

## Morphology of Fabric Finishes Consisting of Acrylic Soil Release Polymers and Durable Press Reagents\*

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### Synopsis

When acrylic emulsion copolymers containing a substantial proportion of methacrylic acid are mixed with durable press reagents such as dimethyldihydroxyethyleneurea (DMDHEU) or dimethylolethyleneurea (DMEU) and applied to fabric in a one-bath application, there is minimal coalescence of polymer dispersion particles. Polymer is embedded in a matrix of condensed methylol reagent which limits swelling of the polymer, in some cases to such an extent that its usefulness as a soil release agent is impaired. The degree of restricted swelling depends upon the soil release polymer and durable press reagents used. Nevertheless, in cases where swelling is severely restricted, excellent soil release is obtained if the matrix is removed sufficiently rapidly in washing. This is more so the case with DMEU than DMDHEU. Some polymer is insolubilized by zinc nitrate used to accelerate reaction of durable press reagent with cotton. Conclusions are based upon electron-microscopic examination of film surfaces of durable press and soil release finishing agents as well as of surfaces of treated fabrics. Further conclusions are drawn from quantitative determination of film solubilities and chemical analysis of insoluble film residues.

### INTRODUCTION

Emulsion copolymers containing a substantial proportion of carboxylic acid, such as 70% methacrylic acid/30% ethyl acrylate, are very effective soil release top finishes for durable press textile fabrics. However, when such polymers are applied with cotton crosslinking agent and catalyst in a one-bath application, both soil release and wash-wear appearance are often inferior to what is obtained with a two-step application.

The crosslinking agents are conventional N-methylol compounds. They are not necessarily crosslinking agents for the polymer. The catalysts are the usual accelerators for the crosslinking reaction with cotton, e.g.,  $Zn(NO_3)_2$  and  $MgCl_2$ . In general, a catalyst is not needed for application of acrylic soil release agents to fabrics.

The degree of inferiority of fabric properties depends upon the crosslinking agent, catalyst, and acid content of the polymer. For example,

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DMEU (dimethylolethyleneurea) is often superior to DMDHEU (dimethyloldihydroxyethyleneurea); N,N-dimethylolalkyl carbamates are intermediate but closer in performance to DMEU. Also, a copolymer with only 33% MAA is often superior to that with 70% when DMDHEU is used as durable press reagent. Considering this evidence, and much more, there is no question that soil release and wash-wear performance of fabrics treated in a one-bath system are sensitively dependent upon the chemicals used. This dependence may be due to either physical or chemical interactions, or both, of soil release and durable press reagents. The importance of the morphology of the finish is emphasized in this article. The significance of possible chemical reactions between durable press reagent, soil release polymer, and cotton will be discussed in a separate publication.

The principal soil release agent investigated was a 70% methacrylic acid/30% ethyl acrylate emulsion copolymer. Low molecular weight polymethacrylic acid and a 33% methacrylic acid/50% ethyl acrylate/17% methyl methacrylate emulsion terpolymer were also investigated to a limited extent. Molecules of soil release polymer are too large to penetrate fibers significantly and therefore accumulate on the surface. Durable press reagents DMDHEU or DMEU were used with the polymers. These reagents are small enough to diffuse into cotton fibers where they crosslink cellulose and improve the resiliency of the fiber. However, there is also appreciable self-condensation of these materials on the surface of fibers where soil release polymers are located.

Electron microscopy was used to examine replicas of films cast from solutions representative of those used in commercial one- and two-bath fabric treatments. Finish on the surface of treated fabrics is also examined by both electron and scanning electron microscopy. Misleading conclusions can be drawn if film surfaces are modified by the replication procedure, or if the surface of the film is not representative of the interior. Therefore, it was desirable to have an independent means of confirming the structures inferred from observation of surface replicas. Solubility of films was found to be consistent with the proposed structures, and therefore the replicas were probably representative of the actual film surfaces. Furthermore, additional valuable information concerning the morphology of the films was deduced from quantitative solubility data.

## EXPERIMENTAL

### Materials

#### *Soil Release Polymers*

- a. 70%/30% (Weight basis) methacrylic acid (MAA)/ethyl acrylate (EA) emulsion copolymer,  $10^5$ - $10^6$  estimated molecular weight, 20% solids.

- b. 33%/50%/17% Methacrylic acid/ethyl acrylate/methyl methacrylate (MMA) emulsion polymer,  $10^6$ – $10^6$  estimated molecular weight.
- c. Poly(methacrylic acid) (PMAA), solution polymer, about 5000 estimated molecular weight, 25% solids.

#### *Durable Press Reagents*

- a. DMEU: Rhonite R-1 (Rohm and Haas Company).
- b. DMDHEU: Permafresh 183 (Sun Chemical Company).

#### *Catalyst*

Zinc Nitrate: Catalyst X-4 (Sun Chemical Company).

#### *Fabric*

65/35 Polyester/cotton shirting, #7406 from Testfabrics, Inc.

#### **Preparation of Films**

Reagents were used as received. Films of about 10 g solids were cast on Mylar in a Cobb ring, either at room temperature or in an oven at 50° or 80°C for 15 hr. Heating promotes coalescence of emulsion polymers and therefore a more homogeneous film. The minimum film formation temperature of the 70/30 MAA/EA polymer was about 60°C. The proportions (product weight basis), soil release polymer/Rhonite R-1 or Permafresh 183/Catalyst X-4 5/5/1, were maintained in solutions used for casting films.

In preparing solutions with polymer and zinc nitrate for films and fabric treatment, N-methylol compound and catalyst were premixed and then added slowly to polymer solution. The reason for this order of mixing will be apparent after the following related experimental results are reported.

If Catalyst X-4 is added directly to completely or partially neutralized PMAA, zinc salts of the polymer precipitate immediately. However, if Catalyst X-4 is premixed with aqueous solutions of DMEU or DMDHEU, and this solution added very slowly to an aqueous solution of PMAA, no precipitate forms; if the mixture is added too rapidly, however, precipitate appears. DMDHEU is more effective than DMEU in preventing precipitation, and precipitation is less difficult to prevent if magnesium chloride is used instead of zinc nitrate. There is IR spectroscopy evidence that metal ions form coordination complexes with N-methylol compounds.<sup>1</sup> Apparently, then, DMEU and DMDHEU can complex catalyst cations and prevent them from precipitating polymer. When solutions where precipitation has been prevented by DMDHEU are dried, films are clear with no observable crystalline material. However, crystalline deposits are readily observed in equivalent films with DMEU.

No precipitate formed when zinc nitrate was added to polymers used in this investigation because they were unneutralized. It is not strictly

necessary, therefore, to premix catalyst and N-methylol reagent, but this was done in the present work because catalyst should logically be associated with durable press reagent. Also, this order of mixing is generally recommended for commercial treatment of fabrics.

### Preparation of Fabrics

Fabrics were padded to about 70% wet pickup with aqueous solutions consisting of (product basis) 25% polymer, 25% Permafresh 183, and 5% Catalyst X-4, fastened to pin frames, dried 110°C/5 min, and cured 160°C/3 min in forced-draft ovens. Treated fabrics were scoured 10 min in a Maytag washing machine with hot water and 0.1% Triton X-100 (nonionic surfactant), rinsed, framed, and dried.

For two-bath treatment, durable press reagent and catalyst were applied initially, and soil release polymer was applied alone in a separate application. Fabrics were dried and cured after each step, and scoured only after the second step.

Total finish on fabric after washing, based upon conditioned weights before and after treatment, was 11.15% for one-bath treatment and 11.75% for two-bath treatment.

### Electron Microscopy

To obtain electron micrographs of polymer dispersion particles, the polymer particles were diluted with sufficient distilled water to prevent them from coalescing when dried upon a Formvar substrate. The isolated particles were then shadowed with germanium and lightly carbon coated.

A two-stage replica procedure was used for both the film and fabric surfaces. The initial replica was made by pressing the sample surface onto a smooth disc of polystyrene that had been heated to its softening point, about 90°C. After cooling, the sample was broken away, leaving a negative replica on the polystyrene disc. This negative replica was shadowed with chromium at a 25° angle. About 200 angstroms of carbon were deposited on the replica, and the polystyrene was dissolved in benzene. A Philips EM-75 electron microscope was used to examine the polymer particles and the replicas.

Fabric surfaces were also examined by scanning electron microscopy. Yarn samples were raveled from fabrics, mounted on stubs, and coated with palladium/gold alloy. A Stereoscan Mark 11A instrument at Engis Equipment Co. was used.

### Solubility of Films

Quantitative estimates of solubility of films were determined by placing approximately 1-g specimens in Whatman 26 × 60 mm extraction thimbles and Soxhlet extracting them with water for four days. N-Methylol compounds undoubtedly self-condense to some degree during

film formation and curing. They may also react with polymer to form esters, although this reaction is believed to occur only to a very limited extent. Products due to condensation reactions should be hydrolyzed nearly completely by the extended extraction. Solubility, then, is dependent upon inherent solubility as well as further solubility due to hydrolysis during the four-day extraction. The term "solubility" is used only in this sense throughout the article.

Solubility was calculated from dry weights of thimbles and their contents before and after extraction. Drying conditions were 110°C, 16 hr. Heat treatment during predrying would be expected to minimize differences due to film formation temperature.

### **Analytical Procedures**

Nitrogen content of residues remaining from extracted films was determined by the Micro Kjeldahl method. Zinc content was determined by atomic absorption spectroscopy.

## **RESULTS**

### **Macroscopic Properties of Films**

Films of 70/30 MAA/EA emulsion polymer cast at room temperature were clear, semicontinuous, and hard. Those cast at 80°C were clear, continuous, and less brittle.

Rhonite R-1 or Permafresh 183 cast with or without zinc nitrate at room temperature retained a good deal of water and did not truly dry to a film. DMDHEU and zinc nitrate film cast at 50°C was hard and brittle and remained so for at least a month. In contrast, an equivalent film with DMEU was more flexible and not as hard. It remained so for about two or three days, but then progressively softened and became more pliable and slightly tacky. Softening is a consequence of reversal of condensation reactions as water is regained by the film.

Films of emulsion polymer and DMEU or DMDHEU, with or without catalyst, cast at room temperature or 80°C, were clear and continuous. Those cast at room temperature were brittle and slightly tacky, more so with DMEU than DMDHEU. Films cast at 80°C were harder and less brittle.

### **Electron Microscopy**

An electron micrograph of polymer particles from a 70/30 MAA/EA emulsion polymer is shown in Figure 1. The particles are unusually irregular, possibly due to a limited degree of polymerization and gelation of MAA in the aqueous phase during emulsion polymerization. There is very little evidence of the original dispersion particles in a micrograph of a surface replica of film cast at 80°C (Fig. 2a). However, in a film of polymer and DMDHEU, discontinuous polymer particles are embedded

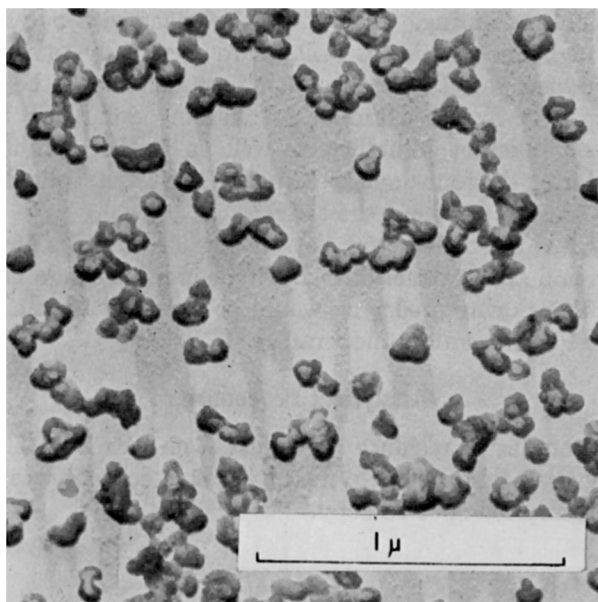


Fig. 1. Electron micrograph of 70/30 MAA/EA polymer dispersion particles.

in a matrix of DMDHEU (Fig. 2b). These particles are of the same size as those of the original dispersion, so it is fair to conclude that the matrix is essentially DMDHEU, although it probably contains a small amount of solubilized polymer as well. Some polymer particles are extracted from the surface during replication. The surface of a film of polymer and DMDHEU cast at 80°C has yet a different structure (Fig. 2c). The polymer particles have coalesced with one another to an appreciable extent, but not with DMDHEU. Polymer particles protrude from the film surface, but in this case were not extracted during replication. They appear as pits in the micrograph, since a negative replica was used.

Fabric as well as film surfaces were examined because morphology need not necessarily be the same in each case. A replica of the surface of DMDHEU-treated fabric, top-finished with polymer (two-bath process), is shown in Figure 3a. There appears to have been only partial coalescence of dispersion particles, and the replicated surface has good continuity. In contrast, when fabrics were treated in a one-bath process, portions of the finish were removed in making surface replicas (Fig. 3b,c). For example, extracted material appears as innumerable dots on the replica in Figure 3b. These dots are poorly coalesced polymer dispersion particles, probably embedded in a matrix of condensed DMDHEU. Results with fabrics treated in a one-bath system were in accord with those of films of polymer and durable press reagent.

Scanning electron micrographs of finish on the surface of cotton and polyester fibers in yarns raveled from the same fabrics are shown in

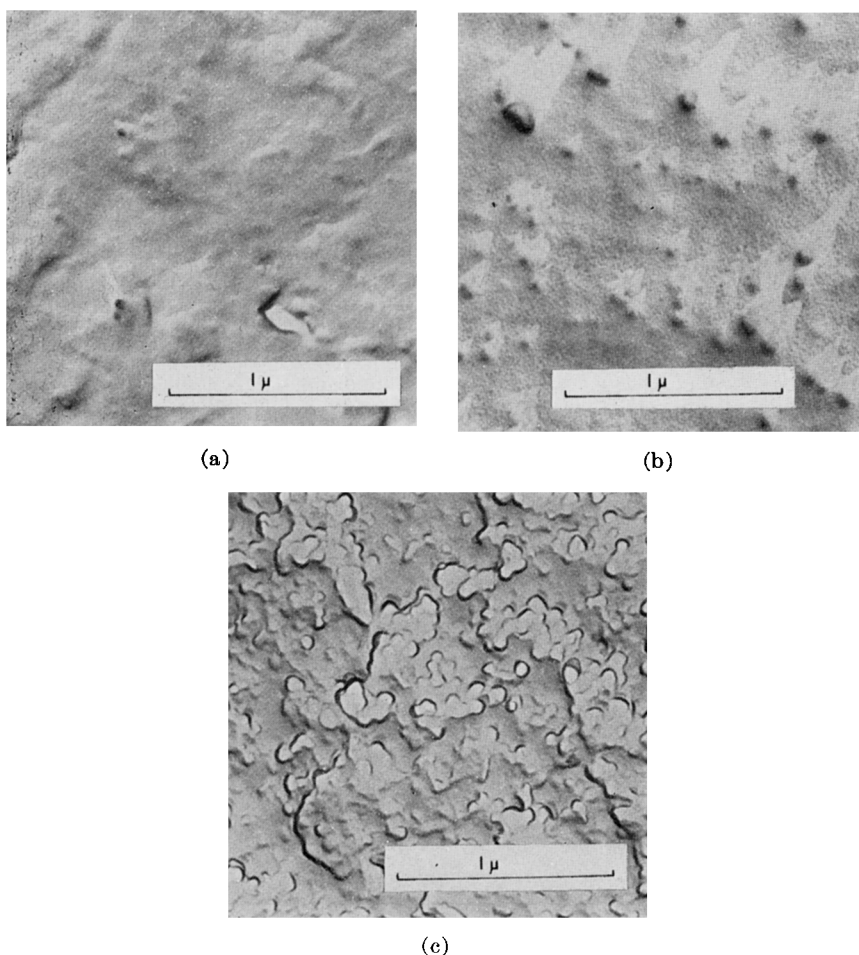


Fig. 2. Electron micrographs of replicas of film surfaces: (a) 70/30 MAA/EA polymer cast at 80°C; (b) 70/30 MAA/EA polymer plus DMDHEU cast at 23°C; (c) 70/30 MAA/EA polymer plus DMDHEU cast at 80°C.

Figures 4 and 5. Morphology appears similar for the one- and two-bath treatments. Coalescence of polymer dispersion particles is poor in each case, although it is somewhat better on cotton fibers in fabrics treated in a two-bath process.

Fabrics were generally dried at high temperatures for short times. These conditions are not conducive to good film formation, especially on irregular fiber surfaces. Coalescence is likely to be poor in certain regions of the fabric, even when polymer is applied separately in a two-bath process. Self-condensed N-methylol compounds generally have a porous structure due to rapid evolution of water vapor during drying and curing. Soil release polymer applied from a two-bath treatment can presumably enter the pores on the surface of this honeycomb structure to some extent.

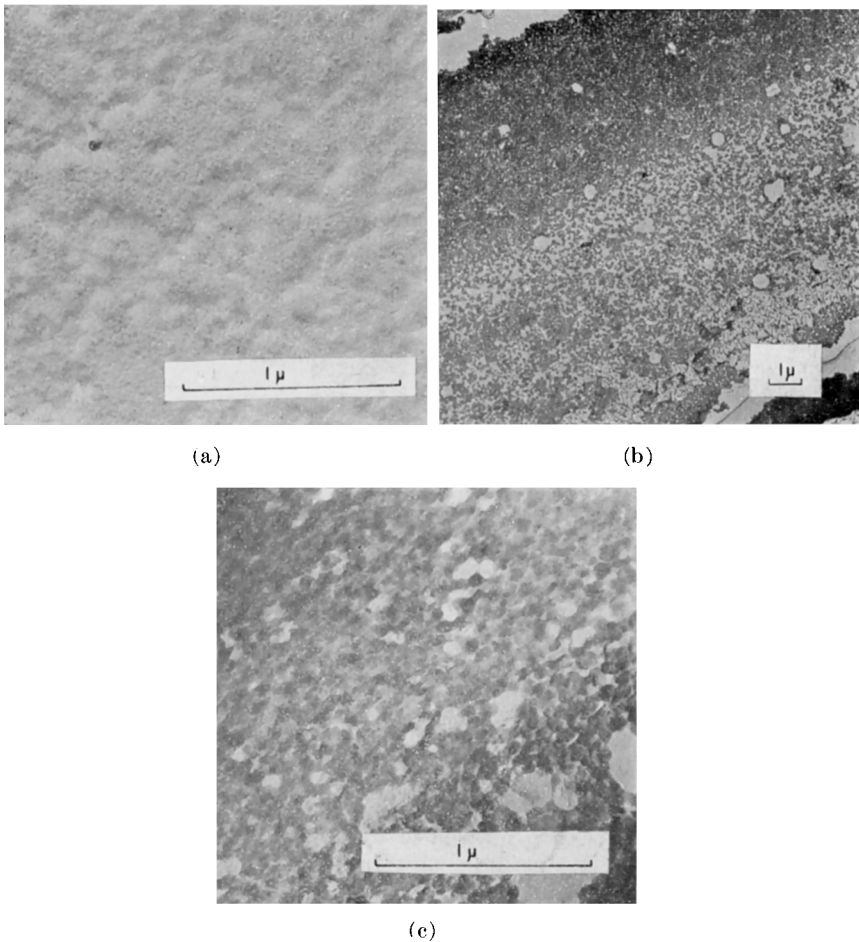


Fig. 3. Electron micrographs of replicas of fabrics treated with 70/30 MAA/EA polymer, DMDHEU, and zinc nitrate: (a) two-bath treatment; (b) one bath treatment; (c) one-bath treatment, higher magnification.

Also, portions of condensed methylol compound may protrude beyond the polymer surface.

In summary, then, coalescence of polymer dispersion particles on fabric is not good in either the one- or two-bath processes; the morphologies appear similar in each case. However, there is an important difference. The finish of a two-bath treatment consists essentially of two amalgamated layers, each relatively homogeneous, while the finish of a one-bath treatment consists essentially of one heterogeneous layer.

#### Solubility of Films

Solubilities after extended Soxhlet extraction with water of films with 70 MAA/30 EA polymer and/or N-methylol compounds are listed in



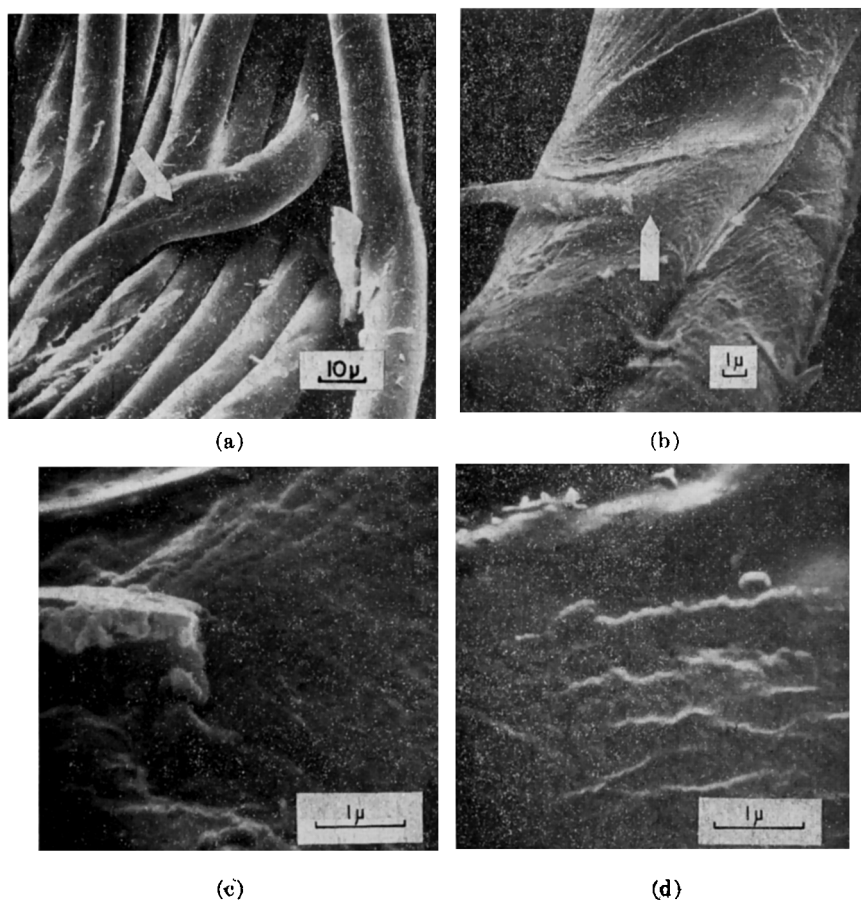


Fig. 4. Scanning electron micrographs of a yarn raveled from a fabric treated with 70/30 MAA/EA copolymer, DMDHEU, and zinc nitrate in a two-bath system (arrows indicate areas shown at higher magnification in succeeding micrographs): (a) general area; (b) cotton fiber; (c) higher magnification at dislodged finish in left center of (b); (d) finish on polyester fiber in center of (a).

Table I. The 70 MAA/30 EA polymer is approximately 3% soluble, somewhat less so when heat treated. Insolubility is due to gel formation during polymerization and film formation.

Solubility of a cured film of DMDHEU and zinc nitrate is considerably less than that of a cured film of DMEU and catalyst, which is nearly completely soluble. These results are in accord with observations from past experience. That is, in general, self-condensed DMEU is water soluble, while self-condensed DMDHEU is much less so due to oligomerization. Also, condensation products of DMEU are more easily hydrolyzed than those of DMDHEU.

When films of polymer mixed with durable press reagents are cast, approximately 3% of the polymer solids originally present in the film

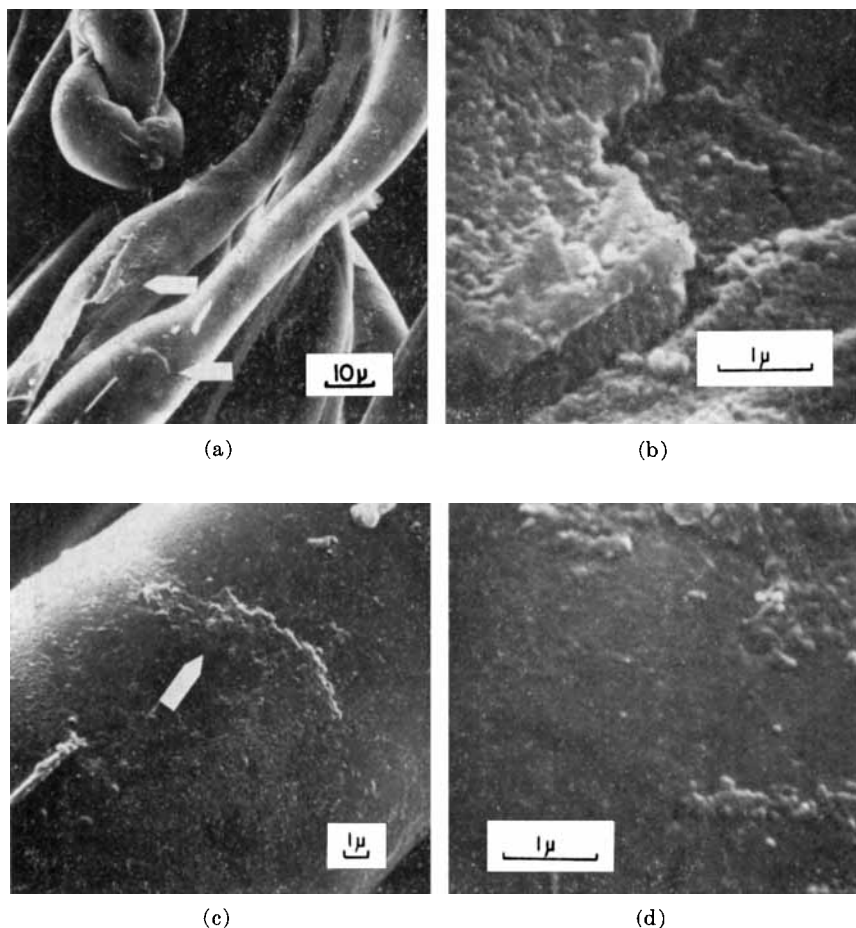


Fig. 5. Scanning electron micrographs of a yarn raveled from a fabric treated in a one-bath system; same reagents as in Fig. 4 (arrows indicate areas shown at higher magnification in succeeding micrographs); (a) general area; (b) at the start of the fold in cotton fiber in (a); (c) at bulge in polyester fiber in (a); (d) higher magnification at finish boundary in upper center of (c).

should be soluble if there is no interaction between polymer and durable press reagents. Hypothetical solubilities listed in Table I were calculated from knowledge of the composition of the films and assuming that all but 97% polymer solids originally present in the film dissolved. Films of DMDHEU and polymer were completely, or nearly completely, soluble, much more so than hypothetically predicted. Enhanced solubility is a consequence of the structure seen in electron micrographs, where uncoalesced polymer dispersion particles are embedded in a matrix of DMDHEU. Very little coalescence results in very little gel formation and, therefore, nearly completely soluble polymer. Films of polymer and DMEU are considerably less soluble than those with DMDHEU.

TABLE I  
Solubility of Films<sup>a</sup>

Film composition	Solubility, %					Hypo- theoretical <sup>b</sup>
	Uncured			Cured		
	23°C	50°C	80°C	23°C	50°C	
Polymer <sup>c</sup>	3.6	—	3.0	3.1	—	3
DMEU	100	100	—	—	—	100
DMDHEU	100	100	—	—	—	100
DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	—	100	—	—	99.5	100
DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	—	100	—	—	66.4	100
Polymer + DMEU	81.0	—	74.2	76.5	—	70
	80.7	—	76.8	—	—	
Polymer + DMDHEU	100	—	100	98.8	—	66
Polymer + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	64.5	—	64.2	66.5	—	73
	66.8	—	—	—	—	
Polymer + DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	69.4	—	66.8	63.1	—	69

<sup>a</sup> Cast at 23, 50, at 80°C, uncured or cured 160°C/30 min, and Soxhlet extracted with water for four days.

<sup>b</sup> Assuming all dissolves but 97% of polymer solids originally present in film.

<sup>c</sup> 70/30 MAA/EA.

DMEU is apparently able to penetrate dispersion particles better, the mixture is less of a two-phase system, and there is better coalescence of dispersion particles. This is consistent with the observed poor stability of soil release emulsion polymers in solutions including DMEU. Additional surfactant must be added to improve stability if the mixture is used commercially. In contrast, stability is excellent in baths with DMDHEU.

Films of polymer and DMEU cast at room temperature were more soluble than those cast at 80°C. The difference is attributable to enhanced diffusivity at 80°C, more coalescence of dispersion particles, and therefore more entanglement of polymer chains. There was little dependence on film-formation temperature with DMDHEU, indicating little diffusion of DMDHEU into polymer coils at either room temperature or 80°C.

Agreement between experimental and hypothetical solubilities was excellent for an uncured film of polymer, DMDHEU, and zinc nitrate cast at room temperature, but not for a cured film of this composition. Cured DMDHEU and zinc nitrate was 66% soluble. If it is assumed that in a film of polymer, DMDHEU, and zinc nitrate, all dissolves but 34% of the DMDHEU solids and 97% of the polymer solids originally present in the film, then the film should be 49% soluble. On the other hand, if it is assumed that all dissolves but 97% polymer solids, the film would be 69% soluble. Experimentally, the solubility of the cured film was intermediate, 63%, and was therefore not consistent with either reasoning.

Cured films of polymer, DMEU, and zinc nitrate were also all less soluble than calculated. These anomalies, which occur in films with zinc nitrate, are explained in succeeding sections.

For comparison, solubility experiments were repeated with a low molecular weight poly(methacrylic acid) solution polymer substituted for the 70 MAA/30 EA emulsion polymer. With one exception, films with PMAA were completely soluble (Table II).

TABLE II  
Solubility of Films with Poly(methacrylic Acid)<sup>a</sup>

Film composition	Solubility, %	
	Uncured	Cured
PMAA	100	100
PMAA + DMEU	100	100
PMAA + DMDHEU	100	100
PMAA + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	100	94.3
PMAA + DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	100	100

<sup>a</sup> Cast at 23°C, uncured or cured 160°C/30 min, and Soxhlet extracted with water for four days.

Soil release polymer is acidic and can catalyze condensation of DMDHEU. If there were self-condensed DMDHEU in residues from extracted films of 70 MAA/30 EA polymer and DMDHEU without zinc nitrate, cured films should be significantly less soluble than uncured films. Experimentally there was very little difference. Considering this result, and the solubility of films with PMAA, it can be inferred that insoluble material in films with emulsion polymer is predominantly polymer and not self-condensed methylol reagent.

#### Nitrogen Content of Residues Remaining after Extraction of Films

There was very little nitrogen in insoluble residues remaining after extraction of films listed in Table III. These results confirm the suspicion that insoluble residues remaining after extraction of films with polymer, methylol compound, and zinc nitrate consist principally of polymer and not of condensed methylol reagent.

TABLE III  
Nitrogen Content of Insoluble Residues of Films with 70/30 MAA/EA Polymer<sup>a</sup>

Film composition	Cure	Nitrogen, %
Polymer	+	0
Polymer + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	-	0
	+	0.73
Polymer + DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	+	0.59

<sup>a</sup> Cast at 23°C, uncured or cured 160°C/30 min, and Soxhlet extracted with water for four days.

### Zinc Content of Residues Remaining after Extraction of Films

Polymers containing methacrylic acid may be insolubilized to some extent by zinc ions. Evidence for ionic crosslinking of 70 MAA/30 EA polymer is presented in Table IV. Less than 3% of the zinc originally

TABLE IV  
Zinc Content of Insoluble Residues of Films<sup>a</sup>

Film composition	Temperature of film preparation, °C	Cure	Zinc, %
Polymer <sup>b</sup> + DMEU	23	—	0.00
DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	50	+	0.47
PMAA + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	23	+	2.17
Polymer + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	23	—	4.80
Polymer + DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	23	—	4.70
	80	—	4.95

<sup>a</sup> Uncured or cured 160°C/30 min, and Soxhlet extracted with water for four days.

<sup>b</sup> 70/30 MAA/EA.

present in a film of DMDHEU and zinc nitrate without polymer remained after extraction. However, about half of the zinc originally present in films with polymer was retained. It can be concluded, then, that zinc is chemically bound to polymer in some manner. If it is assumed that no durable press resin is present in the residue, then in the residue from films with emulsion polymer and zinc nitrate there is present about 1 mole of zinc for every 10 moles of MAA. Zinc is probably concentrated at the periphery of polymer dispersion particles.

The solubility of the cured film of 70/30 polymer, DMDHEU, and zinc nitrate can now be explained. Some zinc is transferred to polymer during film formation and curing. There is, therefore, less oligomerization of DMDHEU, and solubility should be greater than that of a film of DMDHEU and zinc nitrate without polymer. Conversely, zinc ions tend to insolubilize polymer through ionic crosslinks, and therefore solubility should be less than that of a film with polymer and DMDHEU without zinc nitrate. Thus, the experimental solubility of the cured film of polymer, DMDHEU, and zinc nitrate is intermediate between the two.

A lesser but significant amount of zinc is present in the residue from the film with PMAA and DMEU. The lower molecular weight polymer is inherently more soluble and therefore insolubilized less by the same concentration of zinc ions. However, an equivalent film with DMDHEU substituted for DMEU is completely soluble. Solutions for film casting were prepared in such a manner that, initially, zinc ions are believed to be associated principally with N-methylol compound rather than polymer. Since there is more diffusion of DMEU than DMDHEU into polymer, more zinc ions would be expected to contact PMAA when DMEU is used. This would account for the lesser solubility of films with DMEU.

An additional, and probably more tenable, explanation is proposed in the next section.

A few films were prepared with magnesium chloride substituted for zinc nitrate. The limited results were similar to those with zinc nitrate. The magnesium salt insolubilizes polymer also, but to a lesser extent.

### **Association Between Self-Condensed DMEU and Poly(methacrylic Acid)**

Most of the residue remaining after extended extraction of films with polymer, N-methylol compound, and zinc nitrate is concluded to be polymer insolubilized by molecular entanglements, hydrogen bonding, or zinc ions. Nevertheless, some data are not adequately accounted for in the discussion of the preceding sections. Two of these anomalies are now emphasized prior to presentation of additional observations used to explain them.

Heat-treated films of polymer and DMEU without catalyst are about 5% less soluble than those not heat treated. This could be explained by assuming that there is more fusion of dispersion particles at higher temperature. However, the difference in solubility between unheated and heat-treated films of polymer alone is less than 1%. It would be necessary, therefore, to assume that DMEU significantly increases the probability that polymer chains become entangled or associated with one another. This is a defensible but arguable explanation, since the 5% solubility difference is rather large. Also, there is a small but significant amount of nitrogen present in residues of extracted films of polymer, DMEU or DMDHEU, and zinc nitrate. Some is to be expected with DMDHEU because of oligomerization, but self-condensed DMEU should be either soluble or hydrolyzed by the extended extraction. It can be inferred, therefore, that condensed DMEU may be less soluble than expected when polymer is present. An explanation for this additional insolubility is developed from observation of extract solutions.

Extracts from films of low molecular weight PMAA and DMEU or DMDHEU are clear. After cooling and standing for a day or so, solutions from films with DMEU, but not DMDHEU, become cloudy. Reheating clears the solution; if water is vaporized, the solution is more cloudy when cooled. If an aqueous solution of DMEU is refluxed for two days, no cloudiness or insoluble residue is evident. This is expected, since condensed DMEU is water soluble. If refluxed DMEU solution is added to an aqueous solution of PMAA, the mixture is cloudy, similar to the extract from the film discussed above. On standing, an insoluble white material slowly settles. This residue must be due to the presence of condensed DMEU because solutions of DMEU and PMAA are completely soluble. The cloudy solutions can be cleared by adding base or hydrogen bond breakers such as acetone, dioxane, urea, and ethylene

glycol. Water-insoluble complexes of poly(acrylic acid) and poly(alkylene oxides) were reported to exist.<sup>2</sup> It would seem, therefore, that there is also an association between condensed DMEU and PMAA. No cloudiness is evident when condensed DMEU is added to an aqueous solution of poly(acrylic acid). This suggests that there may not only be hydrogen bonding between carboxyl groups of PMAA and amide or ether groups of condensed DMEU, but also hydrophobic bonding between methyl groups of PMAA and the ethylene portion of the DMEU ring.

Refluxed solutions of DMDHEU are completely compatible with PMAA; no cloudiness or insoluble material is observed. Condensed DMDHEU should be more irregular in structure than condensed DMEU and, therefore, less prone to associate intimately with PMAA.

It is concluded that condensed DMEU may be slightly less soluble than expected in the presence of poly(methacrylic acid) due to an association phenomenon. At this point, the reader may question the relevance of a complex with PMAA when 70 MAA/30 EA was the principal polymer of interest in this investigation. The reason the former polymer was used is that the latter polymer is a high molecular weight emulsion polymer. If there were gelation or chemical crosslinking during film formation, partially soluble polymer might be extracted from the film and remain dispersed in the extract, which would subsequently appear cloudy. The extract from cured films of 70 MAA/30 EA polymer alone is somewhat cloudy, although less so than that from films with PMAA, DMEU, and zinc nitrate. Therefore, a low molecular weight PMAA was used to simplify this portion of the investigation by avoiding the possibility of confounding solubility observations with the marginal solubility of a high molecular weight polymer.

When extracts from Soxhlet extraction of films containing 70 MAA/30 EA emulsion polymer, DMEU, and zinc nitrate were cooled, solutions were cloudy, similar to those from equivalent films with low molecular weight PMAA. Distribution of the monomers in the copolymer chain is probably not truly random due to the solubility difference between MAA and EA. There may be some homopolymerization of MAA in the aqueous phase, and MAA may also be concentrated at the exterior of the dispersion particles. Muroi<sup>9</sup> has presented experimental evidence for such a distribution in copolymers of acrylic or methacrylic acid and ethyl acrylate. Portions of the 70 MAA/30 EA copolymer may, therefore, be more similar to poly(methacrylic acid) than otherwise expected. It is highly likely, therefore, that condensed DMEU associates to some degree with 70 MAA/30 EA emulsion polymer. Nevertheless, association between condensed DMEU and polymer is believed to be responsible for only a small proportion of insoluble material in appropriate films. The complex is apparently quite soluble, and therefore most condensed DMEU is soluble, whether it is associated with polymer or not. Most condensed DMEU is probably hydrolyzed during extraction in any case.

### Supplementary Results with 33/50/17 Methacrylic Acid/Ethyl Acrylate/Methyl Methacrylate Emulsion Polymer

A 33/50/17 MAA/EA/MMA emulsion terpolymer was substituted on an equal solids basis for the 70 MAA/30 EA copolymer used previously in order to test the generality of the conclusions drawn.

Films of 33% MAA polymer alone and with DMEU were similar to those of equivalent films with 70% MAA polymer. However, if zinc nitrate was also included, the film with 33% MAA polymer was white and nearly opaque, while that with 70% MAA polymer was clear. The same was true when DMDHEU was substituted for DMEU. Opacity is probably due to formation of zinc salts of the polymer during film formation. This suggests that there is more diffusion of N-methylol compounds into the 33% MAA polymer.

A solution of 33% MAA polymer and DMDHEU does not dry to a true film at room temperature, but rather a viscous liquid, similar to DMDHEU alone. A "dry" film was obtained with 70% MAA polymer, probably because it is more acidic. Acid promotes self-condensation of DMDHEU, resulting in a hard film.

TABLE V  
Solubility of Films with 33/50/17 Methacrylic Acid/Ethyl Acrylate/Methyl Methacrylate Emulsion Polymer<sup>a</sup>

Film composition	Solubility, %
Polymer	3.4
Polymer + DMEU	72.4
Polymer + DMDHEU	92.7
Polymer + DMEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	60.8
Polymer + DMDHEU + Zn(NO <sub>3</sub> ) <sub>2</sub>	63.5

<sup>a</sup> Cast at 23°C and Soxhlet extracted with water for four days.

Solubilities of extracted films are listed in Table V. The polymer alone has about the same solubility as the 70% MAA polymer. The viscous mixture of 33% MAA polymer and DMDHEU is not completely soluble, whereas an equivalent film with 70% MAA polymer is. Films with 33% MAA polymer, DMDHEU or DMEU, and zinc nitrate are less soluble than equivalent films with 70% MAA polymer.

It is concluded that the same general trends in solubility data occur with each emulsion polymer. There is somewhat more diffusion of both DMEU and DMDHEU into 33% MAA polymer than 70% MAA polymer. In each case, the diffusivity of DMEU is greater than that of DMDHEU.

### Relevance of Results to Soil Release of Treated Fabrics

The mechanism by which acrylic soil release agents function is a topic worthy of extensive discussion in its own right. However, such a dis-



ussion is beyond the scope of the present article. Nevertheless, it is important to relate the morphology of the finish to the degree of improvement in soil release of treated fabrics. To do so, it is sufficient to state a belief that acrylic soil release polymers must swell substantially in order to be effective. For example, soil release polymer generally becomes less effective with increasing chemical crosslinking.

There is very limited coalescence of polymer dispersion particles when 70 MAA/30 EA polymer is applied to a fabric together with DMDHEU. Cured finish is essentially a two-phase system in which polymer is embedded in a hydrophobic matrix of condensed DMDHEU. This restricts swelling of the polymer necessary for soil release and accounts for the poor soil release which is sometimes observed with fabrics treated with polymer and DMDHEU applied from a single bath.

It was concluded that more DMEU than DMDHEU diffuses into polymer dispersion particles and that there is, therefore, better coalescence and less tendency toward a two-phase system. Other factors are probably more important with respect to soil release, however. Self-condensed DMEU is water soluble while self-condensed DMDHEU is much less so. Furthermore, condensed DMEU is more easily hydrolyzed than condensed DMDHEU. Thus, in washing, much more condensed DMEU is removed than DMDHEU. Removal of the matrix surrounding polymer particles allows polymer to swell more and function better as a soil release agent. The solubility of condensed DMEU accounts for the greater probability that excellent soil release will be observed with fabrics treated with polymer and this reagent applied from a single bath.

Soil release is generally better when the copolymer with 33% MAA rather than that with 70% MAA is used with DMDHEU in a one-bath system. This may be owing partly to better penetration of 33% MAA polymer by DMDHEU. A more probable explanation is that copolymer with 70% MAA is more acidic and therefore contributes more than polymer with 33% MAA to catalysis of DMDHEU condensation reactions. If mineral acid is added to reduce the pH of baths with 33% MAA copolymer to that of baths with 70% MAA copolymer, soil release of treated fabrics is approximately equivalent. In general, soil release of fabrics treated in a one-bath system is probably sensitively dependent upon bath pH for most durable press and acrylic soil release reagents in common use.

Soil release emulsion polymers are often more durable to washing when applied from a one- rather than two-bath system. This is due to entrapments of polymer in resin and also insolubilization of polymer by cations included in the formulation to accelerate reaction of N-methylol compounds with cotton.

Excellent soil release is obtained, regardless of the durable press reagent used, when soil release polymer is applied separately to fabric pretreated with durable press reagent. In this case, polymer is on top of, and not within, condensed durable press reagent. Its swelling is, therefore, not suppressed. It is the entrapment of polymer in a matrix of condensed

methylol reagent in the one-bath system which is the critical difference with respect to soil release.

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### References

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