CHAPTER 10

SOIL-RELEASE FINISHES

Soil release is the term used to describe the cleanibility of fabrics by the laundering process. The preceding chapter dealt with finishes that made fabrics more resistant to soiling; however, in practice it has been found that soils have a way of penetrating even the best of repellent finishes, the textile item must be cleaned anyway. From a consumer point of view, a stain is perceived to be the worst case of soiling. With use fabrics tend to develop an overall grey and dingy look and this too is undesirable. But unless the consumer has the original fabric to compare with, the loss of whiteness is not objectionable unless it is severely discolored. A visual stain on the other hand, even a mild one, is more objectionable.

I. SOILS

Soils can be defined as unwanted substances at the wrong place. Most common soils fall into one of four categories: 1. water borne stains, 2. oil borne stains, 3. dry particulate soils and 4. composite soils involving oil and grease adsorbed on particulate matter. Water borne stains are not much of a problem, the stains are soluble in the wash water. Food stains and dried blood, although not water soluble, are responsive to proteolytic enzymes found in most commercial detergents. Dry particulate soils such as flour, clay and carbon black are mechanically entrapped in the yarn interstices and reside on the surface of the fiber. Removal of particulate soils depends on overcoming the work of adhesion between the particle and the fiber surface, facilitating the transport of detergent solution to where they reside and transporting the particle into the wash water. Mechanical energy (agitation) is important for latter.

Oily soils, e.g. salad oil, motor oil, food grease are particularly difficult to remove from synthetic fabrics such as polyester. The sorption forces between the oils and the synthetic fiber surfaces are so strong that it is virtually impossible to completely remove them by conventional laundering. For this reason oily soils, as a group, are particularly difficult to remove from many washable fabrics made from 100 % polyester and polyester blends. Lipstick, make-up, printing ink, used motor oil and atmospheric soot are examples of composite soils where bonding to the fiber is a function of the oily component. The removal of these stains is accomplished by overcoming the sorptive forces between the oil carrier and the fiber.

A. How Fabrics are Soiled

Soil can be airborne particles that settle by gravitational forces or are electrostatically attracted to the fabric. Soot is a troublesome airborne particulate that is difficult to remove from fabrics. Drapes, carpets and upholstery are items prone to being soiled by airborne soils. Soils can transfer by contact with a dirty surface and they can be ground in by pressure or rubbing. Soils can also transfer by wicking, liquid soils in contact with fabrics will wick into the structure by capillary action. Soils removed in the laundering process may redeposit back onto the fabric, emulsified oily soils may break out of solution unless the emulsion is well stabilized. Also the ionic charge of the emulsified soil may be attracted to an opposite charge on the fiber.

II. SOIL REMOVAL

A. Particulate Soil

The adhesion between particulate soil and the fiber depends on the location within the fabric structure, the forces of attraction between the soil and fiber, and the area of contact. Studies have shown that as more energy is used to grind the particulate soil into the fabric, the more difficult will it be to remove it. Both the area of contact and the location within the fabric are influenced by the force. Removal of particulate soil is brought about by breaking the adhesive bond between the particle and the fiber, wetting out the particle to make a stable dispersion, and then carry off the dispersed particle into the bulk of the wash water. The greater the area of contact, the more difficult it is to break the adhesive bond. Fine particles have a greater area of contact. The tighter the fabric, the smaller are the interfiber voids which make also make the outward transport more difficult.

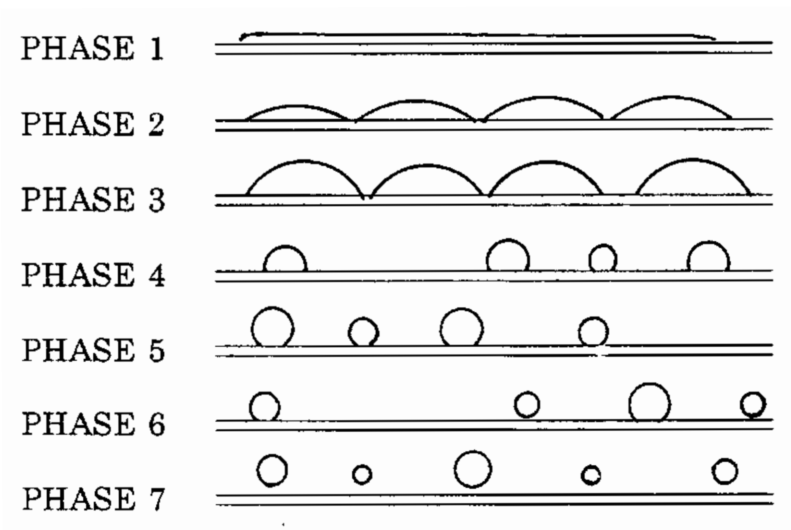
B. Oily Soils

The basic interaction between a liquid and a solid was discussed in the previous chapter on repellent finishes. It was shown that the thermodynamic work of adhesion is given by the Young/Dupree equation, $W_A = \gamma_{L/A} (1 + \cos \Theta)$. From this it follows that liquids that spread on a surface will have a zero contact angle. Since the cosine of zero is 1, the work require to remove that liquid will two times the surface tension of the liquid. Most oils have a surface tension of about 30 dynes/cm so they will completely spread on nearly all fibers except teflon.

1. Roll-up Mechanism

Oily-soil removal will depend on the three phase boundary interaction that occurs in the detergent solution. The roll-up mechanism first postulated by Adams argues that for removal to take place, the surface forces generated at the three phase boundary of fiber/detergent solution/oily soil results in progressive retraction of the oil along the fiber surface until it assumes a contact angle of 180 degrees. Here the work of adhesion is zero (Cosine of 180 degrees equals -1) and displacement is complete. The various phases of the roll-up mechanism is shown in figure 57.

Figure 24. Rolling-up Process of Soil Release



2. Roll-up Thermodyamics

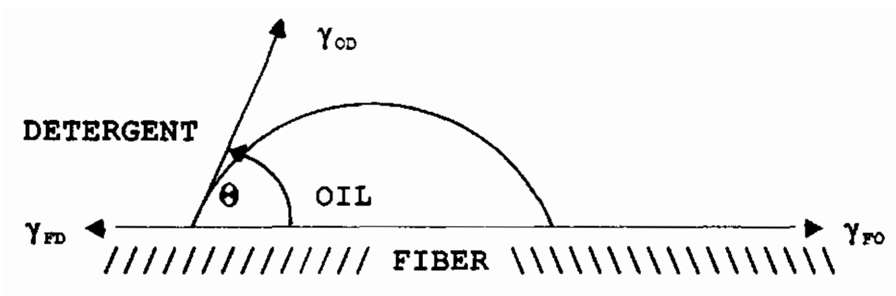
The surface forces responsible for three phase boundary between fiber-detergent and oil can be represented as interfacial tension vectors shown in figure 58. The forces responsible for roll-up is the resultant (R) of interfacial tensions as expressed by the equation:

$$R = \gamma_{F/O} - \gamma_{F/D} + \gamma_{O/D} \text{Cos}\ \Theta_d$$

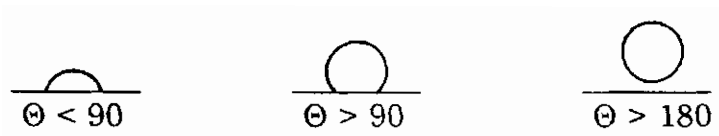
where: $\gamma_{F/O}$ = the interfacial tension between fiber and oil
$\gamma_{F/D}$ = the interfacial tension between fiber and detergent
$\gamma_{O/D}$ = the interfacial tension between oil and detergent

Θ_d = the dynamic contact angle.

Figure 25. Fiber-Oil-Detergent Interaction



In order for the dynamic contact angle (Θ_d) to change from zero to 180 degrees, the resultant (R) must be positive. R is positive when the quantity - (fiber/oil minus fiber/detergent interfacial tension) - is greater than the oil/detergent interfacial tension ($\gamma_{F/O} - \gamma_{F/D} > \gamma_{O/D}$). It follows then that when R is greater than zero, the contact angle increases.



On the other hand when R equals zero, the contact angle is in equilibrium and the oil drop stops receding. However if R is less than zero, the contact angle is smaller and the drop spreads on the surface.

From this it follows that roll-up and spontaneous release occurs when:

$$\gamma_{F/O} - \gamma_{F/D} > \gamma_{O/D}$$

and that redeposition occurs when:

$$\gamma_{F/O} - \gamma_{F/D} < \gamma_{O/D}$$

It is well to remember that: 1. zero interfacial energy exist when the attractive forces operating between molecules of a liquid exactly equal the attractive forces operating between the outermost molecules of a solid. Cotton or other hydrophilic fibers will have very low interfacial tensions with water because of hydrogen bonding. 2. High interfacial energy exist when one surface is non-polar and the other is polar, for example, hydrocarbon oils in contact with hydroxyl or ionic charged solid surfaces.

It is known that cellulosic fibers have good oily soil release. For cellulosic surfaces, $\gamma_{F/D}$ is low and $\gamma_{O/F}$ is high. On the other hand polyester fibers are known to have poor soil release. For polyester surfaces, $\gamma_{F/D}$ is high and $\gamma_{F/O}$ is low. It follows therefore that for spontaneous soil release to occur, the fiber surface must be hydrophilic and the balance of interfacial energies must be:

$$\gamma_{O/F} > \gamma_{O/D}$$

Table 17 illustrates the effect of the influence of outermost molecules on a fiber surface. From thermodynamic considerations, non-polar finishes such as silicones, polyethylene and fluorochemicals increase the interfacial tension between the detergent bath and the fiber and therefore should make soil release worse. The data support these thermodynamic predictions since both the fluorochemical and the silicone finish on 100% cotton fabric reduced the amount of soil removed.

Table 17.

Effect of Hydrophobic Surfaces on Soil Release

Fabric Treatment	% Soil Removed*
Unfinished cellulose	95
Acrylic latex finish	88
Fluorochemical	60
Silicone	45

* Soil was a mixture of iron oxide suspended in oleic acid. The detergent contained an anionic surfactant. Fabric was 100% cotton.

III. SOIL RELEASE CHEMICALS

The introduction of polyester/cotton blends in the early 1960's brought to light the need for soil release chemicals. Up until that era, most all washable fabrics were constructed of 100% cotton. The laundry processes included high wash temperatures, harsh chemicals (caustic, lye, bleach) and starch. Most all normal stains could be removed from these fabrics. When polyester entered the picture, oily stains became more difficult to remove. About the same time, home laundry procedures were changing; lower wash temperatures and less harsh chemicals evolved to prolong the life of durable press finishes. Also starching became unnecessary as the garment didn't require ironing.

Milliken can be credited for being first to introduce soil release durable press fabrics to the consumer. They incorporated an acrylic acid copolymer into their electron beam curable DP finish and merchandised the fabric under the VISA ^{R} label. Shortly thereafter, the rest of the industry followed suit with a host of different soil release finishes. In general, soil release finishes are film forming polymers capable of imbibing water. Today the number has stabilized into three distinct varieties. Two types work well on durable press finished cotton/polyester blends, e.g. acrylics and dual-action fluorochemicals. These are added into the final DP finish bath. A third type is engineered specifically for 100% polyester fabric, e.g. exhaustibles. They are best applied in the dye cycle (thus the name exhaustible) although they may be applied by pad-dry-cure.

A. Acrylic Soil Release Finishes

The chemical composition of acrylic SR finishes may be generalized as follows:

$$-[CH_2-\underset{COOR}{CX}-]_a-[CH_2-\overset{COOH}{CX}]_b-$$

Where: X = H (acrylic) or CH_3- (methacrylic)
R = Methyl or ethyl
a = 30 to 100 % b = 70 to 30 %

1. Polymethacrylic Acid PMAA

Poly(methacrylic) acid is completely water soluble and functions as a soil release finish. However the proper amount of cross-linking is necessary before the finish to functions properly. Table 9 shows that the soil release rating are influenced by the inclusion of a diepoxide crosslinking agent. When PMAA is crosslinked with only the diepoxide, marginal SR ratings are obtained. However if a small amount of diepoxide is added with DMDHEU, the soil release ratings are vastly improved. Increasing the amount of diepoxide causes the SR rating to drop again. This data supports the contention that the ultimate properties of the cured film deposited on the surface of the fiber determines soil release.

Table 9

Poly(methacrylic acid) Soil Release Finishes

Effect of Crosslinking

	SR Rating
PMAA + 14 % Diepoxide	2.0
PMAA + 21 % Diepoxide	2.5
PMAA + DMDHEU + 1.2 % Diepoxide	4.5
PMAA + DMDHEU + 3.0 % Diepoxide	2.5

2. Methacrylic Acid - Ethyl Acrylate Co-Polymers

Monomers containing carboxylic groups can be polymerized with vinyl and acrylic co-monomers to yield a range of co-polymers with varying carboxyl content. Co-polymers of methacrylic or acrylic acid and ethyl acrylate have been found to be particularly useful as soil release agents. An acid content of 70% or less give relatively high molecular weight emulsion polymers whereas higher proportions of acid renders the polymer water soluble and of lower molecular weight. A particularly good combination for soil release is 70% methacrylic acid and 30% ethyl acrylate. The effectiveness of co-polymers can be seen in Table 19. The data shows that when a 70/30 MAA/EA co-polymer is added to a typical durable press finish containing DMDHEU, the fabric possesses excellent soil release with fair durability. The data also shows that the SR ratings are substantially lowered if a diepoxide over cross-links the polymer.

Table 19

70/30 Methyacrylic Acid - Ethyl Acrylate SR Finish

Effect of Crosslinking

	SR Ratings		
	Initial	1 wash	5 washes
70/30 MAA/EA copolymer + DMDHEU	4.0	3.5	3.0
Above + 10 % Diepoxide	2.0	2.0	2.0

a. Mechanism

The mechanism by which these finishes work involves the imbibition of water by the cured polymer deposit. Cured polymer film were shown to swell in alkaline solutions and films with water weight gains of 550% or higher correlated with fabrics with improved soil release. Below this, no improvement in soil release was noted. Durability is also a function of crosslinking. The greater the crosslinking, the better the durability. However its a delicate balance that must be struck to give optimum results. Better soil release occurs at a pH of 11 than at a pH of 8. In fact the soils can be seen to roll up and float away without the need of a detergent at a pH of 11. The reason for this is that the polycarboxylic acids are weakly anionic as the free acid. When neutralized with alkali, they become 100% ionic and develop a strong anionic charge. Under these conditions, they are extremely hygroscopic and being polyelectrolytes, increase the interfacial free energy at the soil/fiber interface.

3. Practical Considerations and Fabric Properties

1. About 6 to 10% acrylic soil release agent is needed to give good results. The polymeric films are stiff and brittle, giving the fabric a stiff and harsh hand. Being brittle and stiff, the finish tends to cause dusting, excessive needle and sewing thread breakage. 2. Most of the finish is lost after the first wash; however, the small amount remaining is effective for many launderings. The fabric is considerably softer after washing. 3. Excellent soil release results can be obtained when the optimum conditions are met. It is the most effective finish against dirty motor oil. 4. The

finish is temperamental. It takes precise condition at the finishing plant to give reproducible results. 5. The finish is cost-effective for work clothing when dirty motor oil release is a significant quality.

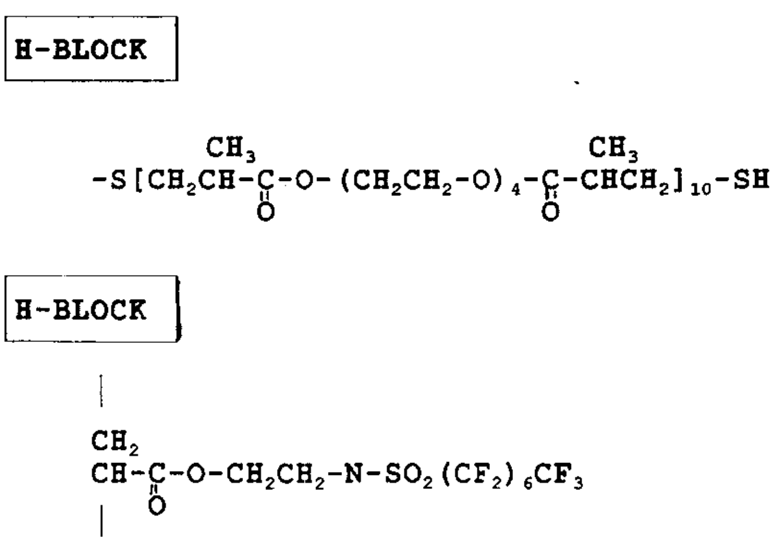
D. Dual Action Fluorochemical Soil Release

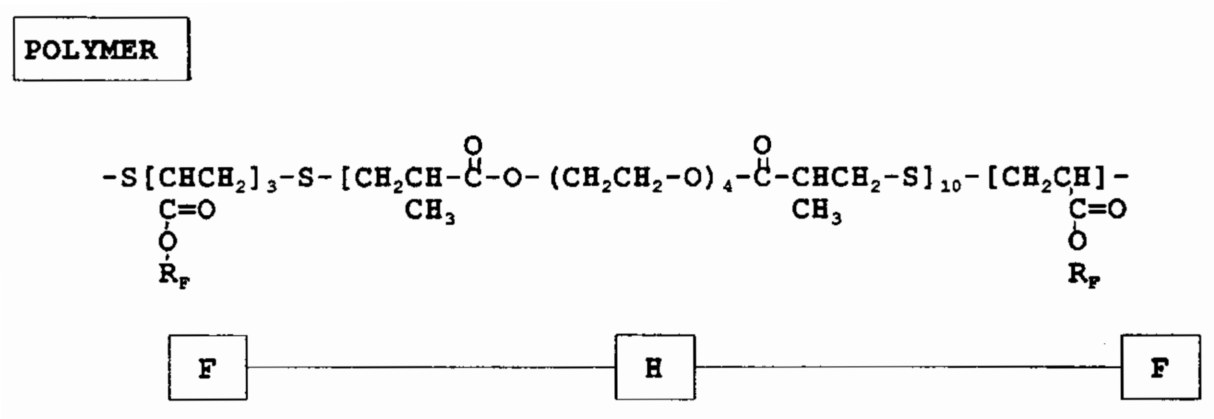
A unique block co-polymer, developed by the 3M company (Scotchgard Brand Dual-Action Fabric Protector) combines oil repellency with soil release. While conventional fluorochemical water and oil repellent finishes have an adverse affect on soil release, the co-polymer overcomes this deficiency. The hybrid polymer backbone is comprised of segments based on polyoxyethylene united with segments containing long-chain perfluoroaliphatic groups. Figure 59 shows the structure of the H portion (the hydrophilic portion), the F portion (the perfluoroaliphatic portion) and the block co-polymer. The H section is a sulfhydryl-terminated co-polymer of tetraethylene glycol dimethacrylate and hydrogen sulfide containing 50% by weight of recurring ethylene oxide units. The F section contains poly(N-methylperfluoro-octanesulfonamidoethyl acrylate). The block co-polymer has recurring units of perfluoro acrylate portion attached to the sulfhydryl-terminated glycol dimethacrylate.

The individual segments alone do not confer effective soil release; however, when combined into a single molecule, the new composition is effective both as a soil release agent and an oil repellent finish. Durable press reactants are necessary to cross-link the finish.

1. Composition of Polymer

Figure 28. Fluorochemical Soil Release Agent



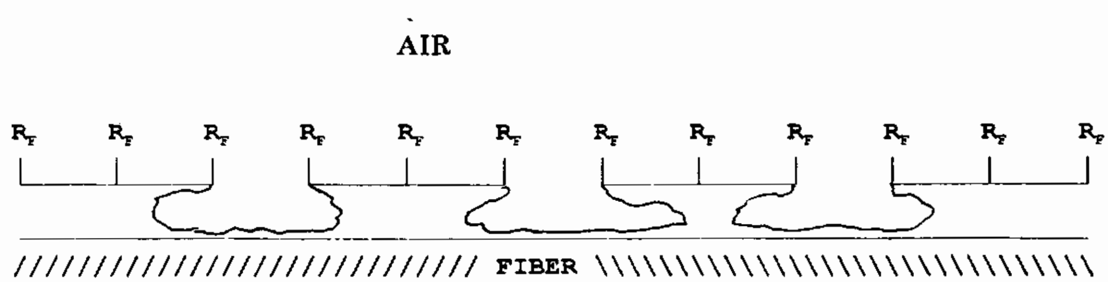


2. Mechanism

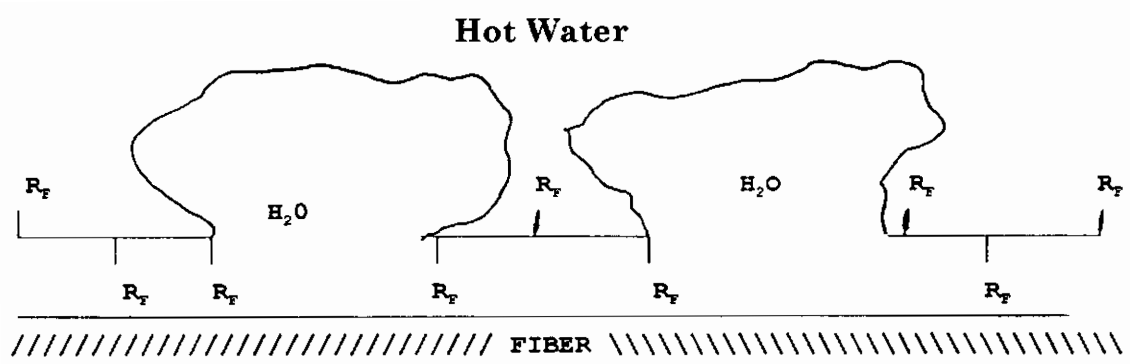
The uniqueness of this material is related to the tendencies of non-polar perfluoro alkyl side chains to orient outward towards air. During the drying and curing stage, polymer mobility allows the tails to orient outward. The oxyethylene segments are forced to the interior of the film and so the outermost film layer is richly populated by the low interfacial energy perfluoro segments. This provides a low critical surface tension which favors oil repellency. In water, the polyoxyethylene segments swell, causing the polymer to "flip-flop". The surface is now hydrophilic favoring the release of soil. The flip-flop mechanism is pictured in figure 60.

Figure 29 "Flip-Flop" Mechanism

Orientation When Dry



Orientation When Wet (During Laundry)



2. Practical Considerations and Fabric Properties

The product is very expensive; however, a small amount goes a long way. Good results can be obtained with about 0.5% add-on. Overall soil release ratings are good; however, this finish is not as effective toward dirty motor oil release as is the acrylic SR finish. The cured film properties and the very small add-on has little or no effect on fabric hand. Sewing, dusting and the other negative fabric properties associated with the acrylic SR finish are non-existent with this finish. It is important to include DP crosslinking resins to make it durable to laundering. For this reason it is used mainly on polyester/cotton blends and not on 100% cotton.

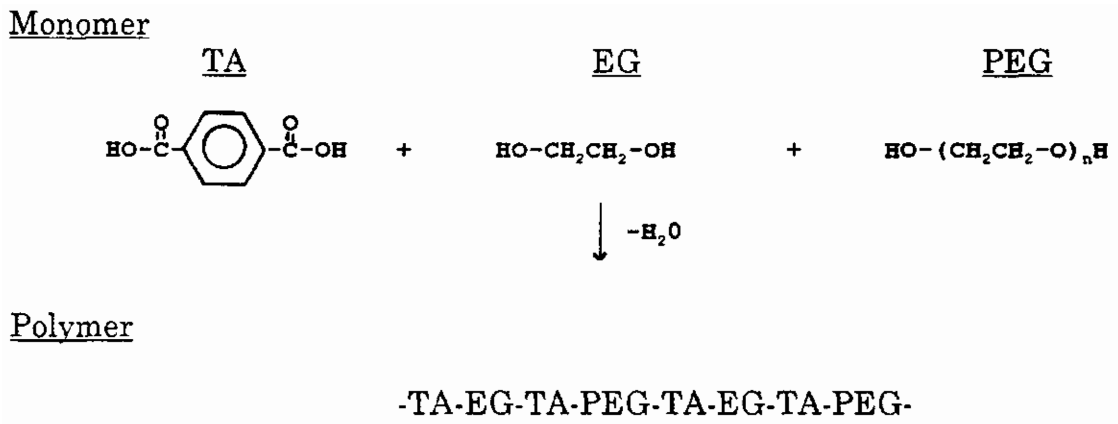
E. Hydrophilic Soil-Release Finishes for 100% Polyester

Effective soil release finishes have been developed for 100% polyester fabrics which are best applied during the dye cycle and are often called ***Exhaustible*** SR finishes. The are also called ***Co-Crystallizing*** SR finishes. This class of SR chemicals are composed of water dispersible, low molecular weight block co-polymers which have recurring blocks of hydrophilic segments attached to short blocks of PET. The hydrophilic segment is either polyoxyethylene or sulfoisophthalic acid. The PET portion provides attachment to the polyester fiber surface through secondary forces. The most effective application conditions are the same as those for exhaust dyeing polyester fibers with disperse dyes. This method results in a uniform deposition of the finish on the fiber surface. Pad applications are sometimes used; however, thermosoling temperatures are needed to get fixation.

1. Polyoxyethylene Co-Polymers

Figure 61 shows a schematic of the monomers used to make this type of co-polymer. Terephthalic acid, ethylene glycol and polyethylene glycol monomers are mixed in proper proportion and condensed to form a low molecular weight polyester. This polymer readily disperses in water and gives a product that is easy to handle and to apply to fabric. The composition of the monomers can be changed to yield products that leave the fabric with a soft slick hand or a dry stiffer hand.

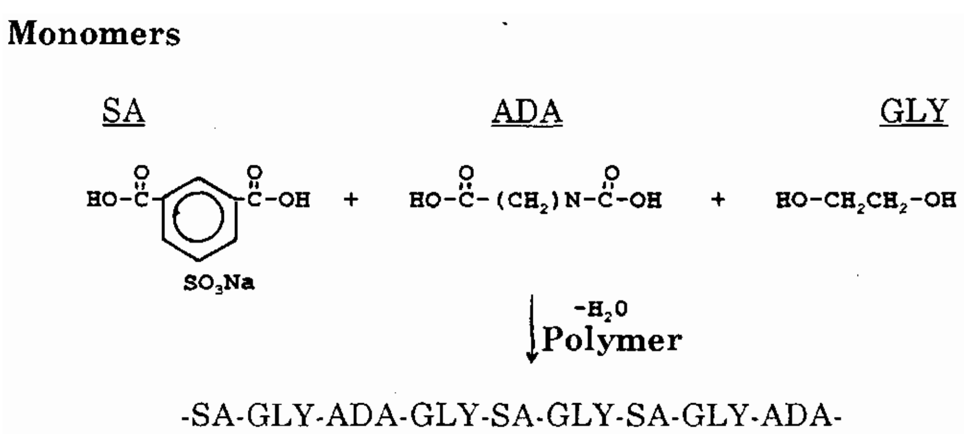
Figure 30. Polyoxyethylene Type SR Finish



2. Sulfoisophthalic Acid Co-Polymers

Figure 62 show a schematic of a second variety of polyester SR finishes. This composition utilizes sulphoisophthalic acid as the hydrophilic portion and an aliphatic dibasic acid to control polymer softening point. The resulting co-polymer is water dispersible and being ionic in nature, requires the inclusion of an electrolyte to facilitate its exhaustion onto the fiber surface.

Figure 31. Sulphoisophthalic Type SR Agent



3. Practical Considerations and Fabric Properties

These finishes work best on loosely structured, textured polyester fabrics. Fabrics made from continuous filament or spun 100% polyester yarns are not responsive to these finishes. The driving force for exhausting the polyoxyethylene type is inverse solubility behavior exhibited by these types of materials. Polyethers are more soluble cold than hot. The high temperatures experienced in the dye bath reduces the co-polymer's water solubility favoring exhaustion. Oily-soil release on the loosely structured knits is fairly good. Oily-soil release on spun yarn and continuous filament fabrics is poor. All polyester fabrics are rendered more water wickable. Water quickly penetrates treated fabrics and is transported away from the source. This quality has been promoted as improved summer comfort, the ability to adsorb and wick away body perspiration. The finish is not effective at all on polyester/cotton blends. The finish imparts good soil anti-redeposition protection to treated fabrics and a modest measure of antistatic protection.

IV. OTHER IMPORTANT CONSIDERATIONS

A. Non-Ionic Detergents

Non-ionic detergents based on polyoxyethylene have the unique feature of becoming less soluble as the temperature rises, exhibiting a cloud point. Cloud point temperature is based on the structure of the surfactant molecule. At this temperature the surfactant is, for all practical purposes, another water insoluble oil. As a non-dispersed oil, it is capable of adsorbing onto the fiber surface and either co-mixing with the oily soil or adsorbing onto the surface of particulate soil. When the temperature drops below the cloud point, the ether linkages again form hydrogen bonds with water and the molecule resumes surfactant qualities. The phase-change induced adsorption of the surfactant onto the fiber and soil promotes the thermodynamic boundary interfacial tensions which favor spontaneous soil release. Table 11 compares the detergent qualities of anionic, cationic and non-ionic surfactants. The soil was deposited on four polymer films representing different fibers.

Table 20

Effect of Surfactant Type on Soil Removal From Polymer Films

	% Soil Removed			
Detergent	Cellulose	PET	Nylon	Teflon
Sodium Laurel Sulfate	92	3	28	22
Cetyltrimethyl Ammonium Bromide	93	7	82	26
Ethoxylated Nonyl Phenol	94	99	99	96

This study showed that: 1. the non-ionic surfactant was equally effective and removed nearly all the soil from all four surfaces since the detergent study was carried out above its cloud point. 2. All three types of surfactants worked equally well on cellophane. One might conclude that the surfactant had little to do with soil release. 3. On the hydrophobic films, (PET, teflon and nylon) the cationic surfactant was effective on nylon but not on the other two. Apparently the fiber has an affinity for the cationic surfactant whereas PET and teflon has none. 4. None of the ionic surfactants work on PET since virtually none of the soil was removed. While the amount removed by the anionic from teflon and nylon wasn't great it was substantially more than was removed from polyester.

B. Soil Release Tests

1. AATCC Method 130

In this test, oily stains are placed on the fabric, laundered and visually rated for the severity of the remaining stain on a scale of one-to-five. The visual judgement is based on contrast, what the eye perceives to be the difference between the stained area and the rest of the fabric. There are variations of the test where a number of different staining materials are used. Regardless of the stain, judgement is still what the eye perceives. Some refinements have been attempted where optics are used rather than humans to make the judgement. From a practical point of view?these tests duplicate what the consumer does. However, from a scientific point of view, the data may be misleading or inconclusive since the quantity of soil removed is what's important. The intensity of the residual stain may or may not reflect the amount of soil remaining since it may be influenced by other factors. For example, the amount deposited on the spot may spread over a wider area during laundering and while it hasn't been removed, the intensity of the stain is less allowing one to conclude that less soil remains. Also there may be light scattering bodies in the fabric which affect the visual appearance of the stain and misleads one as to the amount of soil removed.

2. Release Point

Release Point (Rp) is defined as the surface tension of a detergent solution where oily soil just separates from fiber surfaces. This technique for quantifying soil release is based on thermodynamic considerations which state that the work of adhesion (the quantity $\gamma_{F/O} - \gamma_{F/D}$) must be overcome by the detergent for oily soil to separate from a solid surface. In a detergent solution, when the contact angle becomes 180 degrees and the oil just separates from the fiber, the interfacial tension between the oil/detergent will equal the work of adhesion.

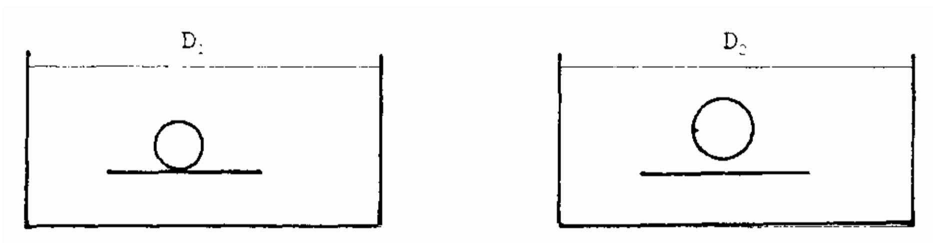
$$\gamma_{O/D} = (\gamma_{F/O} - \gamma_{F/D}).$$

The quantity $\gamma_{O/D}$ is influenced by the adsorbed surfactant. Therefore the surface tension of a bath where release just occurs is proportional to the work of adhesion between the oil and fiber surface.

a. Rp Determinations

The surface tension of a solution where oil just separates from a surface can be closely approximated by exposing the soiled surface to a series of solutions with decreasing surface tension. Consider figure 63:

Figure 32. Roll-up of Oil in Detergent Solutions



D_1 represents the roll-up condition in a detergent where the contact angle is nearing 180 degrees. The oil is just about to separate. D_2 is the detergent where the contact angle is 180 degrees and the oil has separated. The work of adhesion (the quantity $\gamma_{O/D} - \gamma_{F/D}$) is bracketed by the surface tension of the two solutions. From a practical point of view, this determination can be made by observing oil roll-up when an oily soiled specimen is subjected to a series of surfactant solutions of known surface tensions. The surface tension of the solution where the oil just floats away from the fabric is recorded as the Release Point (Rp).

b. Application of Rp Measurements

The Rp technique has been used to study the relationship between hydrophilic SR agents applied to a variety of 100% polyester fabrics. The test was conducted statically and dynamically. In the static test, the soiled samples were placed in the surfactant solution at room temperature. The dynamic test consisted of carrying out the observations in an ultrasonic bath.

Table 21 compares the data obtained on a series of SR treated polyester fabrics. Knit and woven fabrics made from the same feed yarn, textured and untextured, were tested both statically and dynamically. The same treated fabrics were stained and laundered. Afterwards, the amount of residual soil was determined by quantitative extraction.

Table 21

Rp Results Versus Residual Soil

	Rp (Dynes/cm)		Residual Soil
	Static	Dynamic	% Remaining
Woven, Spun Yarn	15.0	24.0	90
Woven Untextured	15.0	27.0	50
Knit, Untextured	23.0	35.5	66
Woven, Textured	25.0	41.0	28
Knit, Textured	28.5	45.0	11

The data shows: 1. there is good correlation between Rp and oil removal. Higher Rp numbers correlated with greater removal. 2. All of the unfinished polyester fabrics showed no release whatsoever, even in the ultrasonic bath. 3. The same experiments carried out on Mylar film gave values of 70 dynes/cm for treated Mylar and no release for the untreated film. 4. The values obtained in the ultrasonic bath were substantially higher than the static ones. This relates to the need for kinetic energy to transport the released oil droplet after the work of adhesion is overcome.

3. Geometry of Yarns and Fabrics

The geometry of the yarn and fabric influences soil release. Both the Rp data and the extraction results show that soil release from woven fabrics made from spun and untextured yarns is worse than those from textured yarns. Textured knit fabrics are more releasing than textured wovens. The data suggests that as the void spaces created by adjoining fibers become smaller, soil release becomes more difficult. Smaller capillaries require greater energy for detergent solutions to penetrate and detach the soil from the fiber surface. Also the small voids make it difficult for the detached soil to migrate to the fabric-bath interface.

V. REFERENCES

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