

A Radiotracer Study of Durability of Acrylic Soil Release Polymers to Laundering*

C. E. WARBURTON, JR., and L. T. FLYNN, †
*Textile Chemicals Laboratory, Rohm and Haas Co.,
Spring House, Pennsylvania 19477*

Synopsis

Cotton/polyester fabrics were treated with ^{14}C -labeled acrylic soil release polymers, either alone or with a durable press reagent, dimethyloldihydroxyethyleneurea (DMDHEU). Both two-bath and one-bath applications were used. Rate of removal of polymer in laundering was determined experimentally by radiotracer methods. Removal was faster in the order polymer alone (no DMDHEU) > two-bath process > one-bath process. The difference was much more significant when high molecular weight emulsion polymer was used than partially neutralized low molecular weight solution polymer. It is concluded that condensed DMDHEU serves as a coupling agent to bind polymer to fabric, thereby retarding removal of polymer in laundering. The significance of the results with respect to soil release of treated fabrics is discussed.

INTRODUCTION

It is of interest to determine the rate of removal in laundering of acrylic soil release polymers applied with durable press reagents to fabrics by different processes. Conclusions concerning interaction between polymer and durable press reagent can be drawn from such data. In the present work, polymer was applied to fabrics alone, or with a durable press reagent, dimethyloldihydroxyethyleneurea (DMDHEU), in a one-bath or two-bath process. Polymers containing $-\text{C}^{14}\text{OOH}$ methacrylic acid were used, and rate of removal in laundering was determined by radiotracer methods. Two soil release polymers were investigated, a 70% methacrylic acid/30% ethyl acrylate emulsion copolymer and a low molecular weight poly(methacrylic) acid solution polymer neutralized to pH 5. In one series of treatments, both polymers were applied with DMDHEU to the same fabric in a one-bath process.

* Presented at the 163rd National Meeting of the American Chemical Society, Boston, Massachusetts, April 9-14, 1972.

† This work was performed while L. T. Flynn was a summer employee at Rohm and Haas Co. Present address: Department of Chemistry, Purdue University, Lafayette, Indiana.

EXPERIMENTAL

Chemicals

70% MAA/30% EA emulsion copolymer, estimated molecular weight 10^5 – 10^6 , 20% solids, ^{14}C COOH methacrylic acid, specific activity 1.6336×10^6 disintegrations/min (dpm)/g polymer.

Poly(methacrylic acid) solution polymer, estimated molecular weight about 5000, neutralized to pH 5 with KOH, 28% solids, ^{14}C COOH methacrylic acid, specific activity 1.9230×10^6 dpm/g polymer.

DMDHEU as Permafresh 183 (Sun Chemical Corp.) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ reagent grade were used.

Fabric Treatment

For two-bath application, durable press reagent and catalyst were applied initially, and soil release polymer alone in a second separate step. Fabrics were dried and cured after each step. Two versions of the two-bath process were used. In one, fabric was washed following each step; in the other, fabric was not washed until after the second step.

For one-bath application, all reagents were mixed and applied in a single step. In one series of treatments, both polymers were applied simultaneously with durable press reagent to fabric in a one-bath application; in certain of these treatments, one polymer was radioactive and the other was not in order to differentiate removal of the individual polymers in washing.

For each treatment, about 24 g 65% polyester/35% cotton shirting fabric, Testfabrics #7406, were padded, two dips, two nips, fastened to a pin frame, dried at $110^\circ\text{C}/5$ min, and cured at $160^\circ\text{C}/3$ min in forced-draft ovens.

Regardless of the order in which reagents were applied, they were used at the following concentrations: 25% Permafresh 183, 6% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 25% (product basis) 70% MAA/30% EA emulsion copolymer, and 30% partially neutralized pMAA polymer solution. However, when both polymers were used in the same bath, only 15% pMAA polymer solution was used.

When partially neutralized polymer was used in a one-bath process, reagents had to be mixed in a specific manner or polymer was precipitated by catalyst cations. A procedure for mixing such solutions so as to avoid precipitation is described elsewhere.¹

Laundering

Fabrics were laundered in hot water (about 60°C) with one cup of Tide in a Maytag machine. Ten cotton towels were added for ballast. At the end of each full cycle, fabrics were removed and tumbled 10 min in a Kenmore dryer at the "hot" setting. Fabrics were conditioned at 21°C , 65% R.H. before and after finish was applied, and also after subsequent washings, in order to estimate total weight of finish on each fabric.

Soil Release Test Method

A 9 in. × 12 in. fabric sample was stained with seven soils, each in a different location on the sample: Nujol mineral oil, used motor oil, Crisco oil, catsup, French's mustard, Ragu spaghetti sauce, and Tabasco sauce. These materials were left on the fabric for 30 min. The excess was then blotted and the fabric air-dried for 10 min. The samples were rinsed for 12 min in cold water in an automatic washer to remove heavily caked-on soil and then laundered and dried as described in the previous section. They were then visually rated for soil release appearance using the Deering Milliken photographic standards. A rating of 1 indicates essentially no removal, and 5, complete removal of soil; 4 to 5 is excellent, 3 to 4, good.

Weight of Polymer on Fabric

After each washing, two 1 in. × 4 in. samples were cut from random positions on the fabric. No samples were taken from within 3 in. of any edge. Each sample was taped into a 10-cm combustion boat and heated in the air stream of a combustion tube for 2 hr. During this period, the temperature of the air was increased from 300°C to 870°C at a programmed rate. ¹⁴CO₂ was trapped in 10.0 ml ethanolamine, of which 4.0 ml was used for counting. Varying amounts of water were produced by combustion, necessitating a volume correction for trapped solution.

Solutions were counted by liquid scintillation spectroscopy. Solutions with CO₂ collected from untreated fabric were used for background counting. Combustion efficiency was determined by "spiking" a solution with ¹⁴CO₂ collected from an untreated fabric with a known amount of ¹⁴C-labeled compound of much greater activity than that of the radioactive polymer. Combustion efficiencies were in the range 92.62% to 98.51%. Counting efficiency was constant, 63.5 ± 1.0%.

The amount of polymer on fabric was calculated from the counts per minute with background subtracted (cpm) as follows:

$$\% \text{ polymer} = \frac{(\text{cpm})(\text{trap vol. corr.})(100)^3}{(\text{combustion eff.})(\text{counting eff.})(\text{spec. activity})(\text{sample wt.})}$$

The average of duplicate determinations was reported.

An attempt was made to account for redeposition of radioactive material during washing by including an untreated fabric in the wash. The count of the trap solution with CO₂ collected from samples of this fabric was used as background count for about the first five washes. After this, there was no significant difference between counts from washed and unwashed untreated fabric, and the latter was used as background. Adsorption was about 0.01% (polymer on weight of fabric) in each of the first five washes. After this, the concentration of polymer in the wash solution was not sufficient for measurable adsorption. The order of magnitude of the adsorption figure and its relatively constant value over five washes suggests

monolayer adsorption. For example, Sullivan and Hertel² calculated the minimum weight of sodium carboxymethylcellulose required to form an adsorbed monomolecular layer on cotton to be 0.0167 g/100 g cotton. This is of the order of magnitude of the value calculated for redeposition of the acrylic polymers.

This method of accounting for redeposition in washing may be questioned because redeposition may be different on treated than untreated fabrics. However, if adsorption is limited to monolayer formation, this difference should not be substantial. Also, the difference should be greatest in the first and second washes when there is abundant polymer already on the treated fabrics. The correction is of little significance for these washes because the amount of polymer already on the fabrics is so much greater than that adsorbed through redeposition. Thus, error in the correction for redeposition is greatest when the correction is of least importance, and the error decreases as the correction becomes more important.

In one treatment, both radioactive polymers were applied to fabric in a one-bath process. Since the specific activities of the two polymers are different, it was necessary to use a weighted specific activity to determine total polymer on fabric. To do so, it was assumed that polymers are removed in each wash in the same ratio as from fabrics treated with the individual polymers and DMDHEU in a one-bath process. This ratio was used to calculate a weighted specific activity for use when both radioactive polymers were applied together.

Weight of Condensed DMDHEU on Fabric

The micro Kjeldahl method was used to determine nitrogen content of finished fabrics. Duplicate determinations were run on each of two samples cut from fabric at random positions. Weight of condensed DMDHEU on fabric was estimated from nitrogen content.

RESULTS

Average soil release ratings of treated fabrics unwashed before staining are listed in Table I. Initial ratings were equivalent for the two-bath

TABLE I
Soil Release Ratings of Fabrics Treated with Acrylic Soil
Release Polymers and DMDHEU (Unwashed Before Staining)

Treatment	Average rating (7 soils) ^a		
	70% MAA/ 30%EA	pMAA ^b	Both polymers
Polymer alone ^c	5	2	5
One-bath process	3	4.5	3.5-4
Two-bath process	5	2	5

^a Rating of untreated fabric = 2.

^b Partially neutralized to pH 5.

^c No DMDHEU used.

process, whether fabrics were washed or not before second-step application of polymer.

Weight of finish on weight of fabric after each washing is reported in Figures 1-5. On the abscissa legends, 0 represents an application step. For example, for the two-bath process, the ordinates at 0[2] are the

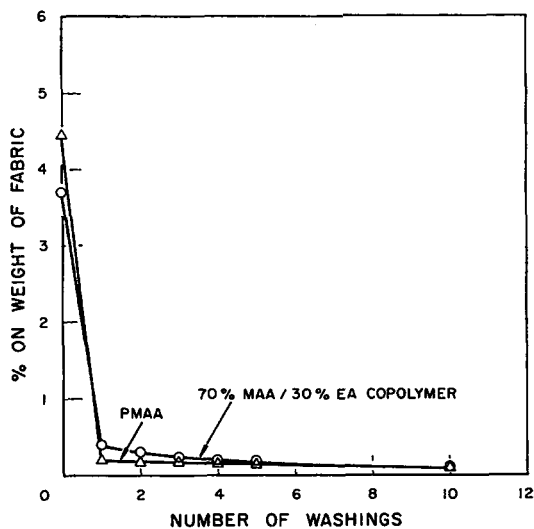


Fig. 1. Loss of 70% MAA/30% EA copolymer or partially neutralized pMAA in laundering. Fabrics treated with polymer only.

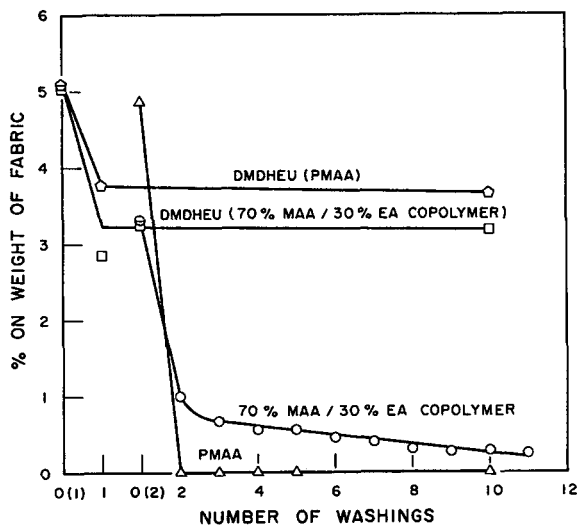


Fig. 2. Loss of condensed DMDHEU and 70% MAA/30% EA copolymer or partially neutralized pMAA in laundering. Fabrics treated in a two-bath process with DMDHEU and one polymer, fabrics laundered once before second step application of polymer.

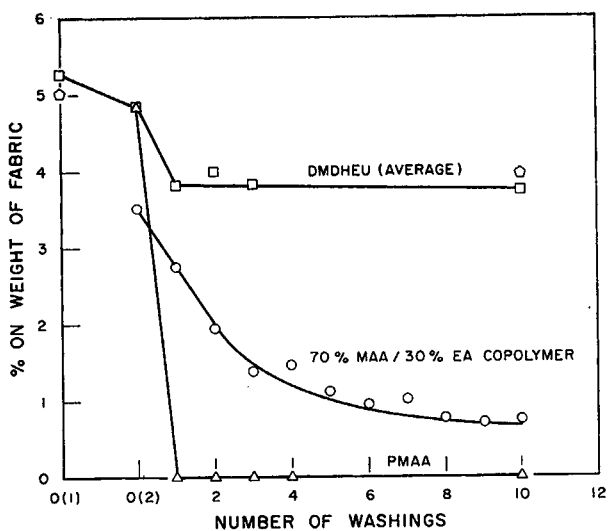


Fig. 3. Loss of condensed DMDHEU and 70% MAA/30% EA copolymer or partially neutralized pMAA in laundering. Fabrics treated in a two-bath process with DMDHEU and one polymer, fabrics not laundered before second step application of polymer: (\square) DMDHEU applied with 70% MAA/30% EA copolymer; (\circ) DMDHEU applied with pMAA.

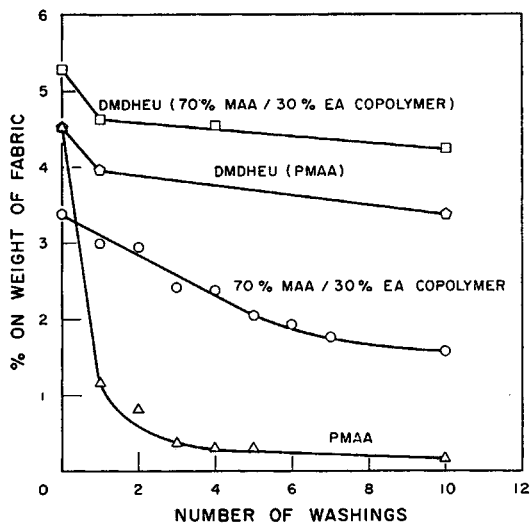


Fig. 4. Loss of condensed DMDHEU and 70% MAA/30% EA copolymer or partially neutralized pMAA in laundering. Fabrics treated in a one-bath process with DMDHEU and one polymer.

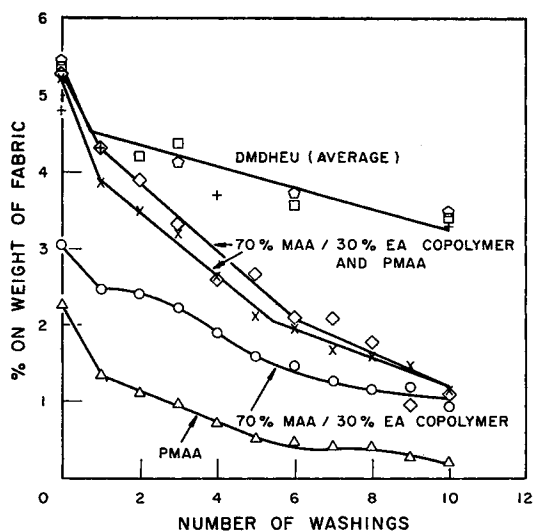


Fig. 5. Loss of condensed DMDHEU, 70% MAA/30% EA copolymer, and partially neutralized pMAA in laundering. Fabrics treated in a one-bath process with DMDHEU and both polymers applied to same fabric: (○) 70% MAA/30% EA copolymer only labeled; (△) pMAA only labeled; (×) sum of (○) and (△) curves; (◇) both polymers labeled; (□) DMDHEU applied with 70% MAA/30% EA copolymer labeled; (◊) DMDHEU applied with pMAA labeled; (+) DMDHEU applied with both polymers labeled.

amounts of polymer and DMDHEU on fabric after second-step application of polymer.

DISCUSSION

Fabric Treated with Polymer Alone

Most applied polymer was removed in the first wash when DMDHEU was not present on fabrics (Fig. 1). A small amount of polymer remained in each case and was removed relatively slowly with further washing.

Partially neutralized low molecular weight polymer was apparently removed so rapidly in the first wash for evaluation of soil release that soil release was not improved (Table I). However, improved soil release through a number of washes has been observed with 70% MAA/30% EA emulsion copolymer applied alone to fabric. Since there was little difference between the amounts of high molecular weight 70% MAA/30% EA copolymer and low molecular weight pMAA on fabric after the first wash, it is concluded that the former is a more efficacious soil release agent.

It is important to realize that rate of removal of soil release polymers is highly dependent upon fabric construction, regardless of whether polymer is applied alone or with durable press reagent. For example, polymers are removed much more rapidly from tightly woven fabrics than bulky-textured ones. Loss of a substantial proportion of applied polymer

in the initial wash is not necessarily catastrophic; excellent improved soil release can be obtained with less than 0.5% polymer on fabric. Such a loss of polymer may sometimes be desirable, such as when the hand of treated fabrics is harsh. It is necessary to apply more than a minimum amount of polymer in order to be sure that it is present in desirable locations. This is not unusual and is also done with durable press reagents. A significant proportion of applied durable press finish is also removed in the initial wash.

Two-Bath Process

Partially neutralized pMAA solution polymer was removed nearly completely in the first wash when fabric was treated with DMDHEU in a two-bath process (Figs. 2 and 3). Removal was even more rapid than when fabric was not pretreated with DMDHEU, probably because surface resin hinders penetration of polymer between fibers of the yarns. For example, yarns pretreated with DMDHEU and then treated with 70% MAA/30% EA emulsion copolymer were stained with berberine sulfate, a fluorescent dye selective to the polymer, embedded in resin, sectioned, and examined by fluorescence microscopy³; polymer was found to have penetrated quite deeply into yarns in each case, but less deeply when fabric was pretreated with DMDHEU.

The 70% MAA/30% EA emulsion copolymer was removed considerably more slowly in washing when fabric was pretreated with DMDHEU. Furthermore, more polymer was retained on fabrics not washed after application of DMDHEU. It is apparent from these results that there is interaction between polymer and durable press finish. A number of explanations can be advanced for interaction. Cations from catalyst used to accelerate reaction of DMDHEU may be retained on fabric. These cations may insolubilize high molecular weight polymer to some extent.¹ Also, there may be a limited degree of ester formation between polymer and condensed DMDHEU. However, this reaction has been shown to occur to only a minor extent.⁴ Condensed DMEU and pMAA in aqueous solution associate to some extent.¹ No evidence was found for association of polymer and condensed DMDHEU in solution. However, the association of polymer with condensed DMEU suggests that there might be appreciable attractive forces between condensed DMDHEU and pMAA in the solid state, if not in the liquid state. It is probable then that 70% MAA/30% EA copolymer is bound to condensed DMDHEU on fabrics principally by hydrogen bonding and van der Waals forces and to a minor extent by covalent bonds.

Observations on film samples cast for use in previous work¹ are pertinent to the present discussion. Films of DMDHEU, $MgCl_2$, and 70% MAA/30% EA copolymer or unneutralized pMAA cast on Mylar were difficult to remove from the polyester surface, more difficult than when polymer or durable press reagent was cast separately. Adhesion was better yet when films were cured and worse when $MgCl_2$ was omitted. Methacrylic acid

polymers are attracted to polyester substrates to some extent, although significantly less so than to cotton. However, the enhanced adhesion of films with polymer and DMDHEU seems to be significantly dependent upon self-condensation of DMDHEU. Acidic polymer probably catalyzes the self-condensation reactions. Since condensed DMDHEU is somewhat hydrophobic, it is probably attracted to polyester as well as cotton. The following results are further evidence for attraction of condensed DMDHEU to polyester substrates.

Approximately equal amounts of DMDHEU were applied to both a 100% spun-polyester fabric and an 80-square cotton fabric in a conventional pad-dry-cure process. Finish on the all-polyester fabric was found to be as durable to washing as that on the all-cotton fabric, even though DMDHEU does not diffuse into or react appreciably with polyester fibers. Condensed DMDHEU is apparently insolubilized and bonded to fiber surfaces. This bonding is again probably due to hydrogen bonding and van der Waals forces.

In summary, condensed DMDHEU is concluded to serve as a coupling agent to bind acrylic soil release polymer to fabrics. Polymer is attracted to resin through secondary bonding forces. There is probably also a limited degree of ester formation between polymer and DMDHEU. At the same time, insoluble oligomerized DMDHEU is attracted to fiber surfaces, also through secondary bonding forces. On cotton surfaces, there is chemical reaction of resin with cellulose as well. The coupling effect of condensed DMDHEU therefore accounts for slower removal of polymer in laundering when fabric is pretreated with DMDHEU.

It can be inferred from data in Figures 2 and 3 that removal of condensed DMDHEU in washing from fabric treated in a two-bath process is not dependent upon which polymer is used and is probably not significantly affected by the presence of either polymer. When fabrics are not washed before application of polymer, a small amount of unreacted or condensed DMDHEU is removed in the pad bath operation when polymer is applied to fabric.

One-Bath Process

Both polymers were removed considerably more slowly in washing when applied with DMDHEU from a one-bath rather than a two-bath process (Fig. 4). Slower removal of the emulsion polymer is a consequence of the morphology reported in earlier work¹; coalescence of dispersion particles is poor, and polymer is trapped in a matrix of condensed DMDHEU on the fiber surfaces, swelling of polymer is hindered, and therefore soil release is inferior to that obtained with a two-bath process.

Partially neutralized low molecular weight polymer was removed much more rapidly in the first three washes than the high molecular weight copolymer, but less rapidly than when it was applied in a two-bath process. Soil release of treated fabric was excellent initially, but there was little improvement over an untreated control after one or two washes. Apparently

then, condensed DMDHEU slows removal of low molecular weight polymer enough to permit excellent initial soil release, but not sufficiently for soil release to be improved after a number of washes. Enhanced retention of low molecular weight polymer applied with DMDHEU is probably due principally to the coupling effect of condensed DMDHEU discussed in the previous section. Poly(methacrylic acid) in aqueous solution exists in a coiled, globular conformation. However, when neutralized to pH 5, the chains are probably substantially solvated. Nevertheless, when mixed with DMDHEU, a "two-phase" morphology of the nature of that obtained with emulsion copolymer probably prevails to a small degree. This would account for slower removal of low molecular weight polymer applied from a one-bath rather than a two-bath process or alone without DMDHEU.

When 70% MAA/30% EA emulsion copolymer was used, more condensed DMDHEU was retained on fabrics treated in a one-bath than in a two-bath process. This may be due to lower bath pH when DMDHEU is applied with acidic polymer, and therefore more catalysis of DMDHEU self-condensation. It may also be partly due to more extensive secondary bonding and chemical reaction of polymer and DMDHEU. Such interactions are more probable in a one-bath process because the probability of the two reagents contacting each other is greater. Similarly, the difference in bath acidity can be used to explain better retention of DMDHEU applied to fabrics in a one-bath process with 70% MAA/30% EA emulsion copolymer rather than partially neutralized pMAA.

Curves in Figures 2 to 4 for removal of condensed DMDHEU are all approximately linear after the first wash. The curve for removal of 70% MAA/30% EA emulsion copolymer applied in a one-bath process is more linear over the entire range of ten washings than any of the other curves representing removal of polymer. The linearity in this case suggests removal of polymer is appreciably dependent upon hydrolysis of condensed DMDHEU. This is consistent with the "two-phase" morphology of this polymer-resin finish.

Emulsion copolymer was removed in washing more rapidly than condensed DMDHEU. It is unlikely, then, that soil release would improve substantially with extended washings because polymer would already have been removed by the time the condensed DMDHEU matrix was removed. However, slight improvements have been observed up to about five washes.

When partially neutralized polymer was used, more DMDHEU was removed in washing from fabrics treated in the one-bath than in the two-bath process. This is believed to result from buffering by the sodium methacrylate portions of the polymer that limits catalysis of DMDHEU self-condensation in the curing stage of the one-bath process. Another possible explanation is that condensed DMDHEU reacts with polymer and is necessarily removed as water-soluble polymer is removed. However, it is very questionable if there is sufficient reaction between polymer and DMDHEU for this effect to be important, especially in the case of a partially neutralized polymer.

One-Bath Process—Both Polymers Applied to Same Fabric

The two lowest curves in Figure 5 were plotted from radiotracer counting data from fabric samples on which only one of the two polymers was labeled. The sum of these two curves is plotted immediately above them. The position of this curve is very close to that of the curve plotted from data obtained when both polymers were labeled. In the latter case, weighted specific activities were used to convert counting data to total polymer weight on fabric. It was assumed that polymers were removed in each wash in the same ratio as from fabrics treated with the individual polymers and DMDHEU in a one-bath process. The close proximity of the curves suggests that the assumption is tenable. Nevertheless, there are probably reasons, other than experimental error, why the curves are not closer together. The following discussion of film solubilities is useful in accounting for the discrepancy.

Films of the two polymers were Soxhlet extracted with water for four days. The procedure was the same as that used in earlier work.¹ A film of 70% MAA/30% EA emulsion copolymer was only about 3% soluble due to gelation during polymerization and film formation. A film of partially neutralized low molecular weight pMAA was completely soluble. However, a film consisting of both polymers, 4.75 g solution polymer/1 g emulsion copolymer (solids basis) was also completely soluble. It was most likely soluble because low molecular weight polymer interferes with coalescence of copolymer dispersion particles during film formation, much in the same manner as DMDHEU does. This additional hindered coalescence of dispersion particles results in somewhat faster removal in laundering of 70% MAA/30% EA emulsion copolymer from fabrics treated with both polymers. (Compare 70% MAA/30% EA curves in Figs. 4 and 5.)

Partially neutralized polymer was removed more slowly from fabrics treated with both polymers. (Compare pMAA curves in Figs. 4 and 5.) This may be due to hydrogen bonding between low molecular weight polymer and emulsion copolymer, which is less easily removed in laundering.

The assumption made in calculating a weighted specific activity for use when both radioactive polymers are applied together does not take into account diminished coalescence of 70% MAA/30% EA dispersion particles and hydrogen bonding between the two polymers. Neglect of the former would result in too low a weighted specific activity, since the specific activity of the low molecular weight polymer is greater than that of the emulsion copolymer. Neglect of the latter would result in too high a weighted specific activity. If both factors are neglected, the errors should tend to compensate. The curve for the case in which both polymers are labeled is somewhat higher than that of the sum of the two curves for the cases in which only one of the two polymers is labeled. If it is too high, then the weighted specific activities used are too low, and therefore, the proportion of 70% MAA/30% EA copolymer on fabric is overestimated. It

can be surmised, then, that in calculating the weighted specific activities, neglecting the greater solubility of the emulsion copolymer is of somewhat more consequence than neglecting the lesser solubility of the solution polymer.

DMDHEU was removed in washing about as rapidly as when partially neutralized solution polymer was used without emulsion copolymer in a one-bath process. As in the latter case, this can be explained by the buffering effect of sodium methacrylate, resulting in less self-condensation of DMDHEU during cure.

SUMMARY AND CONCLUSIONS

Acrylic soil release polymers are removed less rapidly in laundering when applied in a two-bath process to fabrics pretreated with DMDHEU than when applied alone to untreated fabric. Rate of removal is slower still if polymer and DMDHEU are applied together in a one-bath process. Self-condensed DMDHEU is believed to function as a coupling agent in binding polymer to fabric. Attraction between polymer and condensed DMDHEU is concluded to be due to hydrogen bonding and van der Waals forces. There may also be a limited degree of chemical reaction between polymer and resin.

Partially neutralized low molecular weight solution polymer is removed more rapidly than emulsion copolymer when applied with DMDHEU in a one-bath process. In the latter case, coalescence of dispersion particles is poor and polymer is entrapped in a matrix of condensed DMDHEU.

If both polymers are applied with DMDHEU to the same fabric in a one-bath process, removal in laundering of emulsion copolymer is somewhat faster, and that of partially neutralized solution polymer is somewhat slower, than when polymers are applied individually with DMDHEU to separate fabrics. Emulsion copolymer is more soluble because low molecular weight polymer interferes with coalescence of dispersion particles. Low molecular weight polymer is less soluble because it is hydrogen bonded to emulsion copolymer.

In summary, then, soil release of fabrics treated with polymer and DMDHEU is not necessarily determined by the quantity of polymer on the fabric. It is dependent upon whether the reagents are applied from a one-bath or two-bath process, and therefore, the morphology of the dual-purpose finish. It is also dependent upon the rate at which polymer is removed in laundering.

The results and conclusions drawn are dependent upon the use of DMDHEU. Significantly different results would generally be obtained with other durable press reagents. For example, self-condensed dimethylolethyleneurea (DMEU) is water soluble and is removed much more readily in washing than is self-condensed DMDHEU. Initial soil release of fabrics treated in a one-bath process is excellent because the matrix of self-condensed DMEU incasing the polymer is removed sufficiently rapidly

in the first wash to allow polymer to swell and function properly. In general, as far as soil release performance is concerned, each combination of soil release polymer and durable press reagent should be considered as unique an entity as the individual components themselves. It is presumptuous to assume that results with one combination will be similar to those obtained with another combination.

Dr. W. R. Lyman supplied ¹⁴C-methacrylic acid and suggested the experimental procedure for the radiotracer portion of the work. Polymers were prepared under the supervision of Mr. W. W. Toy. Fabric samples were combusted and counted by Mr. N. Matthews under the supervision of Dr. G. Foster.

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Received October 1, 1971