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Interactions in Coatings Formulations. Part 3: The Influence of Hyperdispersant Systems on the Formulation and Properties of Selected Pigment Paste Assemblies

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ABSTRACT

The studies described herein relate to the nature of assembled paste concentrates containing rutile TiO_2 in each of two liquids, namely methoxypropyl acetate and toluene. The approach taken involved the use of inverse gas chromatography, adsorption behaviour, size exclusion chromatography and thermal analysis. Stability criteria were established for pastes which had been let-down in various media.

In general, EFKA 401 dispersant was found to be the more generally sympathetic and forgiving dispersing agent. However, its behaviour is not simple. This was shown through breakdown patterns associated with the dispersant during formulation.

INTRODUCTION

Interactions which develop between molecular components of coatings formulations, whether between the same or different species, are the key to many, if not all, of the properties of those coating formulations. This

applies to both the liquid state and to the solid state of the formulations.

Such interactions have various dependencies for their magnitude and longevity, e.g. dependence on temperature, concentration, the mixing procedure, etc. Each of these is underpinned by the nature of the intermolecular interactions between the molecular species.

Coating systems commonly consist of a colloidally dispersed solid phase (the pigment) in contact with a solvent (or combination of solvents) and a resin precursor or film-former (or combinations of these). In the finally cured system, the resin precursor will have developed its three dimensional, perhaps crosslinked, structure.

The affinity of the pigments for their medium is the key to satisfactory performance of the resulting fluids in the liquid and in the solid states. It is convenient to address the dispersion from the point of view of the pigment, e.g. TiO_2. The behaviour of TiO_2 dispersed in a solvent/film-former composition is controlled by the critical surface properties of each pigment particle and by the acid–base nature of all the components present. However, the TiO_2 is the major insoluble component. Factors related to the solution of the film-former in the solvent need to be considered.[1,2] Interest develops, therefore, in pigment–solvent interactions, pigment–film-former interactions, pigment–pigment interactions, the way in which these manifest themselves and the manner in which they can be modified by the use of additives. The additives of interest include wetting and dispersing agents, flow modifiers, anti-flood and anti-float additives, together with other stabilising systems such as preservatives, anti-skinning aids and biocides. Each of these contributes to the total interactive nature and intraactive nature of the formulation, as seen in the performance,[3] the rheological properties,[4] film formation, wetting, adhesion and drying.[5] However, additives are commonly effective only in particular phases of coatings assembly and use. For this reason, such use must be controlled and the consequences of use should be monitored throughout the life-cycle of the coatings assembly.

Reports of this type are necessarily selective. Such selection concerns the components of formulations, the experimental procedures adopted and the methods of data manipulation. This allows strategies to be developed which provide a basis for understanding the systems.

EXPERIMENTAL

Materials

The high durability titanium dioxide (TiO_2) pigment (rutile form-KRONOS 2310) was supplied by Kronos-Titan GmbH, Leverkusen, Germany. This

form is stabilised by Al, Si and Zr compounds. The oil absorption (DIN 53199) was 15·16. This form of TiO_2 has a relative scattering factor of 102, a density of 4·0 g cm^{-3} and a surface area of 15 m^2 g^{-1}. EFKA 401 (E401) was supplied by Efka Chemicals B.V., Hellegorn, Holland. It is stated to be a modified polyacrylate with 50% active constituents. The amine value (DIN 53176) is 50 ± 2 mg KOH/g. DISPERBYK 163 (DB163) was supplied by Byk-Chemie GmbH, Wesel, Germany as a 45% solution in a mixed solvent system. The amine value (DIN 53176) is 8–12 mg KOH/g. LAROPAL A81 (A81) was supplied by BASF, Ludwigshaven, Germany, as a 100% solid resin. It is stated to be a polycondensation product of urea and aliphatic aldehydes. Each of these dispersing aids was used without further purification.

The solvents, toluene, xylene and methoxypropyl acetate were supplied by Merck, Darmstadt, Germany, as reagent grades and also used without further purification.

Measurement procedures

Inverse gas chromatography (IGC)

The measurements were carried out following the procedures described elsewhere.[1,2] Aspects of interest include column conditioning, column packing and characterisation and data manipulation. The data were processed according to protocols described in Refs 1, 6, 7 and 8. In establishing each system, a range of column loadings of the stationary phases was examined across a series of flow rates for the carrier gas over a temperature range for the column. The injector was constantly heated at 250°C and the detector at 300°C. All the temperatures were controlled to ±0·1°C.

Adsorption studies

(a) Dispersion aids

Adsorption of the E401, the DB163 and the A81 onto the TiO_2 surface was achieved by shaking 30 g TiO_2, 250 g standard glass beads (2 mm diameter) and 90 g methoxypropyl acetate solution of each dispersant at seven different concentrations for each dispersant. The components were weighed into a 250 cm^3 capacity glass vessel and shaken for 20 min on a 'Red Devil' shaker. The initial temperature was 22°C and the final temperature, after shaking, was 45°C. On cooling to 22°C, the dispersion was centrifuged at 15000 rpm at 10°C for 20 min. A clear liquid was always obtained above the treated pigment. The equilibrium concen-

tration of the dispersing agent, in the clear liquid, was calculated by isolating the clear liquid, heating to dryness at 130°C over 2 h, cooling and weighing.

The same procedure was adopted for the E401–toluene combination.

(b) Solvents

The adsorption of toluene, xylene and methoxypropyl acetate was assessed using the IGC technique. The data were collated and processed according to procedures described elsewhere.[9] In essence, 0·1 μl of solvent was injected onto a 0·5 m column, ⅛ (i.d.) with 0·174 g of TiO_2 at the required temperature (100°C). Measurements were carried out on a Perkin-Elmer Sigma 3 GC unit coupled with a Perkin-Elmer Sigma 10 data station. A nitrogen carrier gas, flow rate 15·2 cm^3 min^{-1} was used. A flame ionisation detection system was employed.

'Colour' measurement evaluations

Paste concentrates were prepared by premixing the components in a dissolver chamber for 20 min. The products were then milled with glass beads (2 mm) in a sand mill until an average particle size of 5 μm was achieved. The concentrations of the dispersant systems and of the Laropal A81 were chosen on the basis of the adsorption isotherm data, acquired as described above. The concentrations were as follows:

For EFKA 401	
E 401 in methoxypropyl acetate (6% (w/w))	33·03 g
Kronos 2310–rutile TiO_2	66·97 g
For DISPERBYK 163	
DB163 in methoxypropyl acetate (4% (w/w))	27·59 g
Kronos 2310–rutile TiO_2	72·41 g
For LAROPAL 81	
A81 in methoxypropyl acetate (4% (w/w))	40·0 g
Kronos 2310–rutile TiO_2	60·0 g

Measurement of the tinting strength was achieved by mixing these pastes with Standard Black 1 pigment (98·5 : 1·5), mass 1·5 g, dispersed in an alkyd–melamine system. The alkyd–melamine system was based on a saflower alkyd and iso-butylated methoxy melamine mixture.

The paste concentrates were also used in different 'let-down' situations involving an alkyd–melamine system based on the saflower alkyd and iso-butylated methoxy melamine. This has a curing temperature of approximately 130°C. Also used were an epoxy-based system (low molecular

mass bisphenol-A-epoxy resin and polyamide-amine adduct), a polyurethane system (saturated polyester and aliphatic isocyanate), and a short oil alkyd system (based on an alkyd made of unsaturated fatty acids and produced in Color, Medvode, Slovenia).

The colour measurement unit was a ACS Spector Sensor system.

Size exclusion chromatography

During some of the studies described above, particularly in dispersions containing the rutile TiO_2, it was felt that breakdown of the dispersing aid might be occurring. Thus, size exclusion chromatography measurements of the continuous medium, before and after the dispersion of the TiO_2, were performed to see if any breakdown did occur. The size exclusion chromatography unit was a SHIMADZU-LCAA with the detector system, UV: SPD 2AS and RI.: RID-6A connected to a Hewlett Packard recorder; THF was used as a mobile phase and Merck Lichnogel PS1 and PS20 columns (5 μm).

RESULTS AND DISCUSSION

Inverse gas chromatographic analysis

The ratio AN/DN, where AN denotes the acceptor number and DN denotes the donor number (within the Lewis convention[1,2]) for E401 was found to be 0·706, indicating basic properties as being the source of interactions in the media. DB163 gives a corresponding value of 0·853 showing near amphoteric character, though slightly on the basic side of duality of interaction. The relevant data are given as Figs 1–3 for the E401 on the Chromosorb W support at temperatures of 60, 80 and 100°C in the column. The dispersive force contribution to the interaction on the column was established using C_6 to C_9 aliphatic hydrocarbons, acetone, THF and chloroform as standard probes. Figs 4–6 give the retention behaviour for the DB163 dispersant on the Chromosorb W support over the same temperature range. Clearly the dispersants operate in a dual fashion. They contain segments which act as Lewis acidic centres, and centres which act as Lewis basic centres. How they operate will depend on the other components of the system in which they are present. Hence, the major interest lies in the dominating characteristics through overall Lewis acidity or basicity. The dispersants are adsorbed on a solid surface. This reduces/removes those interactions between the dispersant molecules themselves. In solution, such interactions will occur to extents which depend on the prevailing conditions, such as temperature and the

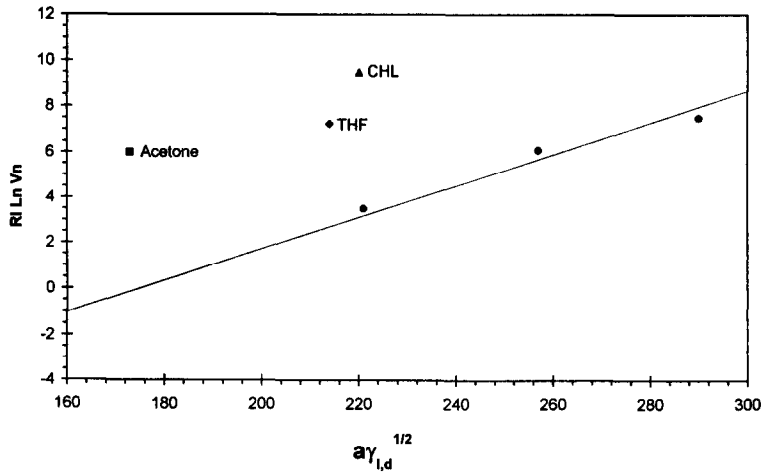

Fig. 1. IGC study of the interaction between various organic probes and E401 on Chromosorb W; 333 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

mixing regime. Essentially, using Figs 1–6, a measure of the interaction can be gained from the 'distance' between the probe (acetone, tetrahydrofuran or chloroform) and the dispersive force interaction baseline.

Laropal A81 cannot be examined in the manner described above. Structural changes/interactions occur at the temperatures specified. Thus, non-equilibrium conditions prevail in the temperature range from 60 to

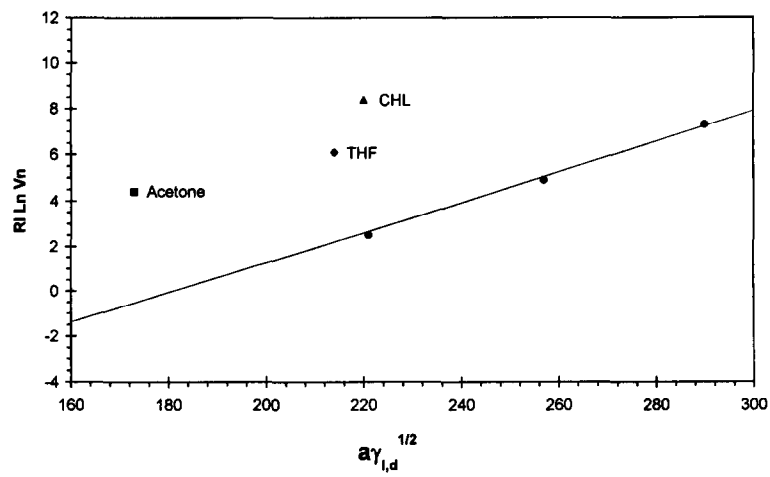

Fig. 2. IGC study of the interaction between various organic probes and E401 on Chromosorb W; 353 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

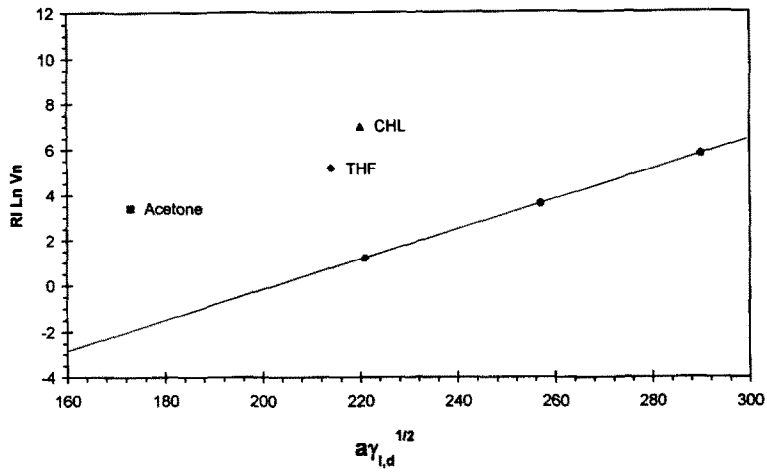

Fig. 3. IGC study of the interaction between various organic probes and E401 on Chromosorb W; 373 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

100°C. This makes the IGC technique inappropriate because of irreproducibility and inaccuracies. This point was confirmed using differential scanning calorimetric analysis. Figure 7 clearly displays the heat flow changes which occur on increasing the temperature from 40 to 100°C. Endothermic melting is indicated, explaining the non-suitability of IGC for examining Laropal A81.

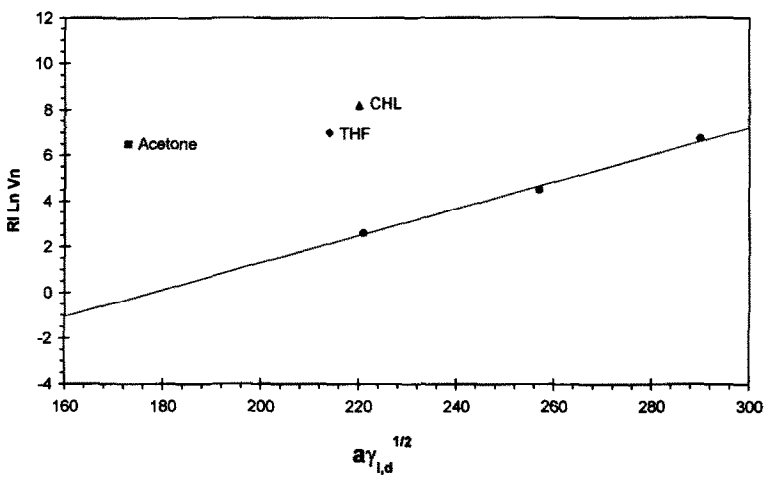

Fig. 4. IGC study of the interaction between various organic probes and DB163 on Chromosorb W; 333 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

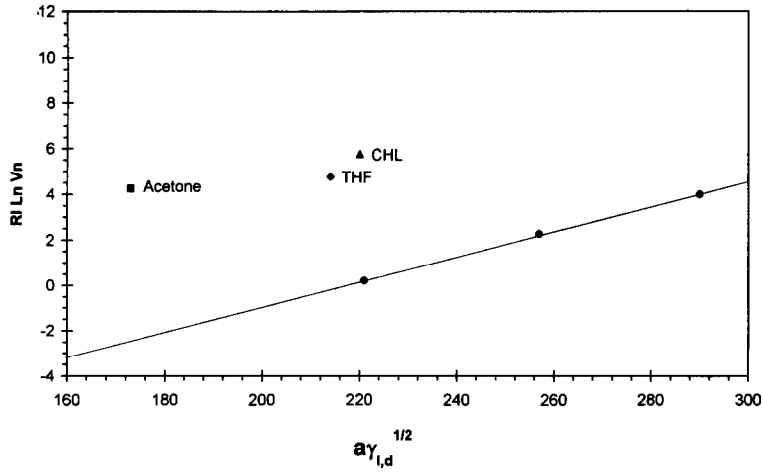

Fig. 5. IGC study of the interaction between various organic probes and DB163 on Chromosorb W; 353 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

Adsorption studies

Figs 8, 9 and 10 represent adsorption isotherms for E401, DB163 and A81 on the rutile TiO_2 surface from solution in methoxypropyl acetate. The same procedure was adopted for E401 from solutions in toluene. This adsorption isotherm is given as Fig. 11. In Figs 8–11, 'A' denotes the

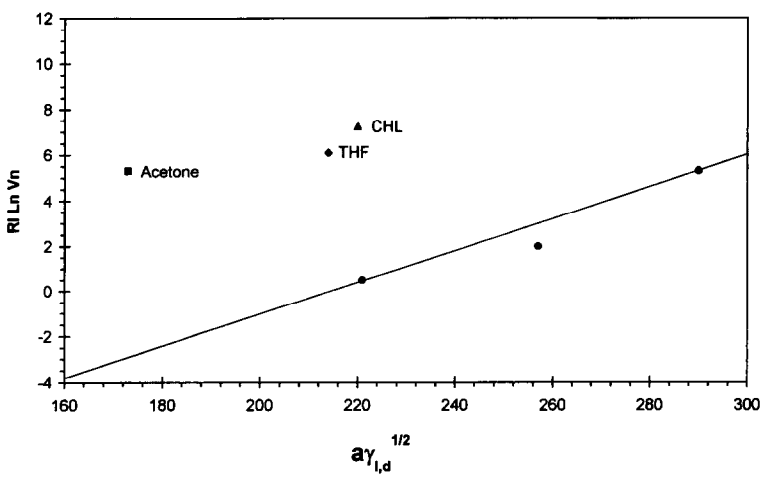

Fig. 6. IGC study of the interaction between various organic probes and DB163 on Chromosorb W; 373 K. THF and acetone as Lewis base probes, chloroform as a Lewis acid probe.

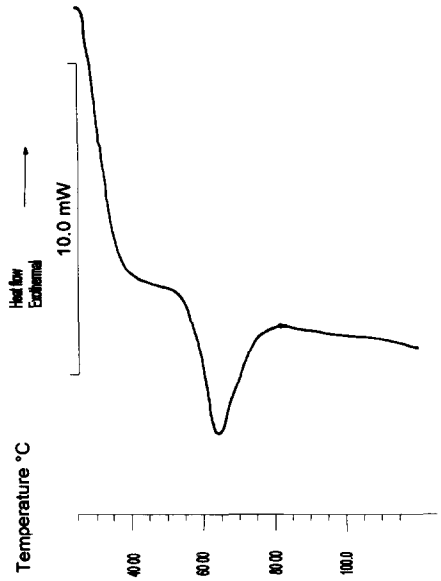

Fig. 7. Variation in heat flow with increasing temperature for Laropal A81.

number of milligrams of adsorbed material per unit mass of treated rutile TiO_2 and 'Co' denotes the loading (% (w/w)) of the particular dispersant (E401, DB163 or A81) in the specified solvent at the specified temperature. The experimental procedures gave rise to highly reproducible data.

The data demonstrate similarities, including the apparent increase in adsorbed material as a function of the amount of dispersant in the continuous medium, but to a maximum. Thus, decreases in the amount

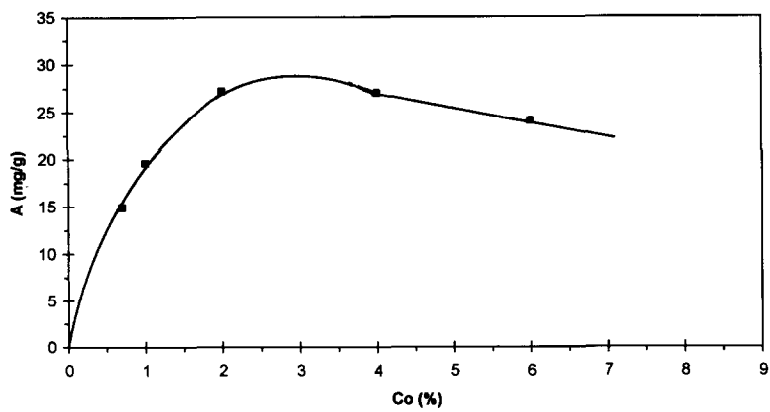

Fig. 8. Extent of adsorption (A) of E401 on TiO_2 from MPAC, as a function of the concentration of E401 in solution, 318 K.

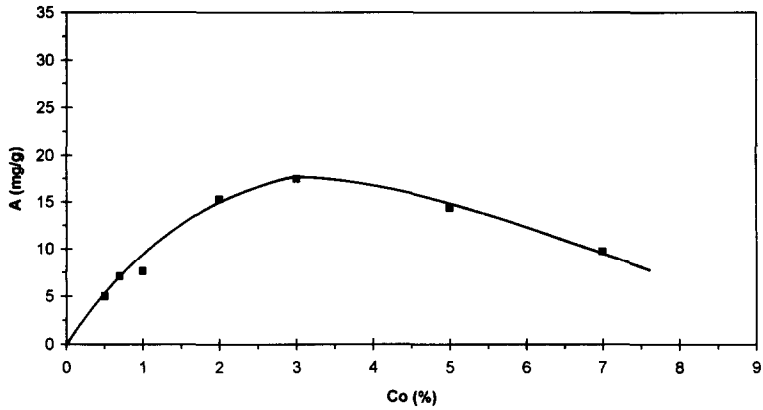

Fig. 9. Extent of adsorption (A) of DB163 on TiO_2 from MPAC, as a function of the concentration of DB163 in solution, 318 K.

adsorbed arise at greater concentrations. It should be noted that the pigment is dispersed in the solutions at the concentration specified and therefore, sequential addition of dispersant is not a feature.

Another similarity relates to the lack of a plateau and the location of the maximum adsorption value, for example in the E401/rutile TiO_2 system, irrespective of the solvent (methoxypropyl acetate or toluene) in which the formulation is located. This can be seen in Figs 8 and 11 to be at a value of Co (%) of 2·0.

Manipulation of these adsorption data, through the studied concentration of dispersant range, shows a consistent trend. The information is given in Table 1 and represented as Fig. 12. In Table 1 and Fig. 12 we

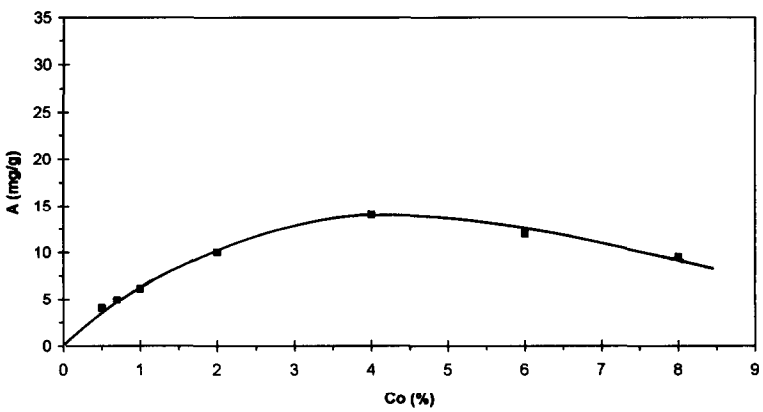

Fig. 10. Extent of adsorption (A) of Laropal A81 on TiO_2 from MPAC, as a function of the concentration of Laropal A81 in solution, 318 K.

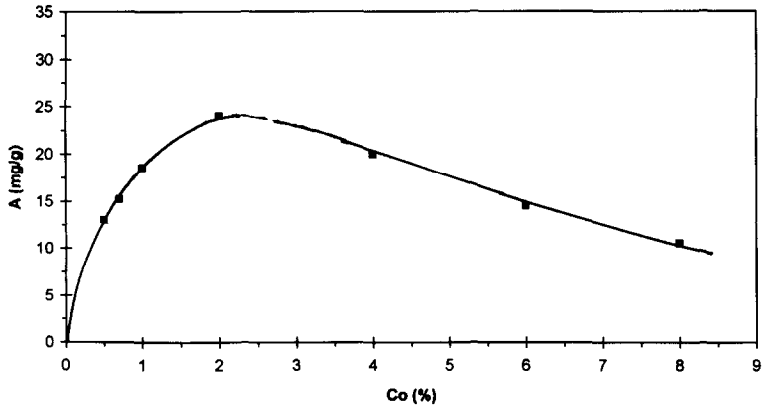

Fig. 11. Extent of adsorption (A) of E401 on TiO_2 from toluene, as a function of the concentration of E401 in solution, 318 K.

are concerned with the amount (g) of dispersant available, (A), to 30 g of rutile TiO_2, in 90 g of a solution containing both, in either methoxypropyl acetate or toluene. We are also concerned with the amount (g) of dispersant adsorbed per g of pigment for the methoxypropyl acetate (B) and the toluene (D) systems, respectively. Columns C and E relate to the total amount of E401 adsorbed on the 30 g of rutile TiO_2. The ratios (C/A) and (E/A) give the proportions of available dispersant, which become adsorbed, for the methoxypropyl acetate and the toluene systems

TABLE 1
Uptake of E401 by TiO_2 from Toluene and from Methoxypropyl Acetate

A *E401 dispersant available*	*B* *MPAC as solvent, E401 adsorbed g/g of TiO_2*	*C* *MPAC as solvent, total amount of E401 adsorbed (g)*	*C/A*	*D* *Toluene, as solvent, E401 adsorbed g/g of TiO_2*	*E* *Toluene as solvent, total amount of E401 adsorbed (g)*	*E/A*
0·45	$1·5\times10^{-2}$	0·45	1·0	$1·3\times10^{-2}$	0·39	0·9
0·68	—	—	—	$1·55\times10^{-2}$	0·47	0·70
0·90	$2·0\times10^{-2}$	0·60	0·67	$1·85\times10^{-2}$	0·56	0·61
1·8	$2·75\times10^{-2}$	0·83	0·46	$2·38\times10^{-2}$	0·71	0·39
3·6	$2·65\times10^{-2}$	0·80	0·22	$1·95\times10^{-2}$	0·59	0·16
5·4	—	—	—	$1·50\times10^{-2}$	0·45	0·08
7·2	$2·40\times10^{-2}$	0·72	0·10	$1·00\times10^{-2}$	0·30	0·04

System: E401 in the respective solvent. Immersion at 45°, 30 g of TiO_2 in 90 g of total formulation.

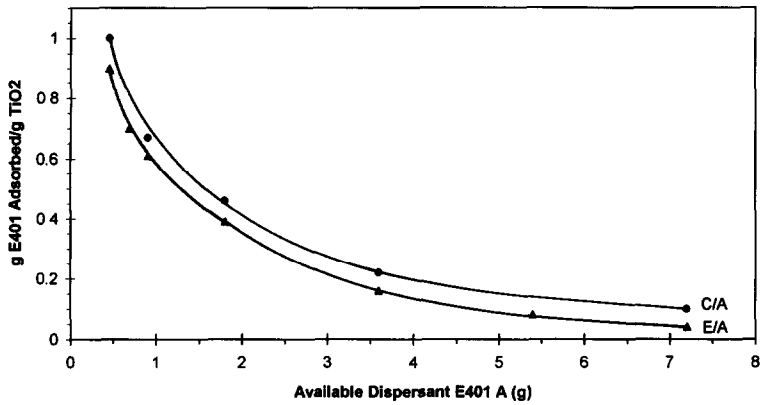

Fig. 12. Variation in the uptake of dispersant E401 as a function of the concentration of the dispersant E401 from toluene (●) and MPAC (▲).

respectively. Thus, in the system containing 0·5% of E401, all of the dipersant becomes adsorbed onto the 30 g of TiO_2. Increasing the amount of surfactant gives a continuous increase in the amount of E401 in the continuous medium. Thus, the medium changes continuously when surfactant concentrations greater than 0·50% (w/w) are employed. Table 1 gives data which imply that the more efficient uptake for the E401/ toluene system lies at a loading of approximately 0·25%. A question arises concerning the contribution made by the dispersant remaining in the solution and that of the dispersant on the pigment surface. Thus, the TiO_2 is converted into a species with which the surfactant/solvent system finds greater compatibility. This is perhaps achieved by the loading corre-

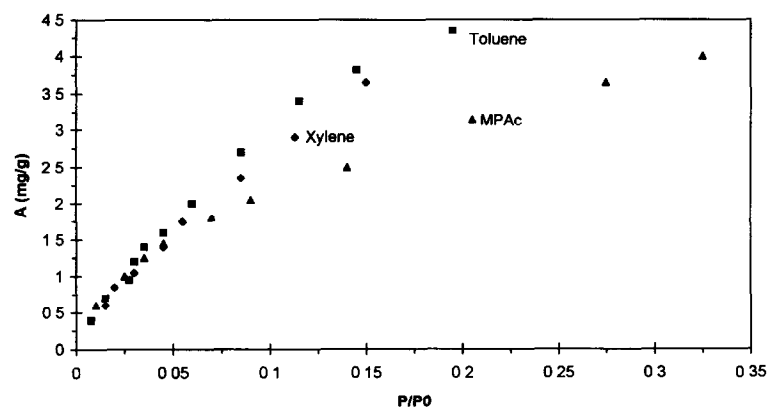

Fig. 13. Adsorption (A) (mg) of probes on TiO_2 as a function of the relative pressure of probe vapours.

sponding to 2% of the dispersant in the continuous medium. Additional work is being undertaken, to clarify these points further.

The results of the use of IGC in studies of adsorption by the rutile TiO_2 of xylene, toluene and methoxypropyl acetate are seen in Fig. 13. In this instance 'A' relates to the number of milligrams of adsorbed vapour per unit mass of TiO_2, located in the column within the IGC system. The column temperature was stabilised at 100°C. The ratio P/P_0 is the equilibrium vapour pressure (P) divided by the vapour pressure of the pure solvent at the specified temperature.[11]

With these vapours we are dealing with various parameters, including molecular size, shape and polarity. The aromatic solvents have similar polarities, but the bulky methyl group will result in less effective molecular packing for the xylene relative to the toluene. Comparisons between those aromatic media and the methoxypropyl acetate can be based on molecular linearity and greater Lewis basicity. This implies that the TiO_2 is behaving as a Lewis base with respect to these three 'solvents'. Thus, the stronger Lewis basic solvent is the least adsorbed perhaps at a reduced level of interaction.

'Colour' measurement studies

The results from the colour measurement studies of the optimised dispersant (E401)/pigment (TiO_2) ratio stated above are given below for the TiO_2/dispersant combinations, as outlined in the experimental section. The optimal paste was mixed with Standard Black 1 in the specified alkyd–melamine composition. The Standard Black 1 was present as 1·5% of the total mix.

Optimal Dispersant in Paste	K/S	Rub out test value
E401	100·0	113·2
DB163	119·3	100·6
A81	131·3	90·9

The measurements were repeated on panels which had been aged at 60°C for 21 days. The corresponding results are:

Optimal Dispersant in Paste	K/S	Rub out test value
E401	100·0	118·62
DB163	132·1	93·0
A81	145·5	91·0

The results show that flocculation of the TiO_2 in the optimal E401-paste system is not a feature. This is shown by the fact that the rub out values exceed 100, which indicates some flocculation of the black pigment. The

data indicate that strong flocculation of TiO_2 occurred in both the DB163-paste system and the A81-paste system.

Following this approach, studies in the let-down compositions were undertaken, again using the devised optimal rates of E401/rutile TiO_2. No incompatibility, flocculation or instability problems were observed on let-down into the polyurethane, the short-oil alkyd composition, the epoxy system or the alkyd–melamine system. However, the DB163 paste concentrate showed strong flocculation when used in the short-oil alkyd coating system. The A81 paste system proved to be useless in the alkyd–melamine composition, where a discontinuous and defective film surface formed. Other, related studies have shown the E401/TiO_2 optimal ratio to give dry films whose gloss, tinting strength capability and mechanical strengths are as good as (or better than) 'classic' coating systems.

Size exclusion chromatography (SEC)

In SEC studies of E401/TiO_2 systems undertaken before and after the dispersion process had been applied, changes in the molar mass distribution of the E401 were observed. The E401 in the undispersed state gave a major peak in the size exclusion chromatogram which centred around 10 000 g mol^{-1}, having a Gaussian shape. There was also a small peak at a molar mass of approximately 600–700 g mol^{-1}. This smaller peak represented approximately 15% of the total E401 dispersant. After 30 min of dispersion of E401 with the rutile TiO_2 under the conditions described, the small peak increased to a value corresponding to approximately 35% of the total E401 present. This process was confirmed by determining the ratio of concentrations between these two peaks acquired for different dispersion times. The implication is that breakdown of the E401 occurs during milling but, perhaps surprisingly, without influencing the dispersion stability. Indeed it may be that such breakdown is a feature of the stability provided by the E401 dispersant system.

The above sequence of operations was repeated, in the absence of the TiO_2 but with the other components normally part of the milling process, in preparation for SEC measurements. Breakdown of the E401 was observed in the absence of the TiO_2. This implies that the TiO_2 was not involved in the breakdown process.

The general implication is that care is needed when using dispersant systems of the types specified if an understanding of their mode of behaviour is to be obtained. Questions still remain concerning the relation which exists between dispersant adsorbed, the intimate nature of the adsorption process, and the quality/stability of the dispersion achieved.

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