

# Improvement of Various Properties of Fiber Surfaces Containing Crosslinked Polyethylene Glycols

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## Synopsis

Modification of a variety of fabric and fibrous surfaces was achieved by insolubilization thereon of crosslinked polyethylene glycols (called POLYTHERM) to impart several useful properties: thermal storage and release, improved resiliency and resistance to oily soiling, static charge, pilling, wear life, and marked increases in hydrophilicity among them. Moreover, these improved properties were durable because up to 70% of the crosslinked polyol was retained after 50 launderings. Such modification was achieved by using average molecular weights of the polyols ranging from 600 to 20,000 by crosslinking with polyfunctional methylolamides (such as DMDHEU) in the presence of acid catalysts by a conventional pad-dry-cure textile finishing procedure. The role of crosslink density of the polyol in determining textile properties was determined by evaluation of films derived from crosslinking the polyols and comparison of selected properties.

## INTRODUCTION

Recent studies have demonstrated that polyethylene glycols with average molecular weights up to 1000 could be bonded or affixed to the surface of various fibrous materials by the discrete crosslinking of polyols with polyfunctional methylolamide reagents. The resultant modified surfaces produced by this crosslinking or network polymerization method have reversible and reproducible thermal storage and release characteristics due to the high enthalpy of melting and crystallization of the polyols insolubilized on the fibrous surface.<sup>1,2</sup> This method of crosslinking polyols (condensation polymerization after removal of solvent) is more facile for affixing them to various surfaces than previously described methods that require exposure to high-energy radiation of the polyols in aqueous solutions to produce insoluble gels.<sup>3,4</sup>

This communication describes the modification of surfaces by insolubilization of polyethylene glycols (PEG) ( $M_n$  600–20,000) by crosslinking with polyfunctional methylolamides such as dimethyloldihydroxyethyleneurea (DMDHEU) and the resulting enhancement of various physical and chemical properties of the surfaces containing the bound polymer. The interrelationship of thermal and other properties to the crosslink density of the polyol bound to various fibers under a variety of conditions is discussed. In addition to their ability to reversibly absorb and release heat, the coated fibrous surfaces have good to excellent resiliency (particularly for cotton cellulose), resistance to abrasion, static charge, oily soil deposition, and pilling. Also, treated fabrics

retain over 70% of the crosslinked polyol after 50 launderings as well as the properties associated with the coated fiber surface. Water absorbency, moisture regain, and related properties of the modified surfaces are also markedly increased due to the hydrophilic nature of the crosslinked polyol gel. It is unusual and significant that thermal and several nonthermal properties are imparted to fibrous surfaces by one process (described as and named POLY-THERM).

### EXPERIMENTAL

The surfaces modified or treated with the crosslinked polyols were in fabric form and included: 100% cotton printcloth (125 g/m<sup>2</sup>), 50/50 cotton/polyester sheeting (139 g/m<sup>2</sup>), 50/50 cotton/polyester jersey knit T-shirt (149 g/m<sup>2</sup>), acrylic fleece (193 g/m<sup>2</sup>), a commercial polyamide-reinforced paper towel (71 g/m<sup>2</sup>), 100% wool flannel (176 g/m<sup>2</sup>), and open mesh fiberglass fabric (105 g/m<sup>2</sup>). Polyethylene glycols (PEG) ( $M_n$  600–20,000) were commercial grade obtained from Union Carbide and/or Fisher Scientific\*. The crosslinking agent was Hylite LF (40% aq. dimethyloldihydroxyethyleneurea or DMDHEU), obtained from National Starch & Chemical Co. Acid catalysts used were combinations of MgCl<sub>2</sub> · 6H<sub>2</sub>O, citric acid (both J. T. Baker reagent grade) and *p*-toluenesulfonic acid (Fisher Certified). Deionized water was used to make up the above solutions.

Fabrics/fibrous substrates were immersed in aqueous PEG solutions containing the resin and acid catalysts and put through squeeze rolls under pressure to obtain pickups of 80–200% over dry substrate weights. Fabrics were then dried for 5–7 min at 70–85°C, cured 2 min at 100–150°C, washed in hot tap water (60°C) containing 1% by weight commercially available phosphate-based detergent, rinsed in additional tap water (25°C), then tumble dried or air dried to constant weight. For low MW (600–1450) PEGs, 50% aqueous solutions containing 8–16% DMDHEU/3.3–4.8% MgCl<sub>2</sub> · 6H<sub>2</sub>O/citric acid (molar ratio 10/1) were used to treat fabrics; for higher MW (8000 and 20,000) PEGs, 45 and 40% solutions, respectively, containing 10% DMDHEU/0.25% MgCl<sub>2</sub> · 6H<sub>2</sub>O/0.025% citric acid/0.5% *p*-toluenesulfonic acid were utilized.

Crosslinked polyethylene glycol films were prepared on glass plates with the same concentration range of solutions used to treat fabrics, but drying and curing times were longer (30 min for drying and 5 min for curing). The films were removed from the glass plates and carefully washed five times with deionized water at 50°C and air dried. Crosslink density (degree of swelling) of the polyol films was determined by the method of Stephenson et al.,<sup>5</sup> using deionized H<sub>2</sub>O as the solvent. Nitrogen content of the films was determined and reported as % N by the Kjeldahl method.

Thermal properties of modified and unmodified polyols and fabrics were determined by differential scanning calorimetry on a Perkin-Elmer DSC-2 with a 3600 Data Base Station. These included:  $T_m$ ,  $T_c$ , and the corresponding  $H_f$  and  $H_c$  of the unmodified and crosslinked polyols and total heat content

\*Use of a company or product name by the U. S. Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

(denoted as  $Q$ ) of the modified and untreated surfaces.  $Q$  (over a given temperature range) is only  $C_p$  (specific heat) of the fiber for untreated surfaces, but is a composite value of  $C_p$  for the fiber plus  $H_f$  or  $H_c$  of the bound polyol for the modified fabrics or surfaces.

Other tests conducted on the fabrics were: Stoll flex abrasion by ASTM D3885-80, breaking strength and elongation at break by ASTM D1682-64, conditioned wrinkle recovery (WRA for warp + fill) by AATCC-66-1984, electrical resistivity at 65% relative humidity (RH) by AATCC-76-1982, stiffness by Federal Test Method 5202, soiling by a modified AATCC 130-81 (amount of soiling expressed as percent of light reflected after soiling and one laundering cycle divided by original amount of light reflected before soiling), and previously described techniques for determining moisture regain<sup>6</sup> and water of imbibition.<sup>7</sup> Durability to prolonged laundering was conducted using untreated and POLYTHERM-treated 50/50 cotton/polyester jersey knit T-shirts which were washed 50 times with a 4-lb load with 100 g of Tide in a commercial-type washer and tumble dried 50 times for 135 min after each wash. Moisture regain values (65% RH/20°C) are based on a "dry weight" after 12 h of oven drying in air at 110°C due to the difficulty of removing all water from polyol-modified surfaces.

## RESULTS AND DISCUSSION

Previous results indicated that a minimum weight increase of 20% of the crosslinked polyol affixed to a surface is required to provide thermal storage and release properties over a given temperature range.<sup>1,2</sup> The reaction of the tetrafunctional reagent DMDHEU with the polyols provides the proper degree of crosslinking to produce a thermally adaptable coating on fibers. The  $MgCl_2 \cdot 6H_2O$ /citric acid catalyst has proven to be the most effective one for insolubilization of polyols, but only for MW/1450 or less. Other acid catalysts either do not promote reaction between the polyol and the resin or cause extensive crosslinking and loss of thermal activity. *p*-Toluenesulfonic acid, or more ideally a mixture of this acid with the  $MgCl_2 \cdot 6H_2O$ /citric acid, was required to insolubilized polyols with molecular weights > 1450 (up to 20,000) on various types of substrates by their reaction with DMDHEU. Table I shows the versatility of using different molecular weight polyols with various substrates to produce insoluble coatings having thermal storage and release properties over a wide temperature range (-13 to +67°C). Surfaces ranging from fiberglas to conventional natural and synthetic fibers and their blends (acrylic, cotton/polyester, paper, wool, and cotton) are suitable substrates for all ranges of molecular weights of the polyols. As noted in earlier and more comprehensive studies with PEG-1000 and PEG-1450<sup>1,2</sup> as well as from selective data in Table I for a wider range of molecular weights, there is some variation in the melting and crystallization temperatures with different fibers containing the same molecular weight polyol. This may be due to the nature of the crosslink and crosslinking with functional groups on the fiber competing with reactions of the polyols with the resin. The thermal energy at  $T_m$  and  $T_c$  of the crosslinked polyol on the surface generally increased with increasing molecular weight of the polymer; this is probably due to lower crosslink densities in higher molecular weight polyols that are characterized by longer,

TABLE I  
Comparative Thermal Properties of Various Surfaces Containing  
Crosslinked Polyols ( $M_n$  of 1000–20,000)<sup>a</sup>

Surface and/or fiber type <sup>b</sup>	MW PEG	% wt Gain	$T_m$ (°C)	$H_f$ (cal/g)	$T_c$ (C)	$H_c$ (cal/g)	$Q$ (heat) (cal/g)	$Q$ (cool) (cal/g)
50/50 Cotton/ polyester	1000	43	27	2.6	0	2.4	18.7	18.3
UT control	—	—	—	—	—	—	9.6	9.7
Fiberglas	1450	21	21	1.7	8	2.4	11.6	11.6
UT control	—	—	—	—	—	—	6.2	6.7
Wool	1450	25	38	4.2	14	4.2	17.2	16.5
UT control	—	—	—	—	—	—	13.7	12.0
Cotton	8000	43	51	4.9	33	8.3	21.1	18.1
UT control	—	—	—	—	—	—	10.9	10.9
Acrylic	20,000	65	52	8.0	32	7.3	24.9	22.4
UT control	—	—	—	—	—	—	11.3	11.1

<sup>a</sup>Ranges for  $Q$  (heating/cooling in °C): PEG-1000 (–3 to +37/+27 to –13); PEG-1450 (+7 to +47/+27 to –13); PEG-8000 (+32 to +67/+47 to +7); PEG-20,000 (+32 to +67/+57 to +17). All samples heated/cooled at 20°C/min.

<sup>b</sup>UT control is corresponding untreated fabric.

more flexible polyol chain segments. Figure 1 shows the DSC data obtained from cotton containing PEG-8000. This typifies the melting and crystallization behavior of crosslinked polyols on various substrates. Untreated substrates used in this study do not melt or solidify in these temperature ranges. Treated fibers listed in Table I had an increase in heat content ( $Q$ ) from 40% to greater than 100% over a given temperature range relative to the corresponding untreated fibers. This was observed both on heating (endothermic) and cooling (exothermic) cycles. Such marked increases in the thermal storage and release of the modified fabrics and substrates relative to the untreated materials make them suitable for a variety of applications that involve buffering of temperature changes; this includes insulation, apparel, protective clothing, and use of modified textiles for protection of plants, animals, and persons from thermal stress in a variety of environments.

Crosslinked films of polyols, derived from reaction with DMDHEU in the presence of appropriate acid catalysts, were also prepared to obtain more information about the nature of the reaction and to determine crosslink density. The water solubility, thermal properties, crosslink density, and % N of these films and reference values for water solubility and thermal properties of the unsubstituted polyols were determined. These data are presented in Table II.

As the molecular weight of the polyol increased, the crosslink density (inversely related to the degree of swelling) became lower, and the solubility of the film in water increased due to greater distances between crosslinks in the polyols. However, even with relatively low crosslink densities, the polyol film derived from PEG-20,000 had a solubility of 1% or less in H<sub>2</sub>O. As the molecular weight of the polyol increased, the heat of fusion and crystallization

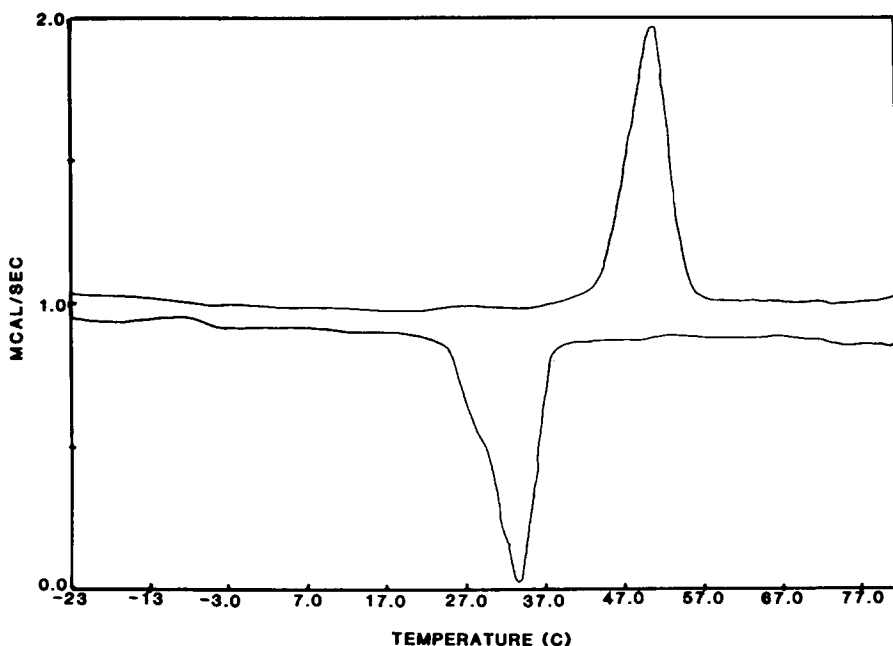


Fig. 1. DSC heating and cooling scans (20°C/min) for  $T_m$  and  $T_c$  of cotton containing crosslinked PEG-8000.

of the crosslinked films increased and more closely approached the enthalpies of the corresponding uncrosslinked polyols. This is desirable because it provides greater thermal capacity to the fibers and may be attributed to lower crosslink density that affords more flexible polyol segments. Melting and crystallization temperatures were generally lower for the crosslinked polyols than for the comparable unsubstituted polyols from which they were derived.

TABLE II  
Properties of Crosslinked Polyethylene Glycol Films

MW PEG	% DMDHEU <sup>a</sup>	Solubility H <sub>2</sub> O (g/100 mL)	$T_m$ (°C)	$H_f$ (cal/g)	$T_c$ (°C)	$H_c$ (cal/g)	Degree swelling	% N
600	0	> 80	20	25.0	0	26.8	—	—
600	8	0.09	8	2.3	—	—	10.3	2.5
600	10.5	0.08	8	4.8	—	—	10.2	3.5
600	13	0.07	6	1.3	—	—	7.7	3.9
1450	0	70	48	40.1	15	38.0	—	—
1450	10	0.40	36	13.9	12	15.0	12.4	3.3
1450	13	0.64	31	13.1	5	13.6	9.4	5.0
1450	16	0.24	37	3.6	11	4.7	6.7	13.0
8000	0	62	60	38.1	27	6.9	—	—
8000	10	0.80	50	23.1	26	21.2	19.8	3.6
8000	15	0.55	39	21.3	15	17.4	16.5	3.7
20,000	0	56	64	42.5	34	35.7	—	—
20,000	10	1.01	54	23.7	32	21.0	18.5	4.2
20,000	15	0.50	56	26.1	33	21.5	12.5	5.3

<sup>a</sup>Uncrosslinked polyols run for comparison of solubility and thermal properties.

However, as the molecular weight increased, these differences also narrowed considerably. A similar effect, namely, comparable enthalpies, was observed in free radical crosslinked and uncrosslinked polyethylenes that melted within a couple of degrees of each other (138–140°C); the highly crystalline crosslinked polyethylene was considered as a suitable thermal storage material in extremely hot environments.<sup>8</sup>

Nitrogen analysis of the crosslinked films suggested that with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid catalysts, low-molecular weight PEGs (e.g., MW 600) were amorphous enough to react rapidly with high concentrations of the polyfunctional resin DMDHEU. However, with PEG-1000 and -1450, excess DMDHEU did not continue to react with the polyol; instead, it homopolymerized to form a yellow rigid thermosetting solid. The 13% N obtained in material derived from the reaction of PEG-1450 with 16% DMDHEU is closer to values expected for homopolymers of the resin. Homopolymerization appears to be optimum at this molecular weight of the polyol. With higher molecular weight polyols, the catalyst systems are different (mixtures of *p*-toluenesulfonic acid and the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid catalyst) and promote reaction even when the number of available hydroxyl end groups is low. Thus, excess DMDHEU continues to react with the polyol at higher resin concentrations instead of undergoing homopolymerization when these catalysts are utilized. This result is verified by the % N values and the melting and crystallization behavior of the crosslinked polyol.

Other selected properties of fibrous surfaces treated with crosslinked polyols over a wide molecular weight range are shown in Table III. These include: resistance to flex abrasion, moisture regain and water of imbibition, % reflectance retained (a measure of oily soil release), and antistatic behavior. As with

TABLE III  
Selected Nonthermal Properties of Various Surfaces Containing  
Crosslinked Polyols (MW 1000–20,000)

Surface/ fiber type	MW PEG	% wt Gain	Flex <sup>a</sup> abrasion	% MR <sup>b</sup>	% H <sub>2</sub> O imbib.	% Reflect. (soiling)	Resistivity (log ohms/sq)
50/50 Cotton/ polyester	1000	43	5640	25.9	90	98	9.3
UT control	—	—	2082	3.5	16	67	10.8
Paper towel	1000	39	—	26.5	130	—	—
UT control	—	—	—	8.6	61	—	—
Fiberglas	1450	21	—	14.5	71	—	10.3
UT control	—	—	—	0.3	3	—	12.3
Wool	1450	25	1947	28.1	220	62	11.6
UT control	—	—	1217	13.7	39	34	12.5
50/50 Cotton/ polyester	8000	43	5284	17.5	72	96	11.3
UT control	—	—	2082	3.5	16	60	10.6
Acrylic <sup>c</sup>	20,000	65	4864	20.3	241	90	11.2
UT control	—	—	652	0.7	4	57	11.6

<sup>a</sup>Cycles to failure.

<sup>b</sup>MR = % moisture regain at standard conditions (65% RH/70°F).

<sup>c</sup>Flex abrasion and resistivity values for treated and untreated acrylic are an average for both sides of the fabric.

the thermal activity, most of these properties are improved in a variety of materials ranging from paper to fiberglas to wool over a broad range of molecular weights. Flex abrasion was markedly increased for modified surfaces relative to untreated surfaces Cotton/polyester fabrics and increases of 150–170% irrespective of polyol MW, wool about a 60% increase, and modified acrylic fabric an increase of about 650% more than the control fabric for this property. Evidently the toughness and elasticity of the crosslinked polyol contribute to this improvement. Because the crosslinked polyol is still hydrophilic, treated fabrics and substrates also exhibited substantial increases in their moisture regain and water of imbibition. Wool containing the PEG-1450 had about twice the moisture regain and over four times the water of imbibition of untreated wool. Inert materials such as glass fibers had almost 50 times the moisture regain and 25 times the water of imbibition of untreated glass fibers. The ability to provide good oily soil release was also independent of substrate; however, optimum soil release appeared to occur at molecular weights of 8000 or less. Soiled cotton/polyester (after washing) containing either PEG-1000 or PEG-8000 was practically indistinguishable from untreated control fabric in its reflectance values, while the soiled control fabric had its % reflectance decreased by at least 30%. Antistatic behavior was also independent of substrate with regard to treated fabrics. Selected data shown in Table III verify that reduction in static charge (relative to untreated surfaces) is more substantial for lower molecular weight polyols (particularly 1000 or less).

Comparative data in Table IV for 100% cotton, 50/50 cotton/polyester, and 100% wool fabrics treated with PEG-1000/DMDHEU and with PEG-1450/DMDHEU at cure temperatures of 145°C and of all cotton fabrics cured

TABLE IV  
Mechanical and Resiliency Properties of Selected Fabrics Containing  
Crosslinked Polyols (MW 1000 and 1450)<sup>a</sup>

Surface/ fiber type	MW PEG	% wt Gain	Cure <sup>b</sup> temp. (°C)	Break. load (lb)	% Elong. at break	Cond. WRA °, (W + F)	Stiffness × 10 <sup>-4</sup> (in lb)
50/50 Cotton/ polyester	1000	38	145	67.2	18.5	276	6.5
50/50 Cotton/ polyester	1450	38	145	73.2	19.5	222	34.5
UT control	—	—	—	80.5	16.2	257	3.2
Cotton	1000	11	100	35.9	7.6	285	6.3
Cotton	1000	38	130	31.2	4.3	304	3.4
Cotton	1000	31	150	27.1	3.7	310	12.0
Cotton	1000	33	160	21.4	3.2	311	11.0
Cotton	1450	38	145	33.6	4.6	216	21.2
UT control	—	—	—	50.4	7.6	169	4.4
Wool	1000	41	145	42.9	56.9	312	9.8
Wool	1450	31	145	48.1	54.6	287	37.2
UT control	—	—	—	31.7	37.4	312	4.2

<sup>a</sup>All properties except conditioned wrinkle recovery (WRA) are in warp direction only; WRA are in warp + fill.

<sup>b</sup>Cure time 2 min for all fabrics. Washed and dried as described in Experimental section.

at temperatures between 100 and 160°C with PEG-1000/DMDHEU, demonstrated the relationship between wrinkle recovery and stiffness as well as breaking strength of these treated fabrics. With the treated cotton/polyester blend and wool fabrics, good to excellent strength retention and improvement in elongation were obtained relative to the corresponding untreated fabrics. However, stiffness also increased and conditioned recovery decreased for these fabrics when the molecular weight of the crosslinked polyol was increased from 1000 to 1450. There appears to be little influence on mechanical properties of the treated wool and treated cotton/polyester blend fabrics cured over a wide range of temperatures (100–160°C). In contrast, the cotton fabrics were extremely sensitive to strength retention when they were cured at different temperatures (e.g., with the PEG-1000/DMDHEU). Most importantly, it was possible to obtain excellent dry wrinkle recovery at moderately low cure temperatures (100 and 130°C) and also retain substantial amounts of strength. It is reasonable to assume that resiliency is imparted by initial reaction of the resin with the polyol at low cure temperatures and increasing extent of reaction of the resin with the cellulosic hydroxyls as the cure temperature is increased. This hypothesis is consistent with the decrease in tensile and wear properties of the treated fabrics as the cure temperature is increased. However, when the cotton fabrics were treated with higher molecular weight polyols (e.g., PEG-1450/DMDHEU), their conditioned wrinkle recovery was substantially reduced due to an increase in fabric stiffness.

Preliminary studies of the durability of the POLYTHERM finish to prolonged laundering were conducted by treating a jersey knit 50/50

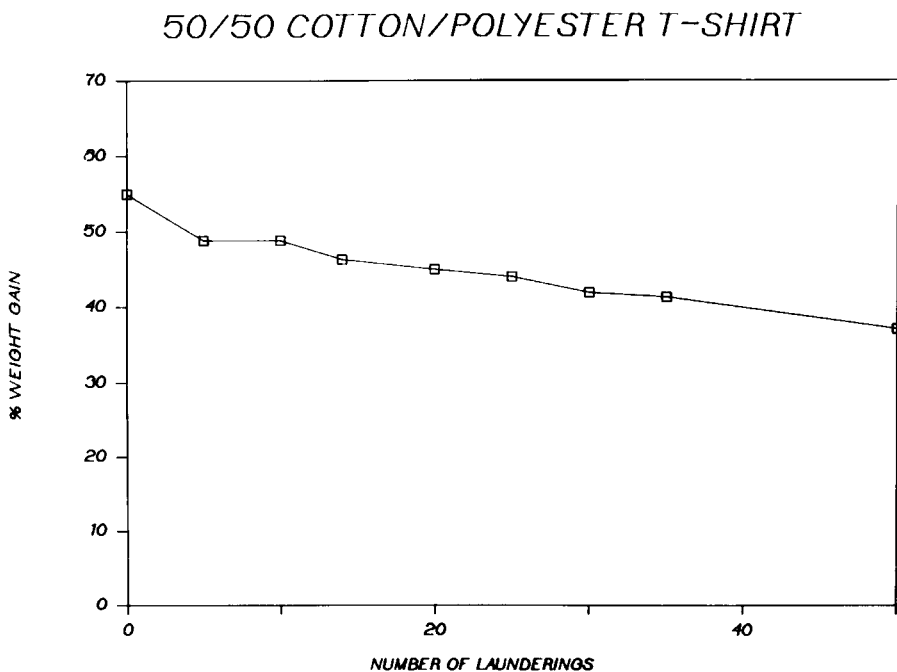


Fig. 2. Cotton/polyester (50/50 blend) jersey knit T-shirt treated with POLYTHERM finish (PEG-1000/DMDHEU): amount of finish retained after laundering.



cotton/polyester T-shirt with the PEG-1000/DMDHEU (2 min cure at 145°C), then subsequently laundering a treated T-shirt and untreated T-shirt 50 times. The % finish retained on the treated shirt (Fig. 2) was almost 70% after 50 laundings; after this extensive laundering, the treated shirt had excellent resistance to pilling (i.e., little or no pill formation) in contrast to the untreated shirt which was extensively pilled. Further studies are in progress to determine optimum fabric construction and fiber type for optimizing durability of the crosslinked polyol on fabrics.

Thus, the modification of a variety of fibrous substrates can be achieved by insolubilization thereon of crosslinked polyols to impart several useful properties: thermal storage and release, improved resistance to oily soiling, static charge, wear and pilling, and marked increases in hydrophilicity and resiliency. Studies are continuing on elucidating structure-property relationships that optimize one or more of these properties to produce modified substrates for many applications in the aerospace, apparel, insulation, specialty chemical, and materials industries.

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