Aspects of Interactions in Complex Polymer Coating Formulations

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ABSTRACT: Acid–base interaction parameters have been measured by inverse gas chromatography for mixed stationary phases of film-forming polymers and pigments. The quantities of adsorbed polymer required fully to coat the pigment surfaces were established, and rheological measurements were used to evaluate the thickness of polymer barriers generated by the adsorption process. Both the barrier thickness and the critical amount of polymer needed to overcoat the pigments were found to be dependent on acid–base interactions. Acid–base considerations also determined the rate of material redistribution when a third component was added to premixtures of two-component polymer/pigment combinations. Time-dependent variations in the surface energies of polymer films were attributed to the component redistribution process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1378–1386, 2000

Key words: acid–base interaction; inverse gas chromatography; adsorbed polymer; surface energies; time dependence

INTRODUCTION

This paper is an elaboration on an earlier study[1] that characterized the acid–base interaction behavior of polymers and pigments intended for use in protective coatings. The importance of the interaction results was demonstrated by relating these to the stability of pigments dispersed in solutions of the polymers involved in the study. Coatings are complex formulations, often combining several polymers and associated solids. A detailed analysis of interactions among the components of such systems remains a desirable but daunting goal. Progress can be made by studying the interaction between combinations of two sol-

ids, relative to solvents used in practical applications. This is the objective of the present work. In stressing the matter of interactions, we recognize the importance of these to a range of properties in polymer systems. That recognition has a substantial history: Early manifestations include the use of Hildebrand's solubility parameters[2] to interpret polymer–solvent states of compatibility.[3–5] Of course, the direct experimental determination of solubility parameter values for polymers poses an inherently intractable problem, a consideration that motivated attempts to adapt the original concept more effectively.[4,5] In spite of these modifications, however, the solubility parameter has only limited value in coping with interactions in polymer systems, notably when nondispersive forces are in play. With the introduction of newer, more powerful analytic techniques, the study of component interactions has taken on new vigor. Of particular interest has become the method of inverse gas chromatography (IGC).[6–8] It is conve-

nient, relatively easily adapted to the needs of academic and industrial laboratories, and capable of furnishing a wide range of data characterizing surface, interface, interphase, and bulk interaction states. The capability of assigning quantitative indexes of acid–base interaction to polymers and to solids used in polymer systems is of particular interest, given the current emphasis placed on acid–base concepts[9–11] as an important tool for the rationalization of performance in such systems. In the present study, acid–base parameters have been determined for two-component combinations of polymers and pigmenting solids. The results have been related to thicknesses of polymer interphases in contact with the selected pigments as determined from rheological measurements. Finally, modeling procedures on industrial practice, contact angle data were used to follow the kinetics of polymer redistribution when a third component is added to a pair brought to equilibrium by premixing. Our intent is to contribute both to a basic understanding of the forces acting within complex polymer combinations and to processes involved in the preparation of protective films.

EXPERIMENTAL

Materials

The polymers and pigments used here were those already described earlier.[1] The polymers, supplied by Nippon Paint Co., were as follows:

NCSC: an acrylic copolymer consisting of styrene, n-butyl methacrylate, n-butyl acrylate, and maleic anhydride, with $M_n = 3000$ and an acid value of 157.

HP: an acrylic copolymer of styrene, methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, and glycidyl methacrylate with $M_n = 3000$, an epoxy value of 90, and an OH value of 90.

ACR: an acrylic copolymer of styrene, ethyl acrylate, methyl methacrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, and methacrylic acid, with $M_n = 21,000$, an acid value of 15 and an OH value of 45.

The particulates were as follows:

R: a rutile (TiO_2) pigment, surface coated by the manufacturer with alumina and zirconia, with a Brunauer–Emmet–Teller (BET) surface area of 11.9 m^2/g, and a density of 4.11 g/mL.

BP: a bare diketo-pyrrolo-pyrol red pigment, with a surface area of 29.0 m^2/g and a density of 1.6 g/mL.

BL: a commercially surface-coated version of BP, with a surface area of 31.0 m^2/g and a density of 1.6 g/mL. The coating composition is unknown.

Procedures

IGC of Mixed Stationary Phases

In ref. 1, standard IGC techniques[5–7] were employed to determine the acid–base interaction constants K_a and K_b for the individual polymers and pigments listed above. The emphasis here is on the evaluation of these constants for pigments with adsorbed polymer at varying pigment/polymer weight ratios, and thus at varying degrees of pigment surface coverage. The pigment coating procedure consisted of adding carefully weighed amounts of pigment to 30 mL aliquots of 1.50 wt % solutions of the polymers in 1:1 (volume) mixtures of p-xylene and ethylethoxy propionate. To achieve dispersion and adsorption, the mixtures were stirred with magnetic stirrers for 24 h at ambient temperature, following which the solids were allowed to settle. Aliquots (5 mL) of clear supernatant solution were withdrawn and evaporated to dryness under vacuum at 60°C. The quantity of adsorbed polymer was calculated from the difference between initial and equilibrium polymer concentrations. The deposited solids were then recovered by filtration, washed with the solvent mixture, and dried to constant weight under the above conditions. Carefully weighed amounts of these solids were then fired in an air oven at 350°C, for 15 min. Preliminary experiments showed that this was suitable for the decomposition/vaporization of the polymer without incurring measurable weight change in the pure pigments. Gravimetric analysis of the fired solids yielded a second value of adsorbed polymer and this agreed generally within 7% with the previous measurement. Averaged values are reported here as the quantity of record. Polymer/pigment mixtures were ground by hand with a mortar and pestle to avoid agglomerates, and then packed directly into previously washed and dried stainless steel columns, 2.4 mm in diameter and 30–40

cm long, to serve as stationary phases in the IGC procedure. Retention data were obtained with a Varian 3400 chromatograph, equipped with ionizing flame and hot wire detectors. Column temperatures were in the range 35–55°C. Prior to collecting retention data, columns were swept with He at 110°C for 24 h. The flow of He carrier gas was controlled at 15 mL/min.

As in our earlier work,[1] the solids were probed by the injection of vapors at extreme dilution, here corresponding to about 2.4×10^{-4} μmol. The vapors used were those of the n-alkanes from nC6 to nC9, and with diethyl ether (DEE), chloroform (CHL), ethyl acetate (EAc), tetrahydrofuran (THF), dichloromethane (DCM), and acetone (AC). The latter group was chosen on the basis of Gutmann's acid–base theory,[11] which assigns electron acceptor (acid) and donor (base) numbers, AN and DN to them. The corrections of Riddle and Fowkes[12] were applied to the AN number in order to overcome the problem of asymmetric units of AN and DN in the original Gutmann tabulation. The corrected value is labeled AN*. Vapor injections were at least in triplicate, with standard deviations from mean values of retention volumes not exceeding 4%. As usual,[1,6] the retention volumes V_n of the alkanes were used to calculate the dispersion contribution to the surface energy of the stationary phases γ_s^d from

$$RT \ln Vn = 2Na(\gamma_1^d)^{1/2}(\gamma_s^d)^{1/2} + c \qquad (1)$$

Here a is the cross-sectional area of the adsorbed vapor molecule, γ_1^d is the dispersion contribution to its surface energy in the liquid state, N is Avogadro's number, R is the gas constant, T the column temperature, and c an integration constant. The procedures developed by Gray,[13] Papirer,[14] and Schultz[15] were applied to obtain experimental values of ΔG^{ab} and ΔH^{ab}, respectively the acid–base contributions to the free energy of adsorption and the enthalpy of adsorption of the vapors on the solids of the stationary phase. The enthalpy values were then used to evaluate K_a and K_b, respectively the acid and base interaction numbers of the solids from

$$\Delta H^{ab}/AN^* = Ka(DN/AN^*) + Kb \qquad (2)$$

Rheological Measurements

The objective here was to evaluate the thickness of the barrier formed by polymer adsorbed on the pigments of this study. The procedure used was similar to that described in earlier work from this laboratory.[16] It was based on the expectation that the relative viscosities of pigment dispersions in standard polymer solutions would follow theoretically prescribed variations with the pigment volume fraction, provided there was no strong interaction between solids and carrier fluids. Accordingly, 30 mL of 10 wt % solutions of the polymers (solvents as specified above) were placed in an earthenware jar, and to these were added measured amounts of solids to represent pigment volume concentrations in the range 5–50%. The mixtures were rotated on a two-roll mill operating at 30 rpm for 24 h, whereupon samples were withdrawn and placed in a Bolin VOR Rheometer at 25.0°C. Viscosities were read over a shear rate range exceeding 3 decades. These were used along with viscosity values for pure polymer solutions to define the relative viscosity η_r. The Maron–Pierce equation[17] was selected as an appropriate statement of the expected interdependence of η_r and the pigment volume fraction ϕ:

$$\eta_r = [1 - \phi/\phi_m]^{-2} \qquad (3)$$

where ϕ_m is the maximum packing factor. This varies from 0.52 for simple cubic packing of solid particles to 0.74 for tetrahedral packing. The exact packing arrangement applying to the present dispersions is not known—hence, a median value of 0.63 was chosen as a reasonable approximation to reality.

Since, in practice, interfacial forces will cause the polymer to adsorb on the pigment particles increasing the effective volume fraction of dispersed solids, strict adherence of data to eq. (3) cannot be expected. Instead, as in ref. 17, eq. (3) is modified to the form

$$[\eta_r]^{-1/2} = [1 - f\phi/\phi_m] \qquad (4)$$

The correction factor f is related to the increment δ of the particle radius due to polymer adsorption and may be regarded as a measure of the adsorbed film thickness,

$$f = [1 + \delta/R]^3 \qquad (5)$$

The effective particle radius R is calculated from the known surface areas and densities of the solids.

Contact Angle Measurements

These data were used to follow the kinetics of material redistribution when a third constituent was added to a premixed pair. The redistribution, or "order-of-addition effect," was expected from the previously documented[1] diverse degrees of acid–base interaction between polymer/pigment pairs, as given by the parameter I_{sp}:

$$Isp = (Ka)_1(Kb)_2 + (Ka)_2(Kb)_1$$
$$- (Ka)_1(Ka)_2 - (Kb)_1(Kb)_2 \quad (6)$$

Here 1 and 2 identify polymer and pigment, respectively. The order-of-addition study was restricted to the systems discussed in the following sections of the paper.

Selected two-component combinations were prepared by premixing polymer and pigment in weight ratios of 45:10, using in this case toluene as solvent for the polymer. Mixing was carried out for 24 h with the equipment noted earlier in this section. A second polymer was then added to the premix, so as to create a three-component system containing equal masses of the polymers, and the system was stirred for an additional 24 h. Films of these compounds were prepared by drawing 2 mL samples of dispersions onto freshly cleaned and dried E-glass slides and drying the films under vacuum at 50°C for 24 h. Contact angle data were collected with a Rame-Hart Goniometer at 25°C, using water, glycerol, and n-decane as contact fluids. Contact angles were monitored for 25 min. and extrapolated to zero contact time to characterize the surface before perturbation by the deposited fluid.[18] An initial datum was obtained on films immediately following the noted drying procedure. Additional contact angle determinations were carried out on specimens that had been aged in air for up to 12 days at 50°C. The experimental data were analyzed according to the quadratic mean convention,[19] to obtain both dispersion and acid-base portions of the film surface energy.

RESULTS AND DISCUSSION

Interaction of Mixed Stationary Phases by IGC

The intent in this portion of the work was to adsorb polymer on pigments so as to achieve both partial and complete coverage of the available surface. Expressed in terms of weight percentages, this amounted to adsorbing polymers in the
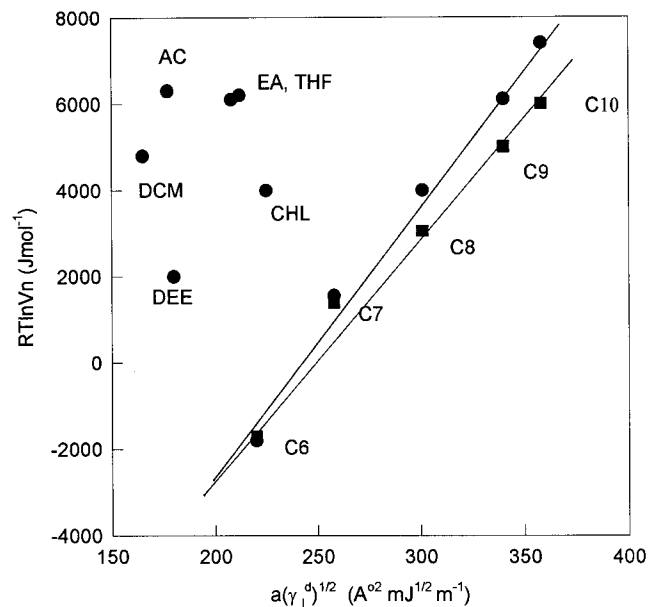
Figure 1 IGC data at 40°C for NCSC on BP, plotted according to eq. 1. NCSC coverage 1 wt % (●) and 4 wt % (■).

range of 0.5–10 wt %, based on the pigment mass. A necessary condition for progress to be made was the applicability of eq. 1 to mixed stationary phases. This condition was met in all cases reported here and is illustrated in Figure 1 for polymer NCSC adsorbed on the organic BP pigment. Partial surface coverage is represented by the data for 1 wt % adsorbed polymer, while coverage near the monolayer is represented at 4 wt % adsorbed polymer. As was the case throughout this work, excellent linear relationships are obtained in Figure 1 for the alkane probes. This makes possible the evaluation of γ_s^d as a function of surface coverage. In the example shown, γ_s^d decreases with surface coverage. This meets expectations since, at sufficiently high levels of adsorbed polymer, the perturbing effect of the underlying surface should disappear, with the surface energy parameter attaining the value for the pure polymer. Evident in the figure is the amphipatic character of the two-component surfaces; acidic probes (CHL, DCM) as well as basic probes (DEE, THF) fall well off the alkane reference line, which represents the interaction due to dispersion, or Lifschitz–van der Waals (LW) forces. As usual, the normal distance from the placement of the polar probes to the corresponding reference line permits an evaluation to be made of ΔG^{ab}, and this datum measured over the defined range of temperatures leads to the enthalpy data needed

Table I   Surface Energy, Interaction Characteristics for Two-Component Systems Based on NCSC Polymer

	γ_s^d (mJ/m^2) at 35°C	K_a	K_b	I_{sp}
Pure NCSC	33.7	0.56	0.29	
Wt % on rutile				
0	58.4	5.9	3.3	−0.70
1.1	49.6	4.8	2.1	
1.8	44.7	4.1	1.6	
3.0	40.7	3.5	1.0	
4.2	40.2	3.1	0.88	
5.1	38.8	2.7	0.71	
7.7	37.5	2.2	0.63	
10.3	36.6	1.7	0.55	
Pure BL	38.2	0.15	0.98	0.23
Wt % on BL				
0.8	36.5	0.29	0.60	
2.1	35.1	0.44	0.42	
3.0	34.4	0.51	0.37	
4.3	34.0	0.53	0.35	
5.1	33.6	0.59	0.31	
8.2	33.7	0.57	0.32	
9.9	33.6	0.55	0.31	
Pure BP	48.0	0.20	0.60	0.12
Wt % on BP				
1.2	47.7	0.52	0.33	
2.4	44.3	0.47	0.37	
3.2	40.1	0.44	0.46	
3.8	37.3	0.44	0.57	
5.0	34.6	0.41	0.36	
8.5	33.9	0.49	0.30	
10.2	33.9	0.51	0.30	

to compute K_a and K_b. Polar probe placement is shown at 1% polymer.

Table I summarizes the results obtained for solids with adsorbed NCSC polymer. Also given in the table are previously published values of the parameters for the pure materials and the I_{sp} datum for each interacting pair. The positive I_{sp} values for NCSC/BL and NCSC/BP indicate the presence of significant acid–base attraction between these pairs, favoring the adsorption of the polymer on the solids. Following the progression of data for NCSC/BL, it may be concluded that at adsorption levels exceeding about 4.5 wt % the surface interaction is essentially equivalent to that of the pure NCSC. The surface concentration of NCSC required fully to obscure the BP surface is somewhat higher, a minimum of 5 wt % of this polymer being required. The difference may reflect the different degrees of acid–base interaction indicated by I_{sp}. In that regard, the results for the NCSC/R pair are particularly interesting. In this case the I_{sp} is negative. No significant acid–base attraction can be postulated, and adsorption may be very restricted. Indeed, even at the highest polymer concentration studied (10.3 wt % polymer), the surface energy, K_a, and K_b parameters are well removed from those of the pure polymer. A likely explanation is the persistence of bare regions of pigment, with their surface characteristics affecting the measured data. An alternative is the posit of a highly perturbed polymer interphase. The former, however, appears to be the more logical choice.

The possible link between I_{sp} and the critical adsorbed mass of polymer, identified as A_{crit}, is further questioned by the data in Table II, which summarize values of A_{crit}, and of γ_s^d, K_a and K_b at the critical point for all the pigment/polymer combinations of this work. Reference1 again has been used to provide corresponding parameter values for the pure materials. Finite values of A_{crit} were

Table II   Adsorption and Interaction Parameters at Full Coverage of Pigment Substrates (Data Refer to Average $T = 35$°C)

Polymer/Pigment Pair	I_{sp}	A_{crit} (wt %)	γ_s^d (mJ/m^2)	K_a	K_b
NCSC/R	−0.70	⩾10.3	—	—	—
NCSC/BL	0.23	4.3	33.6	0.59	0.31
NCSC/BP	0.12	5.0	34.6	0.41	0.36
HP/R	−0.20	⩾10	—	—	—
HP/BL	0.14	5.0	32.0	0.58	0.49
HP/BP	0.06	6.0	31.8	0.55	0.48
ACR/R	−0.40	⩾10.3	—	—	—
ACR/BL	0.10	5.5	34.7	0.42	0.30
ACR/BP	0.05	7.0	34.6	0.40	0.32
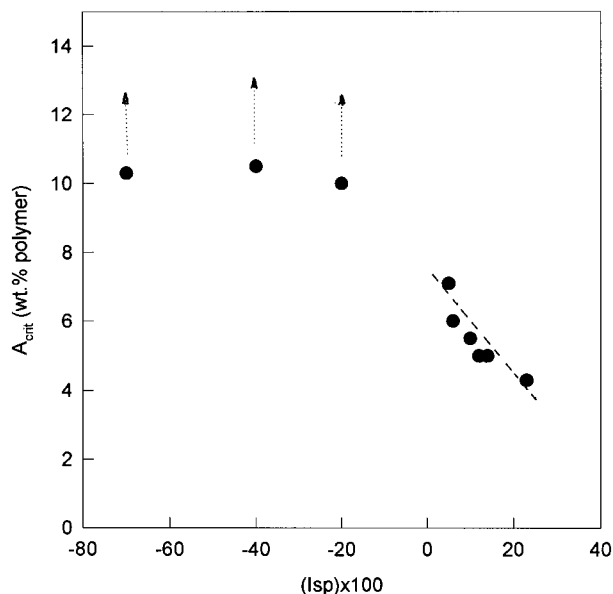
Figure 2 Apparent relationship between critical adsorbed mass of polymer and acid-base interaction parameter I_{sp}. Systems are NCSC on rutile, BL, and BP substrates.

obtained for each of the pigment/polymer pairs with positive I_{sp}, while the A_{crit} values remained indefinite for each of the pairs using rutile, where the Isp was negative. The implied correlation is substantiated in Figure 2. Here, results for positive values of I_{sp} follow an apparent inverse linear relationship. Thus, acid–base interaction at the polymer/solid interface defines the quantity of polymer needed to obscure the underlying substrate and produce a surface layer of unperturbed polymer. In the case of rutile, the LW forces in play appear inadequate to produce adsorbed polymer layers sufficiently thick and/or uniform to overcome the contributing effects of the pigment to surface energy, and acid–base interaction values. Additional information on this is given by the rheological data discussed below.

Barrier Characteristics from Rheological Data

The viscosity/shear rate relationship of pigments dispersed in the polymer solutions differentiated between the behavior of rutile and organic pigment dispersions. In the former case, the nearly Newtonian behavior of pure polymer solutions was maintained for all pigment concentrations. In contrast, as illustrated in Figure 3 for the NCSC/BP system, dispersions of organic pigments in the three polymers displayed increas-

ingly shear-thinning behavior. It may be assumed, therefore, that little significant adsorption took place in the polymer–rutile systems, their Newtonian viscosities increasing with the pigment concentration according to expectations arising from expressions such as eq. (3). Where the organic pigments were involved, however, significant adsorption appears to be the cause of the increasingly non-Newtonian behavior documented in the figure. Accordingly, deviation from eq. (3) is to be expected. Again, using the NCSC polymer as the demonstration vehicle, confirmation is noted in Figure 4, showing the variation of relative viscosity vs pigment volume fraction. The strong deviation from the Maron–Pierce equation of organic pigment dispersions contrasts with the behavior of rutile dispersions, where adherence to the behavior predicted by the equation is quite good. The deviations from eq. (3) noted in the case of polymer/organic solid systems, call for the application of the modified Maron–Pierce equation, leading to the determination of the barrier thickness parameter δ. This is given in Table III.

The apparent barrier thicknesses for polymers on solids BL and BP are near and above 10 nm. Those for the rutile pigment fall below 3 nm. Again, a clear indication is given that acid–base interactions affect the configuration of adsorbed polymers, as was noted already in considerations
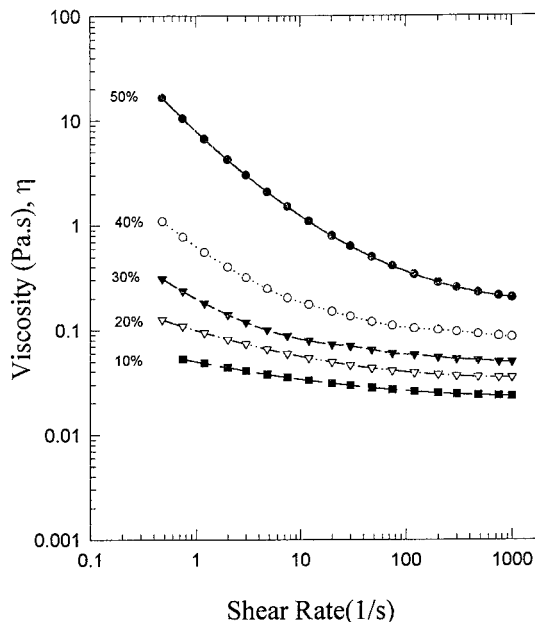
Figure 3 Viscosity–shear rate dependence of dispersions of NCSC polymer and BP pigment, at indicated concentrations.
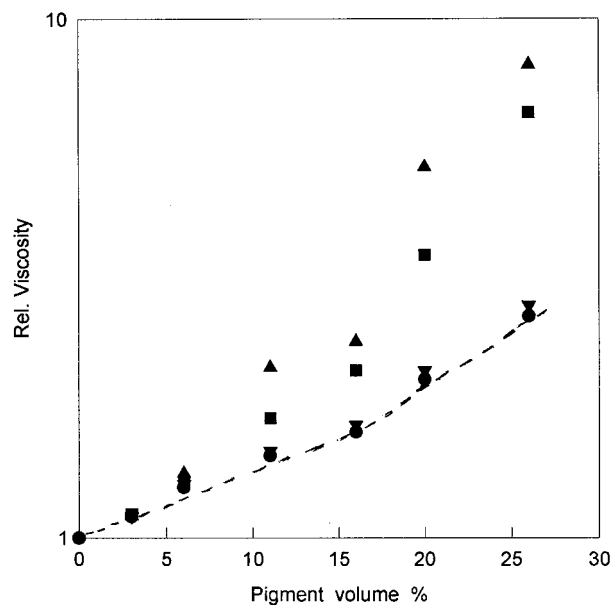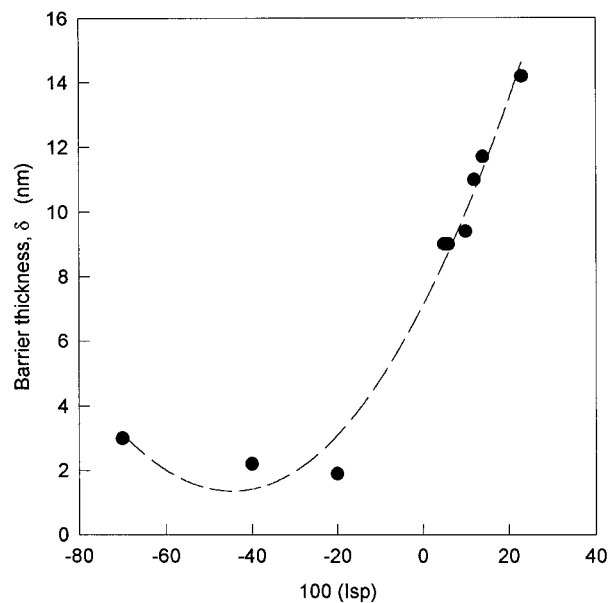
Figure 4   Showing Maron–Pierce (●) and experimental values of relative viscosity vs pigment volume relationship for dispersions of pigments in NCSC polymer. Pigments are rutile (▼), BL (▲), and BP (■).

Figure 5   Barrier thickness of adsorbed polymers on pigments as function of acid–base interaction.

of the stability of pigment dispersions.[1] Figure 5 supports the suggestion, in showing a substantial dependence of δ on I_{sp}. However, although the correlation coefficient of 0.966 for the third-order regression curve shown is very good, the indicated correlation must be viewed with reservation. A full evaluation of the interaction balance in systems of the type considered here should evaluate polymer/solvent and pigment/solvent interactions, in addition to the polymer/pigment forces taken into account. Since no data for the former two are available, Figure 5 can offer no more than an approximate account of the interdependence.

Table III   Barrier Thickness Parameter for Polymer/Pigment Pairs

System	Barrier Parameter δ (nm)
NCSC/R	2.7
NCSC/BL	14.2
NCSC/BP	11.0
HP/R	1.9
HP/BL	11.7
HP/BP	9.0
ACR/R	2.2
ACR/BL	9.4
ACR/BP	9.0

Moreover, the apparent linearity of the plot at I_{sp} > 0 cannot extend indefinitely to higher values of the interaction parameter. This follows because, as shown in earlier publications,[1,16] at very high I_{sp}, indicative of very strong acid–base coupling across the interface, the polymer chain would tend to collapse and adhere strongly to the substrate. Thus, δ would go through a maximum, corresponding to the adsorbed polymer chain configuration marking maximum dispersion stability.

Contact Angles and Order-of-Addition Effect

This portion of the work was restricted to the NCSC and HP polymers and to the organic BL and BP solids. In detail, the following three-component systems were studied: NCSC/BP + HP, HP/BP + NCSC, NCSC/BL + HP, and HP/BL + NCSC. Premixed pairs are noted first, with the third component following. A summary of the surface energy data is reported in Table IV. If only the total surface energies (γ_s) were available, the conclusion could be reached that the order of addition exerted little influence on the initial surface properties of the dried film and that these properties were unchanged over the 296 h aging period. Both the dispersion and more particularly the polar (acid–base) components of the surface energy challenge such a conclusion. Focusing on systems with BP as the substrate, the addition of

Table IV   Order-of-Addition Effect: Summary of Initial and Time-Variant Surface Energy Data

Polymer	γ^d (mJ/m^2)	γ^p (mJ/m^2)	γ_s (mJ/m^2)
NCSC	28.3	6.1	34.4
HP	24.1	12.1	36.3
NCSC/BP + HP			
Initial	28.2	8.7	36.9
24 h	26.2	10.5	36.7
48	25.5	11.0	36.5
72	24.4	11.6	36.0
148	23.4	11.9	35.3
296	23.3	12.1	35.3
HP/BP + NCSC			
Initial	26.6	10.3	36.9
6 h	26.1	11.1	36.9
12	25.7	11.6	37.1
24	25.5	11.7	37.2
48	24.8	12.0	36.8
72	24.3	12.4	36.7
148	24.2	12.2	36.4
296	24.0	12.4	36.2
NCSC/BL + HP			
Initial	28.3	7.4	35.7
24 h	26.1	9.8	35.9
48	25.6	10.0	35.6
72	25.2	10.4	35.6
148	24.5	11.3	35.8
296	24.1	11.5	35.6
HP/BL + NCSC			
Initial	27.9	10.3	38.2
24 h	25.9	10.7	36.6
48	25.4	11.2	36.6
72	25.1	11.7	36.8
148	25.1	11.4	36.5
296	25.0	11.3	36.3

polymer HP to the NCSC premix creates a substantial "shock," the polar surface energy rising by about 50% over a 3–4 day period. The reverse procedure of adding NCSC to the HP/BP premix causes a 20% increase in γ^p, with a more rapid attainment of equilibrium. The equilibrium value of 12.1 mJ/m^2 is identical to that of polymer HP, indicating that the film surface is predominantly populated by chains of this polymer. As a result, chains of NCSC polymer would be preferentially located in the body of the film and in the interface of the BP substrate. A rationalization on the basis of the relevant I_{sp} parameters is indicated (NCSC/BP = 0.12; HP/BP = 0.06). These favor the NCSC/BP pairing by a ratio of 2.0. The NCSC/BP interface therefore would appear to be relatively stable, the more weakly interacting HP

polymer slowly displacing some of the preadsorbed NCSC to reach an equilibrium in which NCSC still predominates at the pigment surface. The replacement of preadsorbed HP by NCSC is more rapid, responding to the greater thermodynamic forces active in this case. Equilibrium here is attained within the first 24 h of aging.

Systems using BL pigment represent a different case, the relevant I_{sp} values being in the ratio of 1.6 (NCSC/BL = 0.23; HP/BL = 0.14). Evidently, both NCSC and HP are more strongly anchored to the BL surface than to BP, but the drive for displacement of one polymer by the other is reduced. This appears to affect the kinetics of the displacement process. The displacement process in NCSC/BL + HP is very attenuated, a steady state barely evident within the time limits of the experiment. The reverse case is somewhat more rapid. The I_{sp} data suggest that, at equilibrium, the film surface should again have a predominance of HP polymer chains, but less so than in compositions involving BP. Thus, the apparent equilibrium value $\gamma^p \sim 11.4$ mJ/m^2, below that of the pure HP, is fully consistent with expectations.

It is reasonable to conclude that the order of addition of constituents in a complex film-forming formulation will exert a significant effect on initial surface, interface, and interphase properties, and will give rise to time-dependent changes in these characteristics as thermodynamic equilibria are sought and attained. Consequently, time-dependent changes may be expected in film properties related to the noted surface and interface effects. Finally, we note again that the component rearrangements taking place at and near the surfaces of these compounds would not have been detected by measurements solely of the total surface energy. A justification may be found therein for the convention, not universally accepted,[20] of dividing the surface energy into its dispersive and nondispersive components.

CONCLUSION

The following may be concluded from the reported work:

- IGC has been applied successfully to two-component stationary phases, based on polymer/pigment mixtures typical of film-forming systems. Acid–base interaction

constants and dispersive components of the surface energy were obtained for a range of polymer/pigment compositions. It was found that the quantity of polymer required fully to cover the available pigment surface varied inversely with the value of the interaction parameter.

- Rheological data were used to compute the thickness of barrier films formed by the polymers adsorbed on the pigments of this work. A tentative correlation was drawn linking barrier thickness with the acid-base interaction parameter. Caution was indicated, however, since the correlation failed to take in account contributions arising from interactions involving the solvents of the system, and was limited by the range of acid–base interactions generated by the materials under study.

- Contact angle measurements have been conducted on films prepared by varying order of component additions. Surface energies calculated from the data were monitored over significant times of film aging. Dispersion, and notably acid–base components of surface energies, were found to vary significantly within these times. The variations were attributed to thermodynamic (acid–base) forces that mandated component displacements at the substrate during times required to attain equilibria. It may be expected that film properties dependent on surface, interface, and interphase compositions will display variations over similar periods.

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