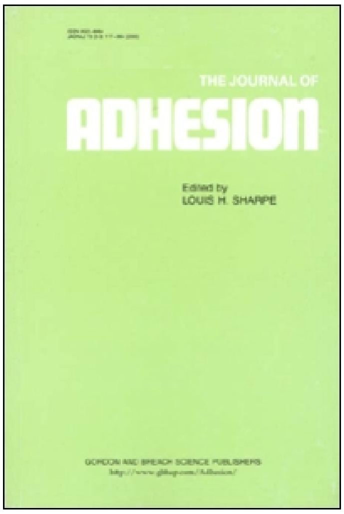

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Crockfastness of Polyacrylate Textile Pigment-Printing Binders: Effect of Binder Mechanical Properties and Adhesion to Fabric[†]

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The effectiveness of ethyl or butyl acrylate copolymerized with a small proportion of acrylonitrile in improving crockfastness of pigment-printed textile fabrics was determined. Crockfastness was demonstrated to be dependent upon mechanical resistance of the pigmented binder to rubbing and adhesion of the binder to fabric. Crockfastness on cotton fabrics correlated with tensile properties of binder films, ethyl acrylate being superior to butyl acrylate. The correlation failed with polyester fabric because adhesion was a more critical factor, the polyester fiber and yarn surfaces being smoother and more difficult to wet thermodynamically than cotton; in this case, butyl acrylate was superior to ethyl acrylate in adhesion and crockfastness. An analysis of surface free energies showed that better adhesion of the butyl acrylate copolymer to polyester was a consequence of lower total surface energy and lower polarity.

INTRODUCTION

In pigment printing of textile fabrics, pigments with little or no chemical affinity for the fibers are bound physically to the fabric by a polymeric, film-forming adhesive. The binder contributes to wash and dry-clean durability of the print and is necessary to minimize crocking, which is the transfer of color from a dyed or printed fabric to another fabric on rubbing. Both mechanical properties of the binder and adhesion to pigment and fabric contribute to crockfastness, good mechanical properties being advantageous in resisting deformation of the coating on rubbing and good adhesion being

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advantageous in preventing transfer of the pigment or coating to rubbing cloth.

If a ranking of the effectiveness of binders within a series is the same regardless of the fabric substrate, mechanical properties of the binders are determinant. If rankings differ with different fabrics, the permutations most likely result from differences in adhesion to fabric because binder mechanical properties are, for all practical purposes, independent of the substrate. In this article, the efficacies of three polyacrylate copolymers in minimizing crocking on cotton and polyester fabrics are analyzed with respect to binder mechanical properties and adhesion to fabric. Differences in adhesion to fabric are accounted for by an analysis of surface and interfacial free energies of binders and fabric substrates.

MATERIALS AND METHODS

Polymeric binders

Three emulsion copolymers, 10^5–10^6 molecular weight: ethyl acrylate (EA)/acrylonitrile (AN)/methylolated amide (MAm), glass transition interval (Tg) = −15°C to 5°C (from ten-second torsional modulus *vs.* temperature curve); n-butyl acrylate (BA)/AN/MAm, Tg = −25°C to −5°C; BA/MAm, Tg = −55°C to −35°C. AN proportion is about 11% by weight, MAm less than 5%. For brevity, MAm is omitted in subsequent nomenclature for these copolymers.

Binders were formulated into a print paste with composition shown in Table I.

TABLE I

Composition of print pastes

	%, by wt.
High molecular weight ammonium polyacrylate thickener	0.7
Epoxidized soybean oil softner	4.0
Polyacrylate binder (46% solids emulsion copolymer)	15.0
Helizarin Blue BT (55% solids pigment dispersion)	2.5
water	to 100%
NH_4OH	to pH 7.5–8.0
Brookfield viscosity, RVF, spindle 6, 20 rpm	190–230 poise

Fabrics

Bleached, mercerized, cotton broadcloth (Testfabrics 419A), 65 Dacron 54/35 cotton blend poplin (Testfabrics 7402), and Dacron 56 polyester taffeta (Testfabrics 704).

Printing

Fabrics were screen-printed in the laboratory using an automatic, magnetically-driven, rolling bar to force the printing paste through a nylon screen onto fabric.

Crockfastness of prints

AATCC (American Association of Textile Chemists and Colorists) Test Method 116–1969, rotary vertical crockmeter (printed fabric conditioned at 21°C, 65% R.H. is rubbed by a standard cotton test swatch under pressure with reciprocating rotary motion).

Transfer of color to test swatches was rated subjectively with reference to the AATCC Chromatic Transference Scale. Also, reflectance of the test cloths was measured using an IDL Color-Eye at a wave length of 700 nanometers. Reflectance, R, was converted to the ratio of the Kubelka–Munk absorption and scattering coefficients, $K/S = (1-R)^2/2R$. Reported data are averages from duplicate samples.

Tensile testing of films

Films were cast from binder latexes at 21°C, 65% R.H. and dried ten days before curing 150°C/6 minute. Dumbbell-shaped samples, 0.25-inch width, 1-inch gauge length, 20–40 mils thick, were cut with a die and extended to failure at 500%/minute rate of extension on an Instron tensile tester. About ten samples from each copolymer were tested.

Abrasion resistance of films

Taber abrasion resistance was measured on conditioned film samples using H-10 wheels and 1000 g weights. Weight losses from three films of each copolymer were averaged.

Peel tests

Pigment printing pastes were coated 10 mils wet onto polyester or cotton fabric using a Gardner knife. Laminates were formed by carefully pressing a second fabric or a sheet of Mylar [poly(ethylene terephthalate)] onto coated fabric. Laminates were dried at 105°C/5 minutes and then cured on a Mann Press, 70 pound gauge (4–5 psi), 150°C/1 minute. Two master laminates were prepared for each adhesive-substrate combination, and five 1-inch width test samples cut from each. Peel strengths were measured on an Instron tensile tester at 2 inch/minute rate of extension. There was no significant difference in peel strengths of samples cut from different master laminates.

EXPERIMENTAL RESULTS

Crockfastness of prints

AATCC crockfastness ratings and K/S of rubbing cloths appear in Table II. EA/AN copolymer is best on cotton and 65 polyester/35 cotton fabric; BA/AN copolymer is best on polyester fabric; BA polymer without AN is worst on all three fabrics. (Ratings of binders on different fabrics should not be compared because the fabrics differ somewhat in yarn density and absorption of print paste.)

TABLE II

Crockfastness[a] of prints on various fabrics with polyacrylate binders

	Cotton		65 Polyester/35 cotton		Polyester		Relative softness of printed fabric[b]
Binder	$K/S \times 10^2$	AATCC rating	$K/S \times 10^2$	AATCC rating	$K/S \times 10^2$	AATCC rating	
EA/AN	1.7	4.0	2.0	4.0	4.5	3.0	3
BA/AN	2.8	3.5	2.5	3.5	1.5	3.7	2
BA	14.0	2.5	19.6	2.0	19.1	2.0	1

[a] Lower K/S and higher AATCC rating indicate less color transfer.
[b] 1 = softest.

Scanning electron microscopic examination of rubbing cloths and rubbed fabrics showed that color on rubbing cloths was principally from fragments of the entire coating and not pigment particles dislodged from the coating surface. Thus, adhesion of binder to pigment did not determine crockfastness ranking of binders. It was not possible to distinguish between cohesive failures of the coatings and adhesive failures at the coating-fabric interfaces.

Tensile properties and abrasion resistance of films of binders

Tensile properties of films of binders were measured in order to determine if there was a positive correlation with crockfastness. Tensile properties of binders are of course altered somewhat by other ingredients added in the print paste, e.g., pigment, softener, surfactants, but previous work has shown that a ranking of tensile properties within a group of binders is seldom permuted by formulation, unless properties of the unformulated binders are very close. Thus, it is fair to attempt to correlate crockfastness of prints with tensile properties of the polyacrylate copolymers.

The EA/AN copolymer is the strongest, most extensible, hardest, toughest, and most abrasion resistant of the three polyacrylates (Table III). Poly(ethyl acrylate) is generally superior to poly(butyl acrylate) in mechanical properties, and acrylonitrile reinforces the network structure of both polymers through interchain cohesive (secondary) bonding, e.g., dipole–dipole interactions.

On cotton, crockfastness of the three binders correlates with tensile properties of films. On polyester fabric, crockfastness of the BA/AN copolymer is best, even though tensile properties are only intermediate.

TABLE III

Tensile properties[a] and abrasion resistance of polyacrylate films

Polymer	Tensile strength (psi)	Ultimate elongation (%)	200% modulus (psi)	Work to break (in.-lb/in.^{3})	Abrasion resistance wt. loss (g.)
EA/AN	446±52	596±49	108±4	1260±230	0.07
BA/AN	318±22	427±26	99±10	568±68	0.60
BA	156±28	319±43	67±9	197±58	1.26

[a] Confidence intervals are 95% limits.

Cotton fibers tend to be elliptical with indentations and convolutions. Their surface is wrinkled and rough, although less so after mercerization. This irregular topography is more conducive to good adhesion than that of polyester fibers, which is more regular and smooth. Furthermore, cotton fabric of necessity consists of twisted, spun yarn, whereas the polyester fabric used in this work consists of untwisted, continuous-filament yarn. The rougher surface of spun yarn is also more conducive to adhesive bonding. Therefore, it is likely that adhesion of all three binders to cotton is good and that differences in crockfastness are determined principally by mechanical resistance of the binders to rubbing. It is also likely that adhesion is a more critical factor on polyester fabric and that BA/AN copolymer adheres to polyester better than EA/AN copolymer.

Peel strength of laminates

To assess adhesion to polyester, laminates were prepared with print pastes as adhesives sandwiched between two cotton fabrics, two polyester fabrics, or Mylar and cotton.

Fabric–fabric laminates failed cohesively in peel tests. As expected, a ranking of cohesive peel strengths in Table IV parallels that of tensile properties of binders. Peel strengths with the same copolymer between cotton and polyester fabrics differ because the applied paste is absorbed to a different degree in each, and consequently the effective thickness of the adhesive layer differs.

Mylar/cotton laminates failed adhesively at the Mylar/adhesive interface. These peel strengths are an unambiguous measure of adhesion to polyester. Peel strengths of laminates with the two butyl acrylate polymers are greater than the peel strength of the laminate with EA/AN copolymer (Table IV). This confirms the suspected better adhesion of the BA/AN copolymer to polyester and accounts for its superiority to EA/AN copolymer in crockfastness on polyester fabric.

TABLE IV

Peel strengths of fabric/fabric and film/fabric laminates with pigment-printing pastes as adhesives

Binder in paste	Peel strength[a] × 10^2 (lb/in.) Cotton/Cotton[b]	 Dacron/Dacron[b]	 Mylar/Cotton[c]
EA/AN	35±3	50±6	2.1±0.0
BA/AN	28±3	30±2	6.2±0.0
BA	7±9	9±1	5.6±0.9

[a] Confidence intervals are 95% limits.
[b] Cohesive failure.
[c] Adhesive failure.

Adhesion to Mylar of the BA polymer without AN is better than that of EA/AN copolymer. However, crockfastness of the EA/AN copolymer is better because the BA polymer resists rubbing so poorly that better adhesion is of no practical advantage.

On the blend fabric, crockfastness of the EA/AN copolymer is best. This may seem anomalous since the proportion of polyester in the blend is greater than cotton, and consequently crockfastness of the BA/AN copolymer might be expected to be best. However, cotton fibers are concentrated nearer the surface of yarns, so the surface is more like cotton than might otherwise be anticipated. Also, the blend fabric, like cotton fabric, consists of spun yarn, which, as mentioned previously, is more conducive to good adhesion than continuous-filament yarn. Thus, adhesion of both EA/AN and BA/AN copolymers to the blend yarn is apparently good enough that crockfastness ratings are determined by binder mechanical properties.

SURFACE FREE ENERGY ANALYSIS

The following analysis was developed to account for differences in adhesion of the EA/AN and BA/AN copolymers to polyester fabric. Adhesion to cotton was considered also.

A necessary condition for good adhesion is that the adhesive wet the substrate and make molecular contact. The spreading coefficient[1] of an adhesive on a substrate is expressed by the equation

$$S = \gamma_s - \gamma_a - \gamma_{as} \tag{1}$$

where γ_s = surface free energy of solid, γ_a = surface free energy of adhesive, and γ_{as} = interfacial free energy. Spreading occurs when $S \geqslant 0$. It is sometimes incorrectly assumed that an adhesive necessarily spreads on a substrate if $\gamma_a < \gamma_s$. This assumption neglects interfacial free energy, which is usually significant between polymers.[2] A positive spreading coefficient does not guarantee the intimate contact necessary for wetting at the molecular level, but for the purposes of this work, it is assumed that adhesion is likely to be better if S is greater.

Owens and Wendt[3] and Kaelble[4] have developed an equation relating interfacial free energy to surface free energy properties of the two materials in contact:

$$\gamma_{as} = \gamma_s + \gamma_a - 2(\gamma_a^d \gamma_s^d)^{\frac{1}{2}} - 2(\gamma_a^p \gamma_s^p)^{\frac{1}{2}} \tag{2}$$

where the superscripts d and p designate dispersion and polar force components of surface free energy respectively, and $\gamma = \gamma^d + \gamma^p$. The polar term includes both dipole and hydrogen-bonding interactions. Procedures for estimating surface free energies and their components for use in this equation are described in succeeding paragraphs. These procedures are rudimentary, but precise, reliable determination would have required considerable experimental effort in itself and was beyond the ambit of this work. Although estimates are generally not desirable substitutes for experimental values, it is noteworthy in this regard that Krause has found that predictions are more accurate when calculated rather than when experimental values of solubility parameters are used in polymer–polymer compatibility calculations.[5]

Critical surface tension of wetting, γ_c, of copolymers was calculated from the equation

$$\gamma_c = \sum_i v_i(\gamma_c)_i \tag{3}$$

where $(\gamma_c)_i$ = critical surface tension of homopolymer that corresponds to monomer i and v_i = volume fraction of repeat unit i in the random copolymer. This equation was adapted from a similar equation derived by Krause for solubility parameter of random copolymers.[5] Since critical surface tension and solubility parameter are related, use of an analagous equation seemed warranted. Equation 3 is also similar to that of Lee,[6] who used mole fractions instead of volume fractions as weighting factors. Implicit in use of such equations for γ_c is the assumption that surface composition of the copolymer is equal to that of the bulk.

Critical surface tensions of poly(ethyl acrylate), 35 dynes/cm, and polyacrylonitrile, 44 dynes/cm, reported by Lee,[7] and poly(n-butyl acrylate), 31 dynes/cm, reported by Toyama *et al.*[8] were used in Eq. 3. γ_c of the methylolated amide homopolymer was assumed to be 40 dynes/cm.

Calculated critical surface tensions of the copolymers are listed in Table V. They differ little from literature values of the respective acrylate homopolymers because the proportions of acrylonitrile and methylolated amide are small. Drops from a series of liquids with surface tensions ranging from 24–38 dynes/cm were placed on films of the copolymers and contact angles measured in order to determine critical surface tensions.[9] Results were in accord with calculated values.

TABLE V

Components of surface free energy (dynes/cm)[a] of binders and substrates

Polymer	γ^d	γ^p	γ	γ^p/γ
EA/AN	20	16	36	0.44
			(40)	(0.42)
BA/AN	20	13	33	0.38
			(35)	(0.37)
BA	21	10	31	0.33
			(27)	(0.33)
Polyester	38	4	42	0.10
Cellulose	18	46	64	0.72

[a] Values in parentheses determined using method of Owens and Wendt (Ref. 3).

Actually, the true surface free energy of the polymeric adhesive should be used in Eq. 1, not the critical surface tension. The latter is actually an interfacial tension equal to $\gamma_s - \gamma_{sl}$ (assuming $\gamma_s = \gamma_{sv}$), where γ_{sl} is the interfacial free energy between the solid and the liquid that just wets the solid (zero contact angle). For poly(methyl methacrylate) and poly(n-butyl methacrylate), γ_c is essentially equal to the actual surface free energy.[10] Therefore, the equality was assumed to exist also for the acrylate copolymers used in this work.

If the polar fraction of solubility parameter is known, Wu[11] has demonstrated that the polar fraction of surface free energy can be estimated fairly accurately from the equation

$$\gamma^p/\gamma = (\delta^p/\delta)^2. \tag{4}$$

Hoy has calculated nonpolar and polar components of the solubility parameters of poly(ethyl acrylate), poly(butyl acrylate), and polyacrylonitrile.[12] γ^p/γ values calculated from these data and Eq. 4 were used to calculate the polar fraction of surface free energy of the copolymers using Eq. 5

$$\gamma^p/\gamma = \sum_i v_i(\gamma^p/\gamma)_i. \tag{5}$$

γ^p/γ of the copolymers was also determined experimentally using the procedure of Owens and Wendt.[3] This method is simple, but the results are not always accurate.[15] Nonetheless, agreement with values calculated for Eq. 5 was excellent (Table V). Total surface free energies determined using the method of Owens and Wendt were somewhat disparate compared to γ_c values calculated from Eq. 3 and those estimated from measurement of contact angles of a number of liquids. The latter estimates of total surface free energy are believed to be more reliable and were used with γ^p/γ values calculated from Eq. 5 in subsequent calculations of spreading coefficients.

Data for the methylolated amide were not available; its polarity was assumed to be the same as that of acrylonitrile.

For poly(ethylene terephthalate), surface free energy components determined by Owens and Wendt were used[3]; polarity is intermediate between that determined for polyester by Wu[10] and Kaelble.[13]

Components of surface free energy of cotton or cellulose were not available in the literature. They were estimated using the procedure of Owens and Wendt[3] with Luner and Sandell's[14] contact angle data for glycerol, formamide, and water on regenerated cellulose. Agreement was good among values estimated using different pairs, which is not always the case using this procedure.[15] The results were averaged to obtain values shown in Table V.

Critical surface tension of cellulose is about 42 dynes/cm.[14] Good has derived the theoretical limits, $\gamma_s/2 \leqslant \gamma \leqslant \gamma_s$ [16]; γ_c and calculated γ_s, 64 dynes/cm, are consistent with these limits. Also, since $\gamma_c = \phi^2\gamma_s$, where ϕ is the Girifalco–Good parameter,[17] $\phi = 0.81$; Luner and Sandell [14] have shown that Lee's [1] extension of the empirical Hildebrand–Scott equation accurately correlates experimental values of γ_c and solubility parameter of cellulose if $\phi = 0.8$. This is further support that the calculated γ_s of cellulose is reasonably correct.

Calculated components of surface free energy of the polyacrylates, polyester, and cellulose are listed in Table V. Spreading coefficients calculated from Eq. 2 appear in Table VI. For polyester, S is negative for EA/AN copolymer and positive for BA/AN copolymer. Thus, the EA/AN copolymer should not spread on a polyester substrate as well, and adhesion should not be as good. This is borne out experimentally by inferior crockfastness of the EA/AN copolymer on polyester fabric and lower peel strength from Mylar. The lesser propensity of the EA/AN copolymer to spread is a consequence of higher total surface free energy as well as higher interfacial free energy (Tables V and VI) because of a polarity mismatch with polyester.

For cellulose, spreading coefficients are high for all three polyacrylate copolymers. Thus, spreading should be facile and adhesion good. Differences in crockfastness on cotton should be determined principally by mechanical resistance of the binder to rubbing rather than adhesion. This is observed experimentally—crockfastness correlates with tensile properties of binder films.

It is noteworthy that calculated interfacial free energies with cellulose are higher than with polyester. However, the differences in surface free energies of cellulose and the polyacrylates are greater than the interfacial energies, so $S > 0$. In contrast, with polyester, the interfacial free energy with EA/AN copolymer is more than this difference, so $S < 0$. These calulations illustrate well how interfacial free energy is more of a determinant in spreading when individual surface energies are close.

TABLE VI

Interfacial free energy, spreading coefficient, and reversible work of adhesion of polyacrylate copolymers on polyester and cellulose substrates

Adhesive-substrate	γ (dynes/cm)	S (dynes/cm)	W (dynes/cm)
EA/AN-polyester	7	−1	71
BA/AN-polyester	5	4	70
BA-polyester	4	7	69
EA/AN-cellulose	8	20	92
BA/AN-cellulose	10	21	87
BA-cellulose	13	20	82

Reversible work of adhesion, $W = \gamma_a + \gamma_s - \gamma_{as}$, is a measure of attractive forces across an interface, higher values signifying stronger bonds. Wu has shown that spreading coefficient correlates better than work of adhesion with bond strengths determined experimentally.[11] This is also the case in the present work; calculated W (Table VI) is essentially equal for EA/AN and BA/AN copolymers on polyester, but the difference in calculated spreading coefficients is consistent with the experimental results.

The preceding surface energy analysis should not be considered definitive. Rudimentary procedures were used to estimate surface free energies; Eqs. 2–5 are, of course, controvertible on theoretical grounds; the surface of cotton is not the same as regenerated cellulose film, and the surface of Dacron is not the same as Mylar. Nevertheless, agreement between the surface free energy analysis and experimental results is gratifying, and the results appear to be helpful in accounting for the observed differences in adhesion and in understanding how both cohesive and adhesive strengths of pigment-printing binders determine degree of crockfastness on different textile fabrics. Hopefully, similar analyses using more materials with well-defined components of surface free energy will be conducted in the future to corroborate the conclusions drawn.

SUMMARY AND CONCLUSIONS

With cotton, crockfastness of three polyacrylate copolymers correlated with tensile properties of films. A surface energy analysis showed that the binders should spread readily on cotton, and therefore adhesion should be good. In this case, then, mechanical properties of the binder were determinant.

With polyester fabric, crockfastness of an EA/AN copolymer was inferior to that of a BA/AN copolymer, despite superior film tensile properties. Adhesion to Mylar of the EA/AN copolymer was inferior. A surface energy analysis showed that the EA/AN copolymer should not wet polyester as well because of higher surface energy and higher polarity. In this case, then, adhesion was determinant.

In conclusion, therefore, crockfastness of pigment printing binders is dependent upon both mechanical resistance of the pigmented binder to rubbing and adhesion of the binder to fabric. Optimal crockfastness is attained when both properties are maximized.

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