CHAPTER IV

SOILING AND SOIL RELEASE BEHAVIOUR OF CROSSLINKED COTTON FABRICS
CONTENTS

4.1 Contradictory Reports on the Topic
4.2 Selection of Fabrics and Soils
4.3 Fabric-Soil Interactions
4.4 Mechanism of Crosslinking
4.5 Mechanism of Oil Spreading on Fabric Surface
4.6 Effect of concentration of Crosslinking Agent
4.7 Kinetics of Oily Soil Accumulation
4.8 Concept of Hydrophilicity
4.9 Effect of Different Additives in the Crosslinking Bath
4.10 Effect of Different Catalysts in the Crosslinking Bath
4.11 Studies with Synthetic Sebum
  4.11.1 Soil Removal Behaviour of Synthetic Sebum
  4.11.2 Interaction of Solid-Solid Soils on the Same Substrate
4.12 Interaction of Solid-Fatty Soils on the Same Substrate
4.13 Mechanism of Particulate Soiling
4.14 Effect of Particle-Size on Soiling
4.15 References
4.1 **Contradictory Reports on the Topic**

The objective of the present studies is to investigate typical fabric-soil interactions and soiling and soil release behaviour of crosslinked cotton fabrics. When a cotton fabric is treated with a crosslinking agent, its physicochemical properties are altered. There are many reports published about the problems of changed soiling and soil removal behaviour of cotton fabric caused by crosslinking. These reports have resulted in equal numbers of different opinions and thus making the complex phenomena of soiling and soil removal even more complex.

According to one report\(^1\), soil uptake remains unaltered upon crosslinking. Another study\(^2\) reports that crosslinked cotton fabric shows a greater resistance to wet soiling. While a third group reports higher soiling of crosslinked fabrics.\(^3\) These divergent findings emphasized the need for a detailed and systematic study of the problem.

Many of these workers\(^6\) used technical recipes, different finishing processes and different soiling methods. As a result, the influence of one particular variate alone, e.g., crosslinking agent, is not visible and hence it is difficult to get a clear picture. For this reason, the present investigations aim to isolate the effects of crosslinking ingredients such as crosslinkers, catalysts,
additives on soiling and soil removal behaviour of treated fabrics.

4.2 Selection of Fabrics and Soils

Cottonoolin samples crosslinked with dimethylol-dihydroxyethyleneurea (DMDHEU) at various concentrations were selected. The catalysts used along with DMDHEU include catalyst DC\textsuperscript{10} in general, and zinc nitrate and magnesium chloride in particular. A few additives with different base chemicals, such as, polyvinylacetate dispersion (PVAD), silicone emulsion (SE), polyethylene emulsion (PE), etc., were also studied along with DMDHEU optionally. The fabrics were treated by conventional pad-dry-cure process.

The other important variables are particulate and oily soils and meaningful soiling method. Dry soil resistance of fabrics is evaluated with particulate soils employing the Accelerator.\textsuperscript{11} The oily soil is applied by the Wicking method.\textsuperscript{12} The accumulation or the build-up of oily soil on fabrics is worked out by repeated soiling and washing cycles. Results thus obtained are presented by soiling values V, S and W or by percent soil retained.

4.3 Fabric-soil Interactions

The term "soiling of textiles" means the unwanted deposition of oily and/or particulate materials on surface of textiles. Soiling of textiles takes place in two steps:
firstly, the transport of soil to the fibre surface and secondly, adsorption of the soil on the fibre. The transport of soil takes place by two mechanisms: static and dynamic. The static mechanism involves soil transport by gravity, air currents or electrostatic attraction. The dynamic one involves soil transport by contact transfer. Which process dominates soiling depends essentially on the end-use of the textile\textsuperscript{13} (Table 4.1).

\textbf{TABLE 4.1}

SOILING MECHANISMS FOR DIFFERENT TEXTILES\textsuperscript{13}

<table>
<thead>
<tr>
<th>Type of textile</th>
<th>Soiling mechanism</th>
<th>Type of soil encountered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drapes, Curtains</td>
<td>Static</td>
<td>Particulate soil, with or without oil</td>
</tr>
<tr>
<td>Upholstery</td>
<td>Dynamic and static</td>
<td>Liquid fatty soil, with particulate matter; particulate soil, with or without oil</td>
</tr>
<tr>
<td>Carpets</td>
<td>Mainly dynamic; also static</td>
<td>Particulate soil, with or without oil</td>
</tr>
<tr>
<td>Apparel</td>
<td>Dynamic</td>
<td>Particulate soil, with or without oil; liquid soil with particulate matter</td>
</tr>
<tr>
<td></td>
<td>Static</td>
<td>Liquid soil, with or without particulate matter</td>
</tr>
</tbody>
</table>
The process of soil deposition displaces fibre-air interface with fibre-soil interface. The possible fibre-soil interfaces are shown schematically in Fig. 4.1. Here, A represents nonwetting oil and B loosely held solid particle on fibre surfaces. A penetrated solid particle C, a wetting oil D, and penetrated oil E are strongly adhered to the fibre surfaces. Lastly, F, G and H show possible solid-liquid-fibre interaction with more complexity.

4.4 Mechanism of Crosslinking

Introduction of crosslinks in cellulose imparts wrinkle recovery properties to cotton fabrics. This is done by application of certain bifunctional compounds such as dimethylol cyclicurea derivatives which form crosslinks with the hydroxyl groups of cellulose. Tovey has reviewed the resin finishing of cotton textiles extensively.

Various types of crosslinking agents and methods of their application have been studied. The physical properties of treated fabrics depend mainly upon the type and concentration of the crosslinking agent applied and in the conditions under which the crosslinks are formed. The conventional process consists of applying the resin solution uniformly on the fabric by padding, drying (at 110°C for 5-10 minutes) and curing (at 150-160°C for 2-5 minutes).

Mechanism of crosslinking reaction, which is
FIG. 4.1: TYPE AND EXTENT OF FIBRE-SOIL INTERACTION
analogous to that of dyeing\textsuperscript{16,17}, is shown to occur in three stages, (a) swelling of the fibres due to adsorption of water, (b) diffusion of the reagent into the fibre, and (c) fixation of the cross-linker on and inside the fibre.

The following reactions take place during curing:

1. Decomposition of metal salt.

\[
2\text{MgCl}_2\cdot6\text{H}_2\text{O} \rightleftharpoons \text{ClMg-O-MgCl} + 5\text{H}_2\text{O} + 2\text{HCl}
\]

2. Protonation of resin molecule.

\[
\begin{align*}
\text{R-CO-NH-CH}_2\text{OH} + \text{H}^+ & \rightleftharpoons \text{R-CO-NH-CH} = \text{CH}_2 \\
\text{R-CO-NH-CH}_2\text{OH}_2 & \rightleftharpoons \text{R-CO-NH-CH} = \text{CH}_2 + \text{H}_2\text{O} \\
& \quad \text{R-CO-NH} = \text{CH}_2
\end{align*}
\]

3. Crosslinking reaction.

\[
\text{CH}_2\text{N-CO-N-CO-N-CH}_2 + 2\text{Cell-OH} \rightleftharpoons \\
\text{Cell-O-CH}_2 - \text{N-CO-N-CO-N-CH}_2 - \text{O-Cell}
\]

In order to study the soiling and soil release behaviour of crosslinked cotton fabrics the effect imparted by the following factors have been considered: concentration of the crosslinking agent, effect of additives and effect of catalysts in the resin formulation. A commonly used crosslinking agent dimethyloldihydroxyethyleneurea (DMDHEU) has been employed and the soil release behaviour of the crosslinked fabrics has been compared with that of the untreated fabric as a control.
4.5 **Mechanism of Oil Spreading on Fabric Surface**

An oily soil transported on a fabric surface gets spread in course of time. The physical interaction during the spreading of oil is presented schematically in Fig. 4.2. There are three important stages in the wicking phenomenon. During the initial state (I) contact angle of oil decreases. Then an oil puddle is observed in the middle of the oil spot as an intermediate state (II). Finally, the oil is spread almost completely leaving a thin film on fibre surfaces (III). The wicking occurs through capillary channels present in the complex contour formed by the fibres in a yarn and the yarns in a fabric.\(^{18}\) The overall phenomenon is affected by the following factors\(^ {19}\):

a. **Oil**:
- Surface tension
- Density
- Viscosity
- Chemical nature
- Contact angle

b. **Substrate**:
- Capillary radius
- Surface energy
- Morphology (compactness)
- Chemical nature

Owing to the spreading, the oil density (\% owf) within the spot decreases in course of time. Thus, it is of interest to investigate a kinetic picture of the process.
FIG. 4.2: WICKING OF OIL ON FABRIC
Since at any instance, a concentration gradient is established from the middle of the spot to the periphery in decreasing order, an average concentration of the oil is considered. Thus, the average concentration of oil (C) is inversely proportional to time (T). Mathematically,

\[ C \propto \frac{1}{T}. \]

An exactly known amount of oil was placed on a marked fabric sample on an embroidery ring. The area of the oil spot was measured by a Planimeter as a function of time. The area of the elliptical oil spot on the fabric was obtained for each measurement. The oil concentration for each area was calculated with respect to the original amount of oil.

A plot of C (% owf) against T (minute) results into a hyperbola (Fig. 4.3) indicating that the C-T relationship is exponential.

Therefore,

\[ C \propto \frac{1}{T^n}. \]

Hence,

\[ C = \frac{P}{T^n}, \quad \text{Eqn. 4.1}, \]

Where P is a constant.

Taking the logarithm,

\[ \log C = \log P - n \log T, \quad \text{Eqn. 4.2}. \]
FIG. 4.3 : HYPERBOLIC RELATIONSHIP BETWEEN OIL CONCENTRATION AND WICKING TIME
It can be seen from Fig. 4.3 that the region of interest lies within 60 minutes.

When C is plotted against T on a log-log scale (Fig. 4.4), a linear relationship is obtained for three different initial amounts of the oil taken on the fabric. The value of the exponent \( n \) can be obtained from the slope. The parallel lines obtained in the Fig. 4.4 indicate that the value of the exponent is independent of the initial quantity of oil placed on fabric. The constant \( P \) is the intercept of straight line and it can be defined as the oil concentration corresponding to unit value of time.

Fig. 4.5 shows C-T relationship for cotton fabrics subjected to the same amount of the oil initially. The value of the exponent \( n \) increases with the increasing concentration of crosslinker on the fabric. The data are given below:

<table>
<thead>
<tr>
<th>Fabric</th>
<th>ml. Used lub.oil</th>
<th>Exponent ( n ) (req.) ± 0.008</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated cotton</td>
<td>0.2</td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.411 (graph)</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.415</td>
</tr>
<tr>
<td>8% DMDHEU treated cotton</td>
<td>0.2</td>
<td>0.480</td>
</tr>
<tr>
<td>16% DMDHEU treated cotton</td>
<td>0.2</td>
<td>0.513</td>
</tr>
<tr>
<td>24% DMDHEU treated cotton</td>
<td>0.2</td>
<td>0.538</td>
</tr>
</tbody>
</table>
FIG. 4A: LINEAR RELATIONSHIP BETWEEN OIL CONCENTRATION AND WICKING TIME ON LOG-LOG SCALE
FIG. 4.5 : EFFECT OF CROSSLINKING OF COTTON FABRIC ON WICKING OF THE OIL
With increasing degree of crosslinking, the cotton fabric becomes less hydrophilic (Table 4.2) that is, more oleophilic. Hence, the oil tends to wick with a faster rate on the crosslinked fabric as compared to the uncrosslinked one. It seems therefore that the exponent \( n \) is analogous to the rate constant of wicking process and indicates the extent of crosslinking of fabric. Thus it is a qualitative measure of surface energy of the substrate.

**TABLE 4.2**

MOISTURE REGAIN AND WETTABILITY PROPERTIES OF COTTON FABRIC CROSSLINKED WITH DIFFERENT CONCENTRATIONS OF DMDHEU

<table>
<thead>
<tr>
<th>No.</th>
<th>Fabric</th>
<th>Column I</th>
<th>Column II</th>
<th>Column III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Moisture regain (% owf)</td>
<td>Rate of water rise in the fabric strip ( \times 10 \text{ cm/sec} )</td>
<td>Water absorbed by the fabric strip (% owf)</td>
</tr>
<tr>
<td>1.</td>
<td>Untreated cotton</td>
<td>7.0</td>
<td>18.0</td>
<td>56.5</td>
</tr>
<tr>
<td>2.</td>
<td>Crosslinked with 8% DMDHEU</td>
<td>6.1</td>
<td>21.2</td>
<td>47.1</td>
</tr>
<tr>
<td>3.</td>
<td>Crosslinked with 12% DMDHEU</td>
<td>5.7</td>
<td>23.5</td>
<td>41.3</td>
</tr>
<tr>
<td>4.</td>
<td>Crosslinked with 24% DMDHEU</td>
<td>4.9</td>
<td>30.0</td>
<td>32.0</td>
</tr>
</tbody>
</table>

After the infinite time of wicking, spreading of oil almost stops. Then the fabric samples can be subjected to washing for comparison of their soil release behaviour. In actual wear life of a garment the oily soil gets accumulated. This effect can be worked out by repeated soiling and washing cycles on the same sample.
4.6 **Effect of Concentration of Crosslinking Agent**

Cotton fabric samples crosslinked with various concentrations of DMDHEU were studied for the accumulation of used lubricating oil. Fig. 4.6 shows accumulation of the oily soil expressed as soiling value $S$. Since the crosslinked samples are having different oleophilicity, the same amount of oil placed gets wicked to different extent on them. Consequently, the oil density per unit area of the oil spot differs from sample to sample. It is evident that in the first cycle the soiling value $S$ is inversely proportional to the crosslinker concentration on the fabric. In the third cycle and thereafter the trend is reversed. This means that the oily soil accumulation must be studied at least for three successive soiling-washing cycles.

Fig. 4.7 shows accumulation of the oily soil expressed as soiling value $W$. The qualitative order of the curves is correct, however, the curves if extrapolated do not pass through the origin. The deviation may be attributed to the different soil densities prior to washing as illustrated in Fig. 4.6.

The meaningful picture is obtained when the accumulation of the oily soil is expressed as % soil retained (Fig. 4.8). Data obtained here unquestionably ascertain that in general, the crosslinked fabric samples retain oily soil to a higher degree than the untreated control. In the
FIG. 4.6: ACCUMULATION OF OILY SOIL EXPRESSED AS
SOILING VALUE S
FIG. 4.7: ACCUMULATION OF OILY SOIL EXPRESSED AS SOILING VALUE W
FIG. 4.8 : ACCUMULATION OF OILY SOIL EXPRESSED AS PERCENT SOIL RETAINED
first cycle, the difference between the treated and the untreated is marginal, which becomes large in the fifth cycle.

When the accumulated soil is plotted as the area covered by the oil spot on the fabric (Fig. 4.9), the accumulation on the crosslinked fabrics is not only heavier but over larger areas also.

The effect of the crosslinker concentration on the fabric towards the soil accumulation is specific. This is revealed when the soil retention is plotted as a function of nitrogen content of crosslinked fabric samples (Fig. 4.10). Here, the soil retention is uniformly increased up to 0.132% mole of nitrogen content (equivalent to 12% owf DMDHEU). Above this concentration, the soil retention increases markedly, and the effect is pronounced with increasing number of cycles.

This behaviour can be explained by a physical property, namely, crease recovery imparted by the crosslinked samples. The nitrogen content is a measure of the amount of the reagent bound to the fibre and the dry crease recovery angle is assumed to give an indication on the extent of the crosslinking of the fabric. Fig. 4.11 correlates these two parameters of the crosslinked samples. The dry crease recovery angle increases up to 0.132% mole of nitrogen content. Beyond this concentration, the crease recovery angle ceases to increase, suggesting thereby
FIG. 4.9: AREA OF THE ACCUMULATION OF OILY SOIL

AREA OF OIL SPOT (SQ. CM.)

FIFTH S-W CYCLE

FIRST S-W CYCLE

NITROGEN CONTENT (% MOLE) OF DMDHEU TREATED FABRICS
NITROGEN CONTENT (% MOLE) OF DMDHEU TREATED FABRICS

FIG. 4.10: CRITICAL DEGREE OF CROSSLINKED COTTON FABRIC DETERMINED BY THE EXTENT OF OILY SOIL RETENTION
Fig 4.11: Relationship between nitrogen and dry crease recovery of cotton fabric samples crosslinked with different concentration of DMDHEU.
consumption of the crosslinking agent as polymeric deposit on surface or side reactions with cellulose.\(^{20}\)

4.7 Kinetics of Oily Soil Accumulation

The amount of soil retained \((R)\) on the crosslinked samples appears to increase linearly with the increasing logarithm of soiling-washing cycle (Fig. 4.12), according to the mathematical function

\[
R = R_0 + m \log N, \quad \text{Eqn. 4.3.}
\]

The slope \(m\) and the intercept \(R_0\) both depend upon the concentration of crosslinking agent on fabric when other factors are essentially constant.

Referring to the above equation, when \(N = 1\), \(R = R_0\), the quantity \(R_0\) may be called soil retainability, which is the amount of soil retained in the first cycle. The soil retainability evaluates the fabrics qualitatively but quickly. The constant \(m\) shows the rate of soil accumulation. It depends upon the concentration of crosslinking agent on fabric so far as the crosslinked fabrics are concerned. It assesses the fabrics quantitatively.

Differentiation of the equation 4.3 gives

\[
\frac{dR}{dN} = \frac{X}{N}, \quad \text{Eqn. 4.4},
\]

where \(X\) is a constant. This expression suggests that the rate of soil accumulation is inversely proportional to the
FIG. 4.12: KINETICS OF OILY SOIL ACCUMULATION

NUMBER OF REPEATED SOILING-WASHING CYCLE

SOIL RETAINED (%) AFTER WASHING

UNTREATED CONTROL

24% DMDHEU
18% DMDHEU
16% DMDHEU
12% DMDHEU
8% DMDHEU
4% DMDHEU
soiling-washing cycle. This may be attributed to the increasing loading of soil by repeated cycles.

When logarithm of the slope $m$ is plotted against the nitrogen content of crosslinked samples (Fig. 4.13), a straight line is obtained. This confirms that the rate of oily soil accumulation is exponentially proportional to the concentration of crosslinking agent on fabric. The percent soil retained per cycle per mole percent nitrogen of DMDHEU is given by the slope, the value of which is nearly 4.0.

In practice, a treated garment undergoes successive wear and wash cycles, and hence, the accumulated soil becomes its intrinsic property. In initial stages of usage, soil accumulation would be low, but on long usage it would be high. Moreover, this behaviour would be 'mild' for the so-called wash-wear level and 'severe' for the permanent press or durable press level of crosslinking agent on fabric.

4.8 Concept of Hydrophilicity

The soil release behaviour of the crosslinked fabric samples studied above can be explained on basis of their hydrophilicity. The hydrophilicity of fabric is determined by two methods, namely, moisture regain and wettability measurements. The data obtained are presented in Table 4.2.

It is evident from column I that the moisture regain and hence hydrophilicity of the fabric samples
Fig. 4.13: Characterization of the crosslinked fabric for retention of oily soil.
decreases with increasing crosslinker concentration on fabric. However, the rate of water-rise (column II) increases in contrast. But, in addition to water-rise, the amount of water (% owf) taken up by the fabrics (column III) decreases with increasing crosslinker concentration on fabric.

These results indicate that water penetrates into fabric structure (slow rate and more absorption) in case of the untreated cotton fabric, but it does not penetrate to the same extent (high rate and less absorption) in case of the crosslinked fabric samples.

The capillary rise phenomenon depends upon two parameters, namely, porosity of the fibre and interaction of water molecules with molecular structure of the fibre. The rise in capillary corresponding to the porosity of fabric can be termed as “capillary hydrophilicity” and that related to the interaction with the molecular structure of fibre as "intrinsic hydrophilicity". As a result of both the interactions, the movement of water is hindered and hence the rise of water on untreated cotton fabric is retarded with higher water absorption. On the other hand, with the increasing amount of crosslinking agent on fabric, the hydroxyl groups of cellulose are progressively unavailable for interaction with water. Consequently, water rises just on the fabric surface with faster rate and less absorption in case of crosslinked samples.
A relation between decreasing moisture regain and increasing soiling tendency of fabrics is reported.\(^3\)

Liljemark and Asnes\(^2\) reported that when polyester fabric was treated with strong alkali the surface was modified chemically. Strong alkali saponify the ester links in the polyester material, thereby changing the amount of carboxyl and hydroxyl groups. Owing to the change, the polyester material became more hydrophilic. The increased hydrophilicity facilitated interaction of water with the fabric.

It may be concluded that the crosslinking agent plays a very important role in oily soil accumulation of crosslinked fabric. Since it makes the bulk fabric structure more difficult to wet due to crosslinking, effectiveness of the surfactant during washing is probably reduced. As a result, oily soils do not get removed completely and they are accumulated on the fabric. That is why these finishes have a deleterious effect on maintaining the original appearance of the fabric.

4.9 Effect of Different Additives in the Crosslinking Bath

In actual practice, some additives are added in the crosslinking bath along with the crosslinking agent for additional improvement of the crosslinked fabric. They are called softeners, builders, stiffners, binders, etc. depending upon their requirement. Since these additives
affect the surface characteristics of the crosslinked fabric, it is necessary to investigate their soil release behaviour.

A few selected additives were applied on cotton poplin along with one crosslinking agent, namely, DMDHEU. The accumulation of used lubricating oil on the crosslinked samples is shown in Fig. 4.14. The additives in general, retain the soil to a higher extent as compared to the DMDHEU control. It is evident from Fig. 4.14 that, in general, the presence of softeners gives rise to high soil retainability.

Since the samples show high soil retention in the first cycle, it is interesting to compare them in terms of their soil retainability as shown in Fig. 4.15. The order of increasing soil retainability is as follows:

DMDHEU CONTROL, P32 + DMDHEU, PVAD + DMDHEU,
SE + DMDHEU, SLNB + DMDHEU

Among the additives studied, silicone emulsion and SLN binder show very high soil retainability. The soil retained in the first cycle perhaps becomes an intrinsic property of the crosslinked fabric which does not get removed on repeated soiling-washing cycles even though the additive is poor in wash-fastness.

The samples treated with silicone emulsion and SLN binder are hydrophobic in character. Mazzero et al.²
FIG. 4.14: ACCUMULATION OF OILY SOIL ON CROSSLINKED FABRIC SAMPLES SUBJECTED TO DIFFERENT ADDITIVES
FIG. 4.15: SOIL RETAINABILITY OF CROSSLINKED FABRIC SAMPLES SUBJECTED TO DIFFERENT ADDITIVES
have explained that the silicone material, which is almost entirely on the surface of fibre, is probably softening and becoming tacky at the washing temperatures so that the carbon particles adhere to the tacky surface. They have substantiated this conclusion by studying the soiling behaviour of film casted on a glass plate.

Other problematic softeners are: paraffin dispersions, fatty alcohol sulfates, and alkyl ethylene urea products.²²

4.10 Effect of Different Catalysts in the Crosslinking Bath

The catalysts used in crosslinking reactions with cellulose do not strictly follow the classical definition of catalyst. They take part in the reaction and are also chemically changed during the course of the reaction.²³ Hence, it is also important to study the effect of different catalysts on the soil release behaviour of crosslinked fabric. In this direction, the cotton poplin samples were crosslinked with one crosslinking agent, namely, DMDHEU and different catalysts. The accumulation of used lubricating oil on the crosslinked samples is shown in Fig. 4.16. The soil retainability as well as the rate of the soil accumulation increases in the following order: untreated control, MnCl₂.6H₂O + DMDHEU, Catalyst DC + DMDHEU, Zn(NO₃)₂.6H₂O + DMDHEU. This behaviour may be attributed to the extent of crosslinking influenced by the catalysts.
FIG. 4.16: ACCUMULATION OF OILY SOIL ON CROSSLINKED FABRIC SAMPLES SUBJECTED TO DIFFERENT CATALYSTS

- Zn(NO$_3$)$_2$$^\cdot$6H$_2$O + DMDHEU
- Catalyst DC + MgCl$_2$$^\cdot$6H$_2$O + DMDHEU
- MgCl$_2$$^\cdot$6H$_2$O + DMDHEU
- Untreated control

NUMBER OF REPEATED SOILING-WASHING CYCLE

SOIL RETAINED (%)
The catalysts studied here are acid catalysts. According to one report, a fibre that is anticrease finished with conventional resins and crosslinked in an alkaline state turns hydrophilic, whilst acid catalysts impart hydrophobicity and additionally, increase soil retention. Although, this behaviour cannot be completely explained but it can be assumed that the differences between alkaline and acidic catalysts are due to different degrees of swelling. And it is reported that the moisture regain, i.e., the hydrophilicity of a crosslinked cotton fabric is directly related to the extent of fibre swelling at the time of crosslinking.

From the above studies it may be concluded that nitrogenous crosslinking agents, hydrophobic additives and acidic catalysts modify the fabric such that build up of oily soil takes place upon repeated soiling and washing cycles. The most obvious reason may be the decreased wettability of finished fabric. It is noteworthy that the DMDHEU concentration beyond 8% owf as studied here are of academic interest only.

Effect of different nitrogenous crosslinking agents is reported by Gagarine. The decreasing order of soil retention and soil redeposition is given as: trimethylol melamine, dimethylol ethyleneurea, dimethyloldihydroxy ethyleneurea, carbamates and formaldehyde. However, the order is a qualitative assignment and a quantitative
evaluation would require extensive work.

4.11 Studies with Synthetic Sebum

Synthetic sebum is a mixture of compounds which in terms of nature and proportion is similar to human sebum. In order to elucidate the soiling mechanisms and the role played by each of the components of synthetic sebum, the individual components and the composite mixture were applied to the cotton fabric from solutions (5-50%) in carbon tetrachloride at room temperature. The fabric samples were dried and conditioned for 24 hours at 65% R.H. and 27°C both before and after immersion in the above solutions as well as after washing and drying. The amount of each component retained after washing was obtained gravimetrically and expressed as % owf.

4.11.1 Soil Removal Behaviour of Synthetic Sebum

Since the sebum components differ in molecular weight and polarity, they must exhibit specific behaviour of removal during laundering. The quantitative retention of the components on fabric after washing at room temperature is computed in Table 4.3. The relative ease of removal of individual components increases in the following order: octadecane, glyceryl tristearate, octadecyl alcohol, stearic acid. It is evident that the polarity of the components increases in the order: hydrocarbon, ester, alcohol, acid. More polar the compound,
TABLE 4.3

RETENTION OF SYNTHETIC SEBUM COMPONENTS AFTER WASHING AT ROOM TEMPERATURE

<table>
<thead>
<tr>
<th>Sebum component</th>
<th>Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecane</td>
<td>53.0 ± 1.0</td>
</tr>
<tr>
<td>Glyceryl tristearate</td>
<td>47.0 ± 1.0</td>
</tr>
<tr>
<td>Octadecyl alcohol</td>
<td>36.0 ± 1.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>28.0 ± 1.0</td>
</tr>
</tbody>
</table>

easier it is to be removed by an ionic surface active agent. Therefore, the ease of removal of each of the component is proportional to its polarity.

However, Fort et al. observed that at higher temperature of washing, this order is not followed. They envisaged a possibility of softening and subsequent diffusion of fatty ingredients into fabric interior. Such a diffusion was confirmed by $^{14}$C labelled radioactive soil on polymer films. They arrived at the conclusion that the extent of diffusion is an inverse function of the polarity and size of diffusing molecule.

4.11.2 Interaction of Solid-Solid Soils on the Same Substrate

The cotton fabric samples were soiled with synthetic sebum components and were subjected to subsequent soiling with ferric oxide in the Accelerator. The amount of ferric oxide used for soiling and the other soiling conditions
were kept constant. The extent of soiling of ferric oxide (Table 4.4) is expressed in terms of the soiling value \( V \) of the soiled samples. The deposition of ferric oxide decreases in the order: hydrocarbon, ester, alcohol, acid. This result may be attributed to the repulsion caused by the polarity of the sebum components.

TABLE 4.4

<table>
<thead>
<tr>
<th>Sebum component</th>
<th>Soiling value ( V ) with 5% (owf) ferric oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecane</td>
<td>5.80</td>
</tr>
<tr>
<td>Glyceryl tristearate</td>
<td>4.48</td>
</tr>
<tr>
<td>Octadecyl alcohol</td>
<td>3.92</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3.33</td>
</tr>
</tbody>
</table>

The extensive deposition of ferric oxide on hydrocarbon-treated fabric is due to the fact that the oily film facilitates soiling. The soil adsorption increases regardless of the chemical nature of the substrate. It is reported that the increase of soiling is related with the ratio of viscosity to the dielectric constant of the oil.

Kissa stressed that the rate of soiling can depend on either of the two steps, namely, the transport of soil and its adsorption on the fibre surface. Usually when a fabric is exposed to soil, the rate of soil
adsorption is rapid at first but decreases with increasing soiling time until the fabric is saturated with soil. When a film of repulsive compound is present on the substrate, the rate of soil adsorption is diminished in the very beginning.

Table 4.5 shows the extent of deposition of ferric oxide on the cotton fabric samples which were soiled previously with 5-25% of the synthetic sebum. The soiling value V is inversely proportional to the synthetic sebum concentration. This means that in case of the sample where the concentration of synthetic sebum is less, more areas are available for the particles of ferric oxide and vice versa. Kissa's view stated earlier can be interpreted as the rate of soiling of particulate soil is governed by the availability of accessible fibre surface area.

**TABLE 4.5**

<table>
<thead>
<tr>
<th>Fabric soiled with synthetic sebum of concentration</th>
<th>Soiling value V with 5% (owf) ferric oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>4.80</td>
</tr>
<tr>
<td>10%</td>
<td>4.60</td>
</tr>
<tr>
<td>20%</td>
<td>3.56</td>
</tr>
<tr>
<td>50%</td>
<td>1.59</td>
</tr>
</tbody>
</table>
4.12 Interaction of Solid-Fatty Soils on the Same Substrate

The laboratory application of synthetic sebum employs non-aqueous solvent such as carbon tetrachloride. But human sebum is always emulsified by water from perspiration. The human sebum with dust particles forms a dark ring usually on collar and cuffs of a shirt.

The cotton fabric samples crosslinked with different concentrations of DMDHEU have been evaluated for their soiling behaviour by two methods, namely, the FIRA tumbler and the Accelerator. The soiling value V is presented in Fig. 4.17 as a function of nitrogen content of the samples.

The results obtained with the tumbler employing unextracted felt cubes show that the degree of soiling is proportional to the concentration of the crosslinking agent on fabric. Surprisingly, the results obtained with the Accelerator show that the degree of soiling is inversely proportional to the concentration of crosslinking agent on fabric.

Upon extracting a set of unsoiled felt cubes, an oily semi-solid material approximately 30% on the weight of felt has been obtained. The analysis of the oily substance characterise it as a wax (Table 4.6). It is
FIG. 4.17: DRY-SOIL RESISTANCE OF CROSS-LINKED COTTON FABRIC

A. TUMBLER, UNEXTRACTED FELT CUBES
B. ACCELERATOR
C. TUMBLER, EXTRACTED FELT CUBES

SOILING VALUE

NITROGEN (% OWF) CONTENT OF CROSSLINKED FABRIC
TABLE 4.6

ANALYSES OF WOOL-WAX

<table>
<thead>
<tr>
<th>IR Analysis</th>
<th>Chemical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharp peaks</td>
<td>Total fat: 94.4%</td>
</tr>
<tr>
<td>2900 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>1725 cm⁻¹</td>
<td>Iodine value: 6.5%</td>
</tr>
<tr>
<td>Medium peaks</td>
<td>Saponification value: 160.7%</td>
</tr>
<tr>
<td>1470 cm⁻¹</td>
<td>Unsaponification value: 2.9%</td>
</tr>
<tr>
<td>1180 cm⁻¹</td>
<td>Ash content: Nil</td>
</tr>
<tr>
<td>720 cm⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

Noteworthy that when a set of unextracted unsoiled felt cubes was employed in the FIRA tumbler, approximately 7.0% wax was transferred to the fabric under the same conditions of tumbling.

Subsequently, the samples were soiled in the tumbler employing the extracted felt cubes. A trend of soiling similar to that obtained by the Accelerator has been obtained.

Several conclusions can be derived from the above results. The crosslinked cotton fabric (finished with DMDHEU without softeners) shows higher dry-soil resistance. In other words, the crosslinking of cotton fabric minimises dry soiling. This may be attributed to the stiffness of the crosslinked fabric.
Upon crosslinking, the fabric becomes more oleophilic (Table 4.2) and therefore, it becomes more susceptible to oily wax. Consequently, with increasing degree of crosslinking, increasing amount of the wax gets adsorbed by the sample. And the film of wax on fabric surface promotes heavy deposition of the particulate soil. In fact, in the tumbling process employing unextracted felt cubes, the soil particles are encapsulated in the wax and get deposited on fabric. A strong adherence of the liquid-solid mixture occurs probably through the so-called fabric-oil-particulate soil bonding.

Scanning electron micrographs revealed the adsorption pattern of soil on fabric. Fig. 4.18(a) is the micrograph of unsoiled cotton fabric as a control. Fig. 4.18(b) is the micrograph of a sample soiled by the Accelerator. It shows that the soil particles are separate and are distributed evenly on the fibre surfaces. Fig. 4.18(c) is the micrograph of a sample soiled by the tumbler employing unextracted felt cubes. It shows that the soil particles are aggregated with an odd distribution thus giving clusters of agglomerated particles on the fibre surfaces. The clusters indicate that the soil particles are embedded in wax on the fibre surfaces.

Soiling the fabric with unextracted felt cubes thus simulates the creation of the dark ring around the collar and the cuff of a shirt on account of sebum, skin cells
FIG. 4.18(a): UNSOILED FABRIC (900X)
(b): FABRIC SOILED BY THE ACCELEROTOR (900X)
(c): FABRIC SOILED BY THE FIRA TUMBLER (900X)
and the air-borne particulate soil.

4.13 Mechanism of Particulate Soiling

A garment made of cotton poolin was extensively used by a child. The naturally soiled garment thus obtained was examined under scanning electron microscope. Figs. 4.19(a), 4.19(b) and 4.19(c) are the micrographs obtained from a portion of the garment which was not in intimate contact with skin. In these micrographs, soil particles appear physically seated on fibre surface. This would indicate that the main cause of soiling is adhesion. The attractive forces causing the adhesion are usually van der Waals forces or dispersion forces. The factors affecting the strength of adhesion are discussed by Bohme et al.

A part of the garment, which was in contact with skin, is shown in Fig. 4.19(d). The fibre surface is covered with sebum and soil particles are attached to the fibres.

The micrographs mentioned above show that particulate soiling of fabric is predominantly a surface phenomenon. The naturally soiled fabric can be compared to laboratory soiled fabrics also. Figs. 4.19 (a,b and c) are similar to Fig. 4.18(b) because they represent fabric soiled with "dry soil". On the other hand, Fig. 4.19(d) is similar to Fig. 4.18(c) as fatty soils are associated
FIG. 4.19(a, b, c): ADHESION OF PARTICLE AND FIBRE IN ABSENCE OF SEBUM (a, 2800X; b, 3900X; c, 2000X)

FIG. 4.19 (d): ADHESION OF PARTICLE AND FIBRE IN PRESENCE OF SEBUM (1400X)
with particulate soils.

The particle-fibre interface formed by the adhesion depends upon geometry and elastic properties of the two adherents. The surfaces of particles as well as of fibre are microscopically rough or irregular, and therefore, the actual contact area between the two is usually small. Four general types of particle-fibre interfaces are shown schematically in Fig. 4.20. A particle may remain just in contact with the fibre surface (Situation I). It may penetrate the fibre at various regions of the interface, possibly under pressure (Situation II). A tough particle may deform the fibre surface (Situation III). Otherwise a soft particle on a hard surface would get flattened (Situation IV).

4.14 Effect of Particle-Size on Soiling

Since the adhesion of solid particles on fibre is dominated by the interfacial contact area, the particle-size of particulate soil would affect the soiling of textile. Particle size affects also the optical properties of soil. At equal weight percentages soil consisting of finer particles is more visible. Moreover, since natural soil consists of particles of various sizes (Chapter III), the particle size is an important variable in soiling and detergency tests.

Carbon soil in different ranges of particle size
FIG. 4.20. POSSIBLE SOIL-FIBRE INTERFACES
(P = PARTICLE, F = FIBRE)
was applied on fabrics by the Accelarotor, keeping the amount of soil used for soiling and other soiling conditions constant.

The extent of soiling on untreated as well as crosslinked cotton fabric is shown as soiling value $V$ in Table 4.7. The degree of soiling of the fabrics

<table>
<thead>
<tr>
<th>Particle range (microns)</th>
<th>Soiling value $V$ of soiled fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>150-75</td>
<td>0.38</td>
</tr>
<tr>
<td>75-50</td>
<td>0.45</td>
</tr>
<tr>
<td>50-40</td>
<td>0.83</td>
</tr>
<tr>
<td>10-2</td>
<td>1.30</td>
</tr>
</tbody>
</table>

increases with decreasing particle size of the soil. The extent of soiling, indicated by soiling values $V$ derived from reflectances, is a function of the amount of soil on the fabric and its "visibility", in accord with the visual effect of soiling. Therefore, it can be inferred that fine particles are deposited more and they produce a very dark "shade" under the same environment of soiling. The effect is similar for untreated as well as crosslinked cotton fabrics. The following explanations
may be put forward:

(a) The smaller the particle, the greater is the total surface area of the particles and the greater is their capacity to cover and adhere on the substrate.

(b) Sorptive forces become the dominant factor in adhesion below 50 microns while mechanical occlusion predominates for larger particles.\(^{34}\)

(c) According to Compton and Hart\(^{35}\), the spaces between fibrils in the secondary wall of cotton are very small and hence can trap particles of finer size. However, this reason is objectionable when fibres of various spaces and irregularities are considered.
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