishing formulations. In the following series of experiments, a few additives with different base chemicals were added at definite concentrations in each case in the crosslinking bath along with the crosslinking agent (DMDHEU). The soil retention behaviour of such finished fabrics is shown in Fig. 8.
Softeners, in general, increase the retention of soil on the crosslinked fabric. Fabric treated with wax emulsion retains almost the same quantity of soil as the control after first wash and the soil retention behaviour changes upon repeated washings. This tends to suggest that soil which is not removed during the first wash is strongly held with the softener on the fabric and this, to some extent, reflects the durability of the softener on the fabric. The fabric samples treated with polyvinyl acetate dispersion and polyethylene emulsion behave in the same fashion. In these samples, soil retention is always higher by 5% than in the control sample. In the case of silicone emulsion treated crosslinked fabric, soil retention is markedly higher after the first wash and it gradually decreases with subsequent washes. Even after the third wash, the retention is as high as 20% compared to the control. The order of soil retention by different softeners is as follows: wax emulsion < polyvinyl acetate dispersion < polyethylene emulsion < silicone emulsion.

The retention of pigment soils on silicone emulsion treated fabric was explained by Mazzeno et al. The above results indicate that (a) the active material content in a softener does not have much effect on its soil retention property, (b) the chemical nature of the softener, i.e., the hydrophobicity of the parent compound does not explain its soil retention behaviour, and (c) most probably, the wash fastness property of the softener plays a major role in explaining its soil retention behaviour.

Soil redeposition on crosslinked fabrics—During washing, there are chances that the soil which has been displaced from the fabric into the detergent solution may deposit onto the fabric. This phenomenon is known as aqueous soiling, wet soiling or soil redeposition. Wet soiling retards the soil release efficiency.

Results of the soil redeposition study revealed that, in general, soil redeposition increases with increase in crosslinker add-on.

In the case of DMDHEU and TMM treated fabrics, soil redeposition is found to be more (~ 7%) than with HMM and DMEU treated fabrics (~ 3%). However, in the presence of CMC, soil redeposition is significantly lower (Fig. 9). This behaviour can be explained considering the hydrophilic and anionic character of CMC. The hydrophilic nature of CMC enhances the effectiveness of the detergent and the negative charge repulses the similarly charged dirt particles and thus prevents redeposition.

Conclusion

Fabric finishes, especially DP finishes, play an important role in the yellowing and greying of cotton fabric on usage. Since such finishes make the bulk fabric structure difficult to wet due to crosslinking, soils do not get removed easily during washing. As a consequence, these finishes have a deleterious effect on the original appearance of the fabric. This effect is promoted by certain softeners present in the crosslinking bath.

Acknowledgement

The authors thank Dr H.C. Srivastava, Deputy Director and Head, Chemistry Division, ATIRA, for his keen interest and guidance, and Dr P.C. Mehta, Director, ATIRA, for his suggestions and permission to publish this paper. They wish to acknowledge the useful discussions with Dr J.J. Willard, Senior Research Consultant of UNDP, Shri H.U. Mehta, and Dr N.E. Dweltz. One of them (AMD) is thankful to the Council of Scientific and Industrial Research for the award of a fellowship.

References