Adsorption at the Solution-Solid Interface: Alkyd Resin on TiO_2 Pigment

R. JANARDHAN, P. H. GEDAM, and P. S. SAMPATH KUMARAN,* *Organic Coatings and Polymer Division,* and R. NARASIMHA and SAJID HUSSAIN, *Analytical Division, Regional Research Laboratory, Hyderabad 500007, India*

Synopsis

Gel permeation chromatography results obtained from the adsorption of alkyd from different solutions on anatase TiO_2 surfaces are reported, and the influences of the solvent–resin interactions in the adsorption process are discussed, covering the thickness of the adsorbed layer, the type of molecular weight species adsorbed, and its dependence on the concentration of the solution. Resin–pigment interaction was found to be influenced by the type of solvents used.

INTRODUCTION

The phenomenon of adsorption of resin on the pigment surfaces plays an important role in the dispersion of pigment particles in the resin solution. The extent of adsorption and thickness of the adsorbed layer determine the shelf-life, the stability, and the performance of a coating.

Several workers[1-6] have studied the adsorption of different polymer molecules on a number of pigment particles. However, the adsorption of oil-modified polyester resin (alkyd resin) on TiO_2 has not been studied so extensively. Rothstein[7] studied the adsorption of alkyd resins of various fatty acids (drying and nondrying) in different solvents on anatase TiO_2, phthalocyanine blue and silica, and found that the amount of adsorbed resin decreased with increased solubility in the solution and the thickness of the adsorbed resin increased with the increase in fatty acid content of the alkyd resin. Rowland et al.[8] reported that, even though the amount adsorbed was almost tripled from the best to the poor solvent, the thickness was found constant due to the formation of compact layer of the adsorbed material. Doorgeest[9] explained the adsorption of alkyd on the pigment particles on the basis of acid and hydroxy numbers of the resin as its molecules possess pendant (—COOH) and (—OH) groups. Felter and Ray[10] used gel permeation chromatography (GPC) for monitoring adsorption process to get detailed information of the adsorbed layers and the concentration dependence on the type of molecular species adsorbed. Adsorption from relatively concentrated solutions was studied by a few workers.[11-13] They found that the adsorption isotherm starts declining after attaining a maximum, which they attributed to the migration of solvent molecules from the resin solution and their getting entrapped in the coils and loops of the adsorbed resin. However, Sprangers et al.[14] attributed this decline

*To whom all the correspondence should be addressed.

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to the adsorption of lower molecular weight species of the resin in the relatively concentrated solution.

The extent of adsorption of polymer on the pigment particles and the thickness of such polymeric chains anchored on the surface of pigment particles by intermolecular attractive forces depend on the combined effect of pigment–binder, pigment–solvent, and binder–solvent interactions, which are likely to help in getting a stable dispersion. For a particular pigment–binder system, the pigment–solvent and binder–solvent interactions play a major role, and choice of apolar system of solvents having least affinity for the pigment, will restrict this phenomena mainly to binder–solvent interactions.

The literature cited above reveals that solvent plays an important role in the adsorption and dispersion process, and there is a need for a detailed study on this aspect. The subject matter of the present study is to investigate the effect of individual solvent and their blends on the adsorption of 66% linseed oil–glycerol–phthalate alkyd on anatase TiO_2 and relate the amount adsorbed and hence stability of the dispersion to the solvent–binder interaction parameter.

EXPERIMENTAL

Materials

Pigment

Anatase TiO_2 with the specific area of 12 m^2/g measured by BET, was used. Specific gravity was 3.84 g/cc and the particle size distribution 50% of the particles with an average diameter of 0.54 μm.

Solvents

Analytical reagent grade benzene (δ = 9.15), xylene (δ = 8.80), methyl ethyl ketone (δ = 9.27), ethyl acetate (δ = 9.10), cyclohexanone (δ = 9.88), cyclohexane (δ = 8.18), and distilled mineral spirit (155–157°C) (δ = 7.82) were used.

Solvent Blends

Blends containing xylene and mineral spirit in 25:75 (δ = 8.55), 50:50 (δ = 8.31), and 75:25 (δ = 8.06) (v/v) proportions were used.

Alkyd Resin

Linseed glycerol phthalate long oil alkyd prepared by the monoglyceride process had the following characteristics: acid value 6.8; hydroxyl value 35.2.

Gel Permeation Chromatography

GPC experiments were carried out in Waters Associates Model ALC/GPC 204. The separation columns were of the μ-Styragel by Waters Associates. The columns of 1000, 500, 500, and 100 Å were connected in a series for better

separation. A 13-min injection time at a flow rate of 1.5 mL/min was used in all the sample analyses. Calibration was made by using polypropylene glycol supplied by Waters Associates.

Methods

Selection of Solvent System

Solution viscosities were measured using Ubbelhode capillary viscometer and AVS/N system for automatic recording of flow time to an accuracy of 0.01 of a second. The intrinsic viscosity $[\eta]$ of the resin in a given solvent was obtained using the equation

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C}$$

where η_{sp} = specific viscosity, C = concentration of resin solution (dL). Selection of a solvent was done by plotting $[\eta]$ of resin in solution vs. solubility parameter (δ) of solvents used (Fig. 1). Among the solvents chosen, resin exhibits highest interaction with benzene, moderate in xylene, and lowest in mineral spirit, and the latter two were selected for the present study as they are commonly used solvents for alkyd resin in industry and benzene for comparison. The other parameters for the three selected solvents are listed in Table I.

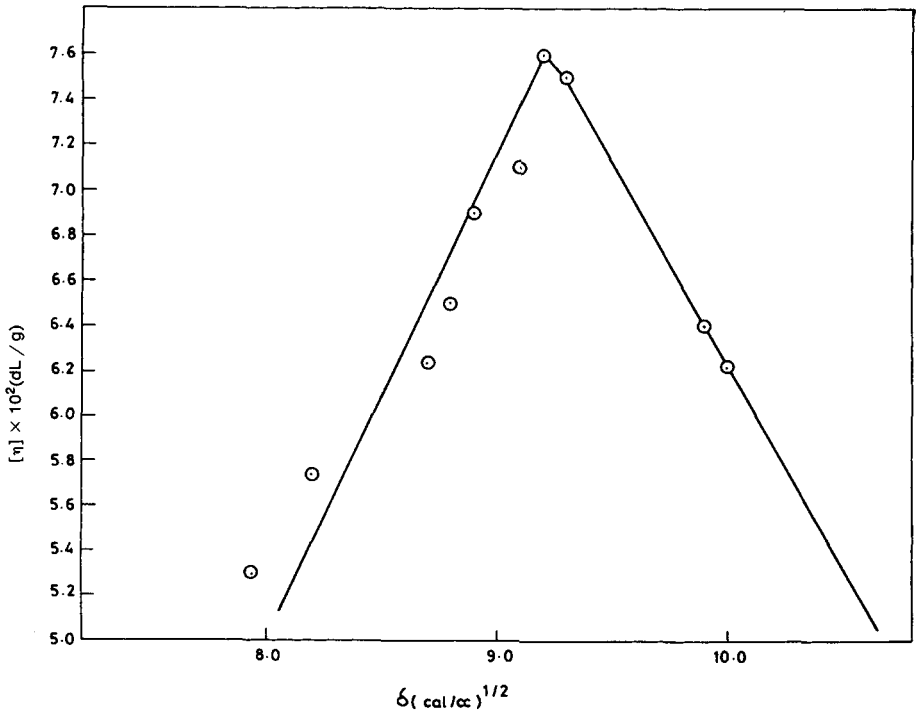

Fig. 1. Intrinsic viscosity vs. solubility parameter of solvents (δ).

TABLE I
Properties of the Solvents

Solvent	Solubility parameter (δ) $(cal/cc)^{1/2}$	Partial solubility parameter			Dielectric constant[c]
		δ_d	δ_p	δ_h	
Mineral spirit	7.82	7.82	0	0[a]	2.014
Xylene	8.80	8.70	0.3	0.7[b]	2.284
Benzene	9.15	8.95	0.5	1.0[b]	2.270

[a] Khaja Mohammed Ali Shareef, Ph.D. thesis, Osmania University, 1985.
[b] C. M. Hansen, *J. Paint Technol.* **50** (640), 86 (1978).
[c] Dielectric constant was measured using Verlustfaktor–McBbrucke fur kondensatoren instrument.

Fractionation of Alkyd Resin

Fractionation was carried out by the fractional precipitation method using dilute solutions of alkyd resin in toluene and anhydrous methanol as precipitant at constant temperature. Four fractions were collected and characterized for their molecular weight averages by GPC method. The molecular weights are listed in Table II along with that of alkyd resin.

Determination of Resin–Solvent Interaction Parameters (χ)

The magnitude of resin-solvent interaction parameter (χ) in these three selected solvents were obtained using alkyd fractions, from the plot $[\eta]/\bar{M}_w^{1/2}$ vs. $\bar{M}_w^{1/2}$ using the Stockmayer–Fixman equation (Fig. 2)

$$[\eta]/\bar{M}_w^{1/2} = K_\theta + 0.51\phi B\bar{M}_w^{1/2}$$

where K_θ and B are the short- and long-range interaction parameters and ϕ is a universal constant (2.87×10^2). The solute–solvent interaction parameter (χ) was obtained from B:

$$B = \frac{2\bar{\nu}^2(0.5 - \chi)}{NV_1}$$

The symbols $\bar{\nu}$, N, and V_1 represent partial molar specific volume, Avagadro's number, and molar volume, respectively. The (χ) values for the three solvents are listed in Table III along with $[\eta]$ of the resin in them.

TABLE II
Molecular Weight Averages for Alkyd Resin and Its Fractions

Alkyd resin	$\bar{M}_n$	$\bar{M}_w$	Dispersivity
Original	1,987	4,430	2.22
Fraction I	11,199	15,384	1.37
Fraction II	10,199	14,884	1.45
Fraction III	7,770	12,544	1.58
Fraction IV	5,860	8,100	1.38

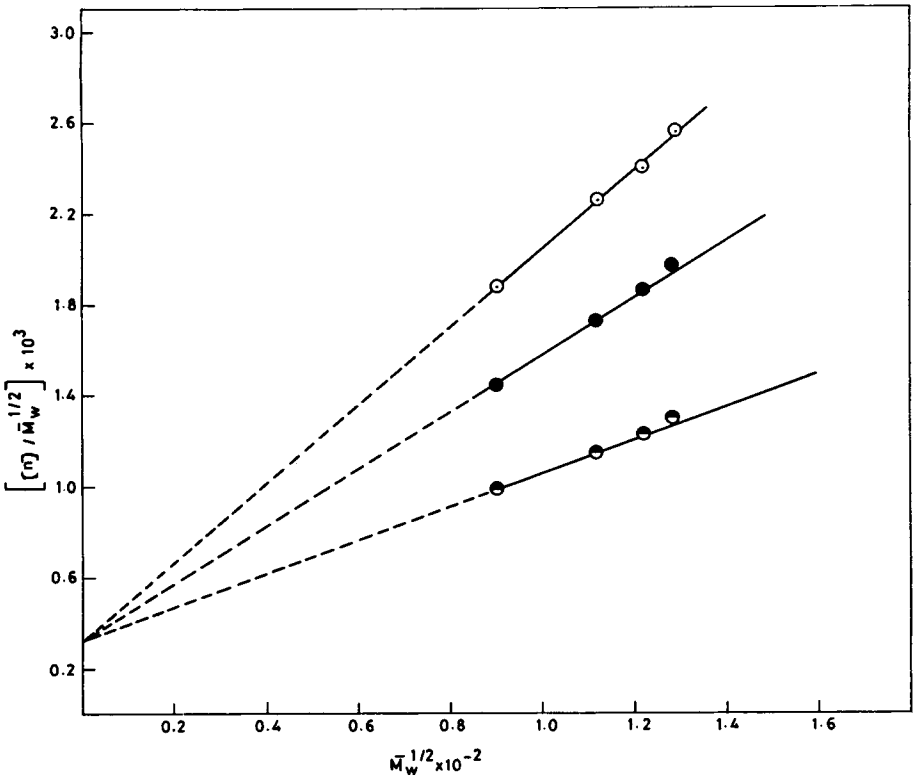

Fig. 2. Stockmayer–Fixman plot for alkyd fractions: (◓) mineral spirit; (●) xylene; (⊙) benzene.

Determination of Resin Adsorption

The time required for attaining equilibrium and the amount of resin adsorbed were determined as follows: The alkyd resin solution of known concentrations, ranging from 0.1 to 10% (w/v), were prepared in the chosen solvents. To 5 g of TiO_2 (previously conditioned at 100°C for 24h and stored over anhydrous $CaCl_2$ in a vacuum descicator) taken in a conical flask, 50 mL of each of the solution were added. The flasks were stoppered and gently swirled for 48 h, maintaining them at a constant temperature of 30°C. The contents of the flasks were centrifuged in a refrigerated (4°C) high speed centrifuge (6000 rpm), and the clear supernatant solution was analyzed by GPC for the amount of unadsorbed resin present in it. This was achieved by

TABLE III
Binder–Solvent Interaction Parameters

Resin	Solvent	$[\eta]$	(χ)
Alkyd	Mineral spirit	0.0539	0.456
	Xylene	0.0682	0.411
	Benzene	0.0782	0.406

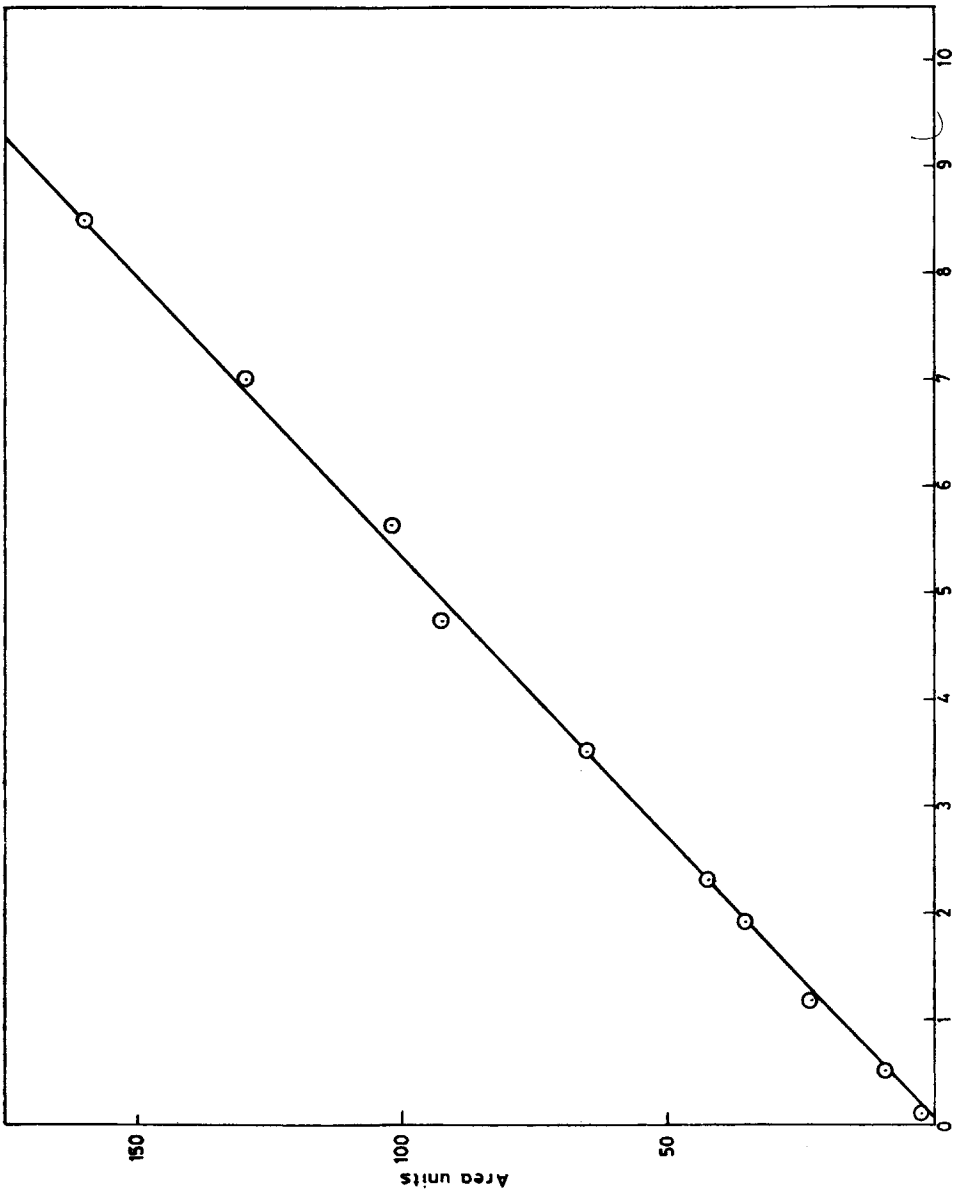

Fig. 3. GPC peak areas vs. resin concentration.

using a calibration graph (Fig. 3) involving area under the GPC Chromatogram versus concentration of the resin. The amount adsorbed was obtained by the difference in the concentration of solution before and after each adsorption experiment. As the determination of polymer concentration from GPC elution curves depends strongly on the accuracy of the injection volume, extreme care was taken in controlling the injection volume.

The amount of resin adsorbed per gram of the pigment was calculated from the relation:

$$A = \frac{500(C_0 - C_e)}{W}$$

where A is the adsorption (mg resin/g adsorbent). C_0 and C_e are the initial and final concentrations of the solutions g/ 100 mL), respectively, W is the weight (g) of adsorbent used.

The time required to obtain equilibrium concentration was found to be 24 h. However, in all experiments, the resin solutions were allowed to be in contact with pigment particles for 48 h and then supernatant solutions were separated and analyzed by GPC. Amounts of resin adsorbed per gram of the pigment (mg/g) were plotted against equilibrium concentrations, and the results for the three different solvents are shown in Figure 4.

The thickness of the adsorbed resin was calculated using Rehacek's methods,[11] which deals with adsorption from relatively concentrated solutions. The amount of resin adsorbed is calculated from the intercept with the ordinate and the concentration of adsorbed layer from the intercept with the abscissa (Fig. 4). Amount of resin adsorbed, concentration of the adsorbed layer, and thickness of the adsorbed layers in nm are given in Table IV, and the plots of χ values against the amounts (mg/gm) and thickness of resin adsorbed are given in Figure 5.

Molecular weight distribution of resin adsorbed from dilute and concentrated alkyd solutions on TiO_2 are given in Tables V–VII. The percentages of each molecular weight species present in the original resin and in the adsorbed layer were calculated and are given in Figures 6–8.

Studies with Solvent Blends

Blends containing xylene and mineral spirit in the ratio of 25 : 75, 50 : 50 and 75 : 25 (v/v) were used for preparing solutions of alkyd resin at only one concentration, viz., 2.5 g of resin per 100 mL solvent blend, as the adsorption of the resin attains maximum at this concentration for the individual solvent systems. Adsorption studies were carried out as decribed above with these blends, using 50 mL of the solution and 5 g of pigment. The supernatant solutions after equilibration for 48 h were analyzed by GPC. The amounts adsorbed (mg/g) of the resin were plotted against composition/solubility parameter of the solvents and their blends, and the results are given in Figure 9. The molecular weight distribution and the percentage of each molecular species adsorbed are given in Table VIII and Figure 10 respectively.

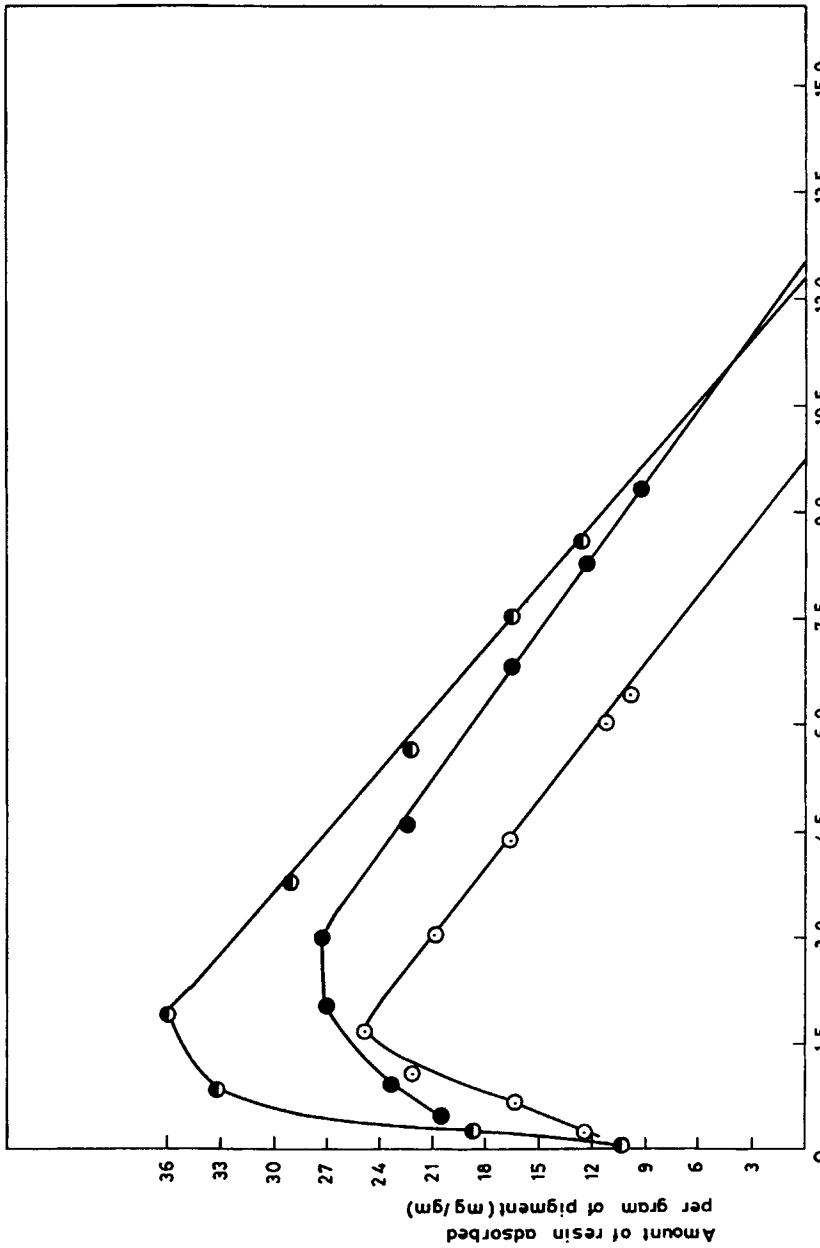

Fig. 4. Adsorption isotherms for alkyd on anatase TiO_2: (◐) mineral spirit; (●) xylene; (○) benzene.

TABLE IV
Thickness of the Adsorbed Layer of Alkyd Resin on TiO_2 Pigment

Solvent	Adsorption (mg alkyd resin/s pigment)	Concentration of the adsorbed layer (g/100 mL)	Thickness of the adsorbed layer (nm)
Mineral spirit	42.1	12.20	28.6
Xylene	35.4	12.75	23.1
Benzene	30.00	9.67	25.8

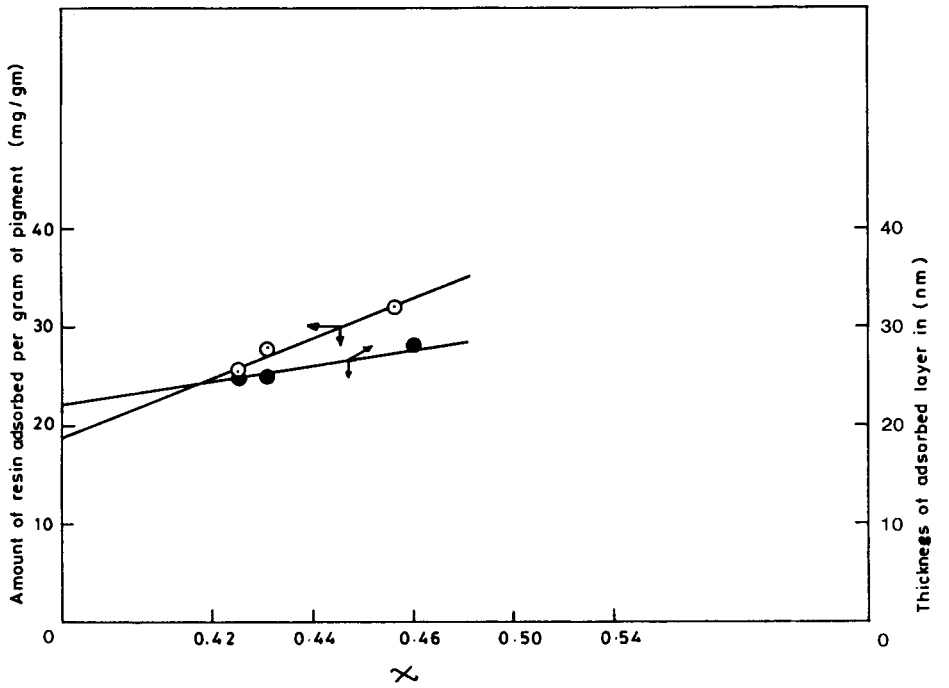

Fig. 5. Amount of resin adsorbed and thickness of adsorbed layer vs. χ (resin solvent interaction parameter).

TABLE V
MWD Averages along the Adsorption Isotherm (Mineral Spirit)[a]

Soln concn (g/100 mL)	$\bar{M}_{wo} \times 10^{-3}$	$\bar{M}_{no} \times 10^{-3}$	$\bar{M}_{ws} \times 10^{-3}$	$\bar{M}_{ns} \times 10^{-3}$	$\bar{M}_{wa} \times 10^{-3}$	$\bar{M}_{na} \times 10^{-3}$	$\bar{M}_{wa}/\bar{M}_{na}$
—	4.43	1.98	—	—	—	—	2.22[b]
0.25			0.86	0.84	6.62	5.63	1.17
0.75			1.92	1.36	6.53	5.52	1.18
0.85			2.98	1.69	6.50	5.59	1.16
2.60			2.44	4.55	6.38	5.12	1.24
3.87			4.13	2.33	6.26	5.09	1.22
7.50			4.47	2.46	6.24	5.22	1.19

[a] $\bar{M}_w$ and $\bar{M}_n$ refer to weight average molecular weight and number average molecular weight, respectively. The subscripts o, s, and a refer to the initial alkyd, the alkyd in supernatant after adsorption, and the adsorbed layer of alkyd, respectively.

[b] $\bar{M}_{wo}/\bar{M}_{no}$.

TABLE VI
MWD Averages along the Adsorption Isotherm (Xylene)[a]

Soln concn (g/100 mL)	$\bar{M}_{wo} \times 10^{-3}$	$\bar{M}_{no} \times 10^{-3}$	$\bar{M}_{ws} \times 10^{-3}$	$\bar{M}_{ns} \times 10^{-3}$	$\bar{M}_{wa} \times 10^{-3}$	$\bar{M}_{na} \times 10^{-3}$	$\bar{M}_{wa}/\bar{M}_{na}$
—	4.43	1.98	—	—	—	—	2.22[b]
0.47			3.89	2.15	7.15	6.15	1.16
0.90			3.18	1.77	8.09	7.68	1.05
1.55			2.85	2.10	8.37	8.17	1.02
2.05			3.95	2.45	7.51	5.61	1.33
4.60			4.20	3.45	6.77	5.97	1.13
6.85			4.61	2.50	6.92	5.68	1.21
8.35			4.89	3.80	6.64	6.00	1.10
9.30			4.95	4.02	6.25	5.98	1.04

[a] $\bar{M}_w$ and $\bar{M}_n$ refer to weight average molecular weight and number average molecular weight, respectively. The subscripts o, s, and a refer to the initial alkyd, the alkyd in supernatant after adsorption, and the adsorbed layer of alkyd, respectively.
[b] $\bar{M}_{wo}/\bar{M}_{no}$.

TABLE VII
MWD Averages along the Adsorption Isotherm (Benzene)[a]

Soln concn (g/100 mL)	$\bar{M}_{wo} \times 10^{-3}$	$\bar{M}_{no} \times 10^{-3}$	$\bar{M}_{ws} \times 10^{-3}$	$\bar{M}_{ns} \times 10^{-3}$	$\bar{M}_{wa} \times 10^{-3}$	$\bar{M}_{na} \times 10^{-3}$	$\bar{M}_{wa}/\bar{M}_{na}$
—	4.43	1.98	—	—	—	—	2.22[b]
0.05			1.25	0.85	8.00	6.52	1.22
0.20			1.03	0.62	8.73	7.92	1.10
0.45			1.01	0.71	8.90	8.35	1.06
0.65			0.98	0.64	9.53	9.42	1.01
1.05			1.18	0.91	8.57	8.03	1.06
1.65			2.80	1.60	7.76	5.62	1.38
3.10			3.20	2.45	6.61	5.71	1.15
4.35			3.68	2.82	6.33	5.61	1.12
5.98			4.25	4.01	5.85	5.02	1.16
6.17			4.34	3.89	5.27	4.72	1.11

[a] $\bar{M}_w$ and $\bar{M}_n$ refer to weight average molecular weight and number average molecular weight, respectively. The subscripts o, s, and a refer to the initial alkyd, the alkyd in supernatant after adsorption, and the adsorbed layer of alkyd, respectively.
[b] $\bar{M}_{wo}/\bar{M}_{no}$.

RESULTS AND DISCUSSION

It can be seen from the plots given in Figure 4 that in all the chosen solvents, after a steep initial rise, the adsorption isotherm starts declining after attaining the maximum at an approximate equilibrium concentration of 2.5 g/100 mL. The steep rise in isotherm is attributed to the stronger affinity of resin molecule to pigment and the decline in the isotherm to the coadsorption of resin and solvents, resulting in a solvated adsorbed layer. The amount of resin adsorbed in mineral spirit is more when compared with those adsorbed in xylene and benzene media (Fig. 5), indicating lesser resin–solvent interaction in the former case, thus enabling more resin to be deposited on the pigment particles. The interaction parameter (χ) between mineral spirit and alkyd (0.456) and low dielectric constant of the solvent explain this finding. In

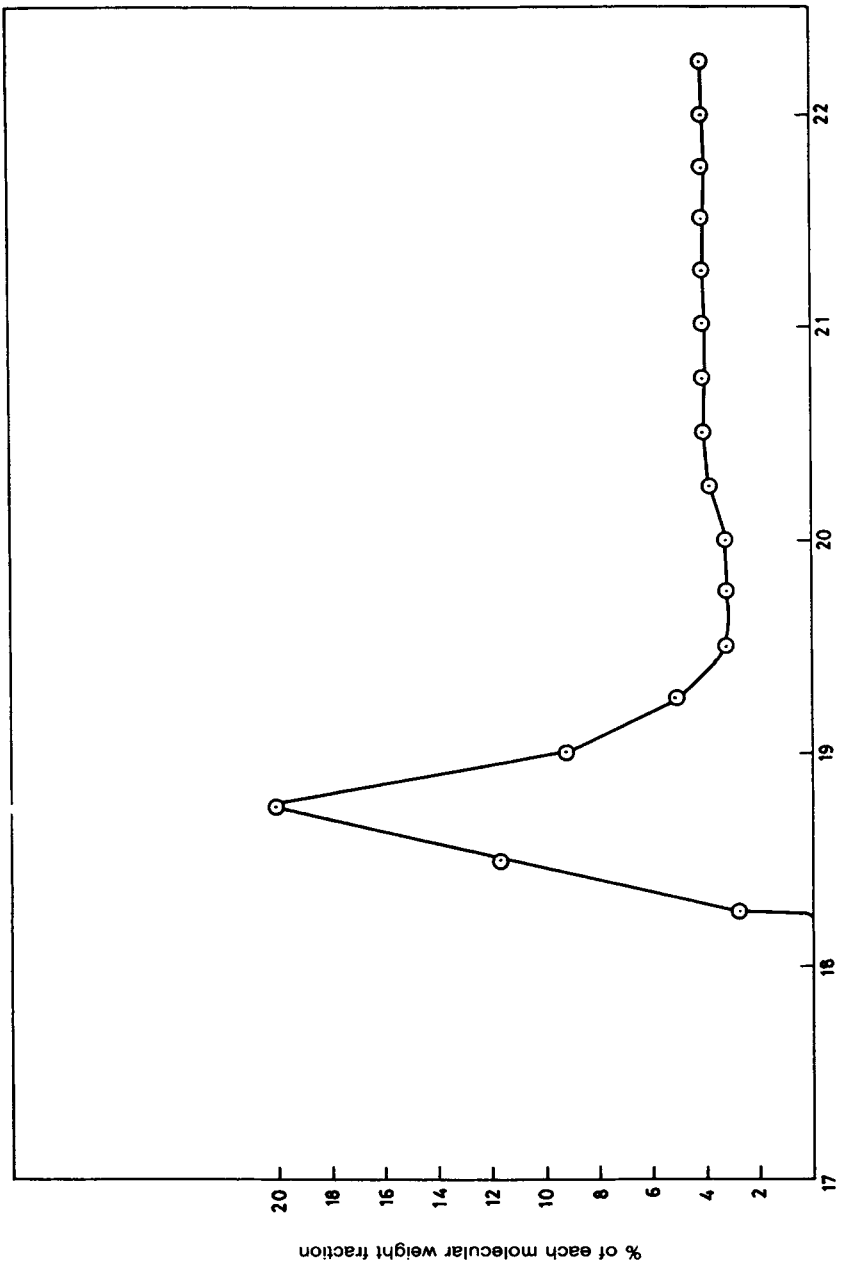

Fig. 6. Molecular weight distribution of initial alkyd resin.

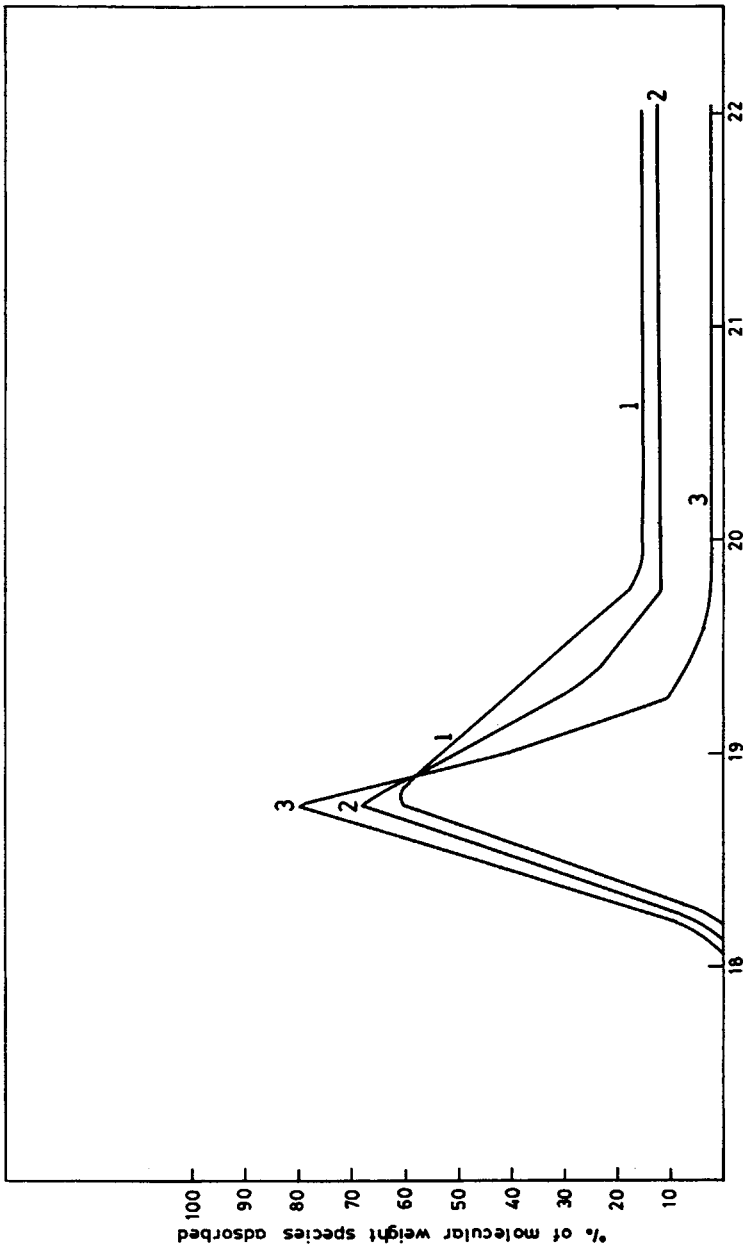

Fig. 7. Molecular weight distribution of the adsorbed alkyd resin in dilute solution: (1) mineral spirit (C_e = 2.25 g/100 mL); (2) xylene (C_e = 2.30 g/100 mL); (3) benzene (C_e = 1.65 g/100 mL).

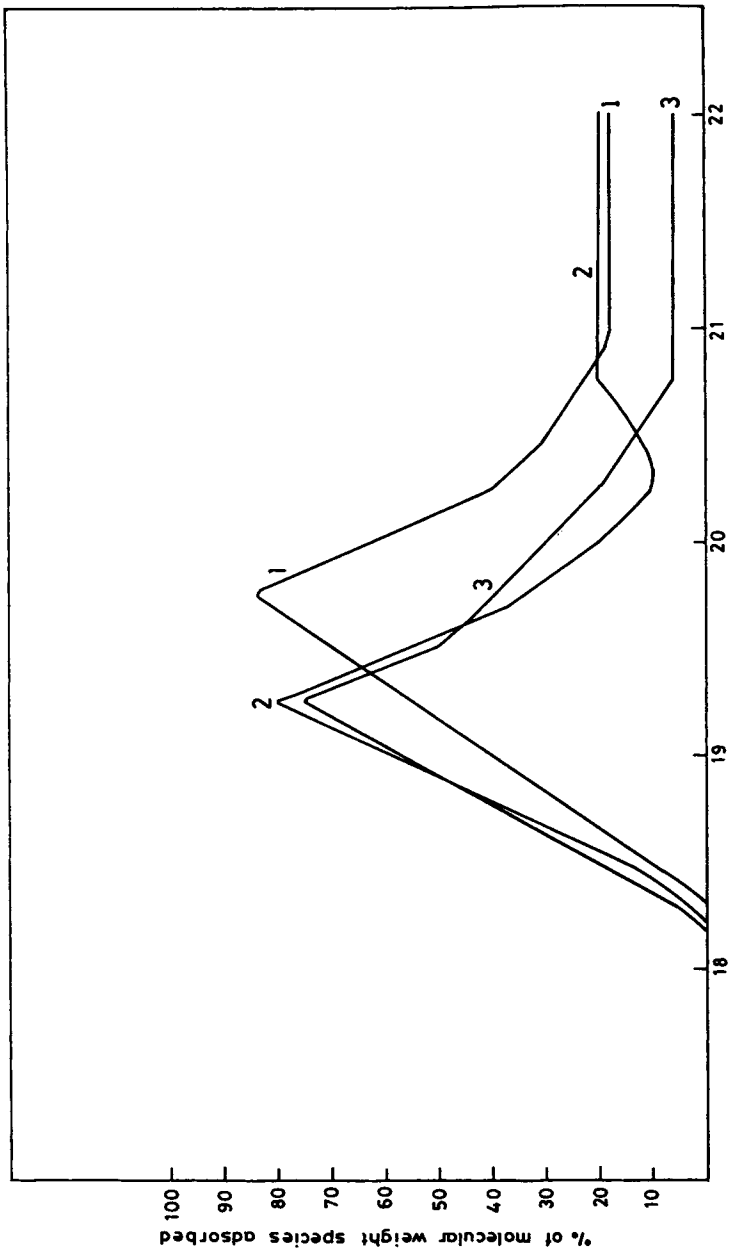

Fig. 8. MWD of the adsorbed alkyd resin in concentrated solution: (1) mineral spirit (C_e = 5.5 g/100 mL); (2) xylene (C_e = 4.6 g/100 mL); (3) benzene (C_e = 4.5 g/100 mL).

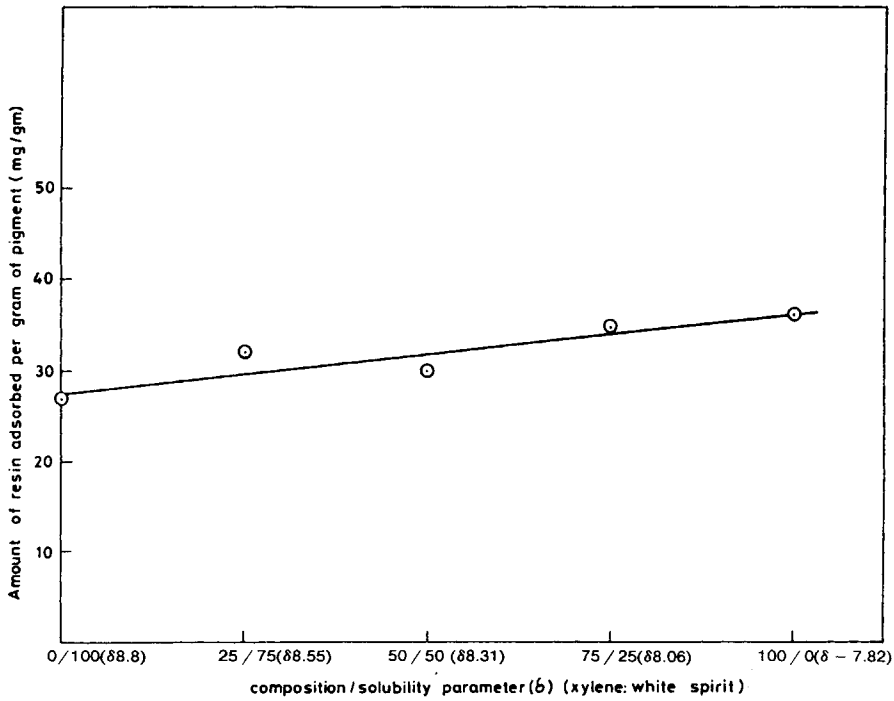

Fig. 9. Amount of resin adsorbed vs. composition of solvent blends/solubility parameter (δ).

TABLE VIII
MWD Averages along the Adsorption Isotherm (Mineral Spirit:Xylene)[a]

Soln concn (g/100 mL)	Composition of Blend (mineral spirit:xylene)	$\bar{M}_{ws} \times 10^{-3}$	$\bar{M}_{ns} \times 10^{-3}$	$\bar{M}_{wa} \times 10^{-3}$	$\bar{M}_{na} \times 10^{-3}$	$\bar{M}_{wa}/\bar{M}_{na}$
2.6	100:00	2.44	4.55	6.38	5.12	1.24
2.5	75:25	4.01	3.35	6.34	5.27	1.20
2.5	50:50	3.65	2.86	7.07	6.11	1.16
2.5	25:75	3.05	2.56	7.66	6.67	1.14
2.05	0:100	3.95	2.45	7.51	5.61	1.33

[a] $\bar{M}_w$ and $\bar{M}_n$ refer to weight average molecular weight and number average molecular weight, respectively. The subscripts s and a refer to the alkyd in supernatant after adsorption and the adsorbed layer of alkyd, respectively.

the case of xylene and benzene, the amounts deposited are in the same order as their χ values and dielectric constants of solvents. Though the amount of resin deposited is more in the case of mineral spirit medium, the calculated thickness of the resin adsorbed is almost the same as those measured in the case of xylene and benzene solution (Fig. 5), indicating that the adsorbed layer is getting compressed in the presence of a poor solvent, a fact also noticed by Rowland et al.[8]

In order to determine which molecular weight species gets preferentially adsorbed, a comparison was made of the molecular weight distribution of the

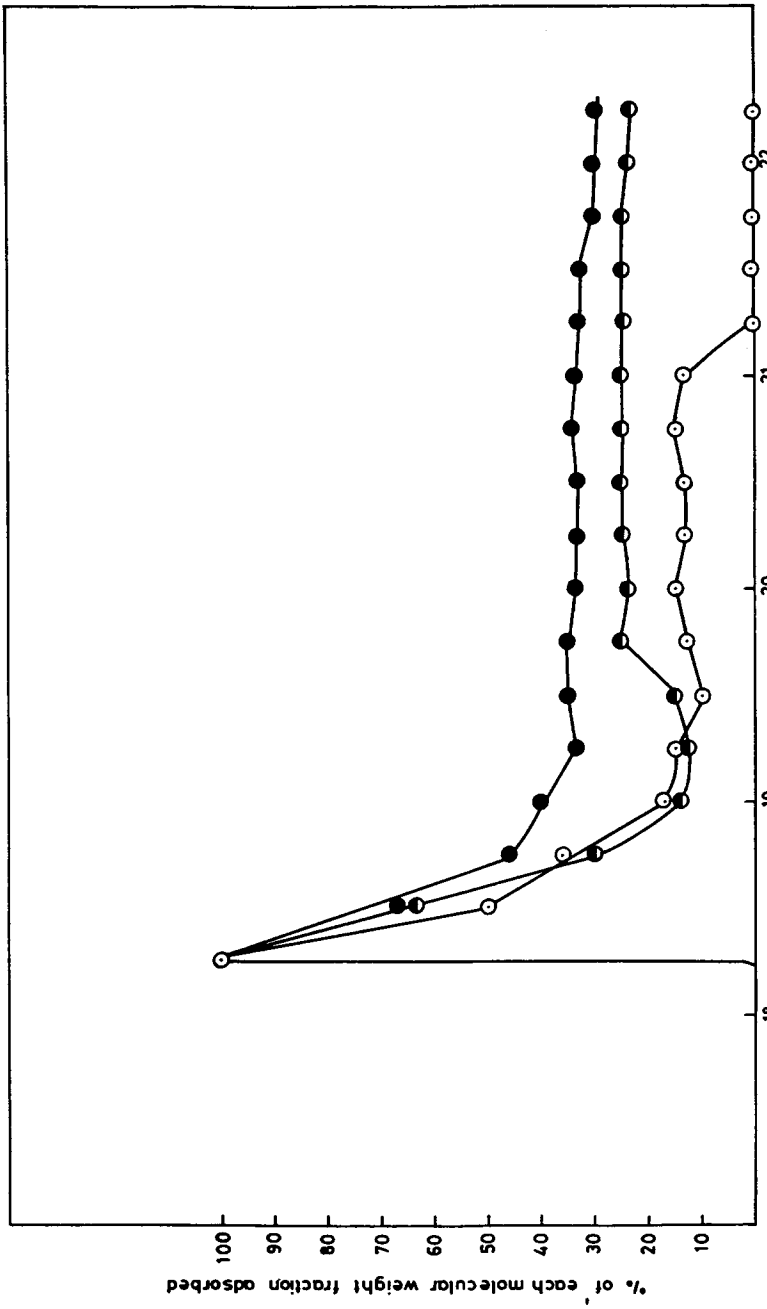

Fig. 10. Molecular weight distribution of the adsorbed alkyd resin in blends (xylene + mineral spirit): (●) 75% xylene:25% mineral spirit; (◒) 50% xylene:50% mineral spirit; (○) 25% xylene:75% mineral spirit.

original resin and residual resin after adsorption. The above study revealed that, for all the systems at low concentrations, high molecular weight materials are preferentially adsorbed and, at higher concentrations, the adsorption preference shifts to lower molecular weight materials (Tables V–VII). These results are in agreement with the finding of Scheutjens and Fleer.[15] All the three solvents used show differences in their preferences for different molecular weight species. In dilute solutions, there is a larger percentage of the adsorption of high molecular weight from benzene solution, less from xylene, and the least from white spirit. At higher concentration the order is reversed, except that the adsorption preference is for low molecular weight materials.

Along the adsorption isotherm, the dispersivity of the adsorbed resin is found to be low (Tables V–VII), indicating a narrow molecular weight distribution compared to that of the original resin; thus, in the adsorption process, fractionation appears to take place, as also noticed earlier by Koopal.[16]

As the concentration of the resin solution increases, the percentage of low molecular weight material increases in the adsorbed layer of resin so that the amount of resin adsorbed on the pigment remains constant. Thus, the decline is the isotherm may be attributed to the entrapment of solvent in the adsorbed layer of lower molecular weight species of resin, as the solvent is having greater affinity for such species, thereby making significant differences in the concentration of resin in supernatant solution, leading to the decline in the adsorption isotherm.

Alkyd Resin Adsorption from Solvent Blends

The experiments carried out with blends of xylene and mineral spirit reveal that the amount of resin adsorbed from solution of xylene, mineral spirit and their blends increases from xylene to mineral spirit, with the blends having intermediate values (Fig. 9).

Among the blends, the mixture having 75% mineral spirit and 25% xylene behaves more like mineral spirit in giving rise to a larger amount of adsorbed resin of lower molecular weight species (Fig. 10) on the pigment for facilitating dispersion and yet retaining a larger proportion of high molecular weight material in the supernatant liquid, which is likely to aid in the subsequent adhesion process on application of the system to a substrate.

CONCLUSIONS

The amount of alkyd resin adsorbed on anatase TiO_2 depends on the dielectric constant of the solvent used and solvent–resin interaction parameter (χ). In a poorer solvent, resin adsorbed appears to be in a compressed state.

The study also reveals that adsorption takes place throughout the molecular weight distribution to a lesser or greater degree depending on the concentration of the solution. In dilute solutions, more of high molecular weight fractions and in the concentrated solutions more of low molecular weight fractions get adsorbed. The decline in the adsorption isotherm in relatively concentrated solutions has been explained due to entrapment of solvent molecules in the loops and coils of the lower molecular weight resin adsorbed, for which the solvents have greater affinity.

In the case of blends, 75% mineral spirit and 25% xylene appear to possess the desired properties regarding dispersion and subsequent adhesion process.

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