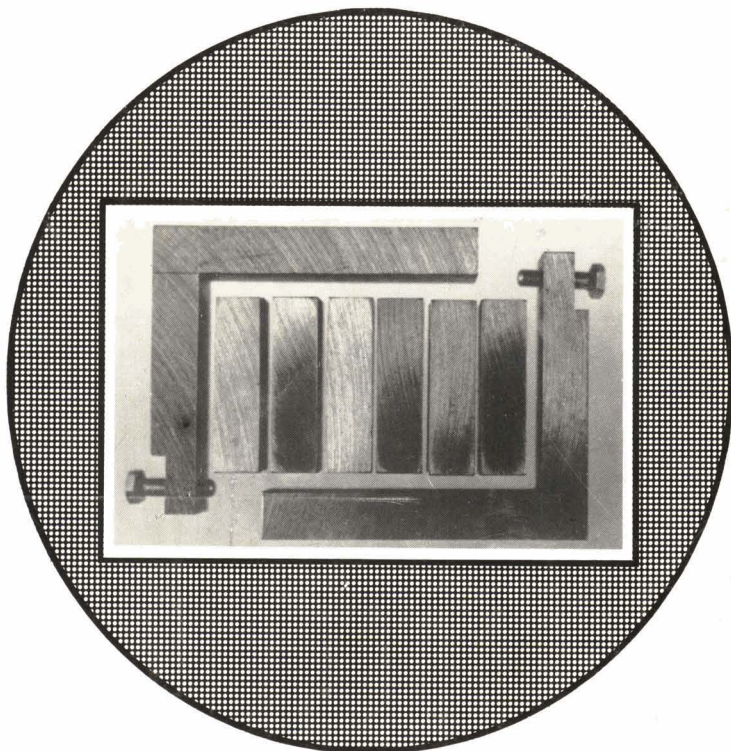# JOCCA

Corrosion monitoring of coated steel using a "Multi-layer sandwich" cell

Also in this issue

- Rheological parameters of red iron oxide-alkyd paints: their dependence on pigment content and on solubility parameters of solvents

- Maleinization of rosin and isolation of maleopimaric acid

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Corrosion monitoring of coated steel using a "multi-layer sandwich" cell

S. Feliu, J. M. Bastidas[†] and M. Morcillo

CENIM, Ciudad Universitaria, 28040-Madrid, Spain

Summary

A new test cell is described for corrosion monitoring of coated steel. Some of its advantages over the classical test cell are explained. The behaviour of an acrylic lacquer applied on surfaces contaminated with NaCl and SO_2 is studied.

1. Introduction

During the last few years some investigators have used co-planar electrodes to calculate corrosion rates mainly in investigations connected with atmospheric corrosion[1]. On the other hand, recent electrochemical studies have increasingly concentrated on measuring the protective capacity of paint layers on metallic surfaces[2,3]. The aim of this paper is to describe a "multi-layer sandwich" cell from which it is possible to examine the initiation and development of the corrosion process on coated metallic surfaces. This new cell has some advantages over the classical test cell (Figure 1).

Figure 2. Photograph of the multi-layer sandwich cell before assembly, with six rectangular segments and the metallic frame

Figure 1. Appearance of the classical test cell, painted steel

2. Experimental technique

The AC impedance technique was used in this investigation. A transfer function analyser (Solartron 1174) together with an electrochemical interface (Solartron 1186) were used. The design of the cell is described in detail in the following section.

3. Design of the "multi-layer sandwich" cell

Figure 2 shows a photograph of the rectangular segments and the metallic frame of the multi-layer sandwich cell used to study the electrochemical behaviour of painted metals. It consists of six rectangular segments (sandwich electrodes) of mild steel (55 x 15 x 8 mm) separated from each other by an insulating plastic sheet 170 μm thick. Each segment is attached to a wire connection so that it can be connected to the monitoring equipment (Figure 3).

A metallic frame gives mechanical support to the assembly (Figure 2). The six sandwich electrodes, the insulators and the metallic frame are mounted together, in a self-hardening resin (cronolite). The test surface is exposed by polishing the side opposite to where the conducting wires are attached (Figure 4). The surface area of each test segment is 825 mm².

The six terminals can behave alternately as anodes or cathodes when the electrochemical measurements are

† Present address: Corrosion and Protection Centre, UMIST, P.O. Box 88, Manchester M60 1QD, United Kingdom
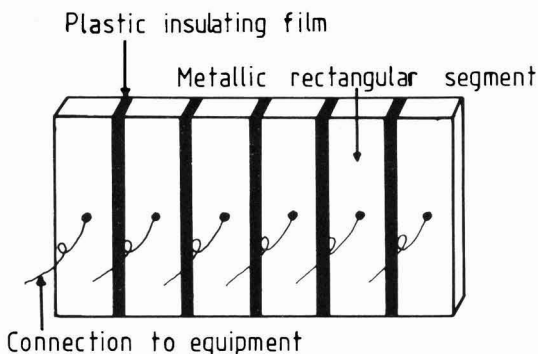
Figure 3. Disposition of the rectangular segments, plastic insulator sheet and wire connections. The width of the plastic insulators is exaggerated in the graph
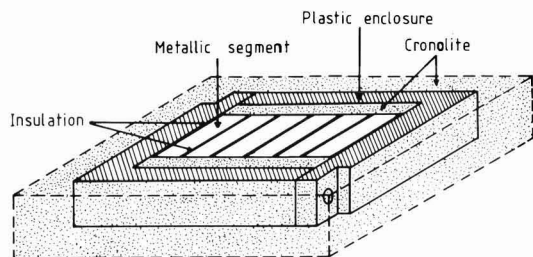
Figure 4. Appearance of the multi-layer sandwich cell after assembly
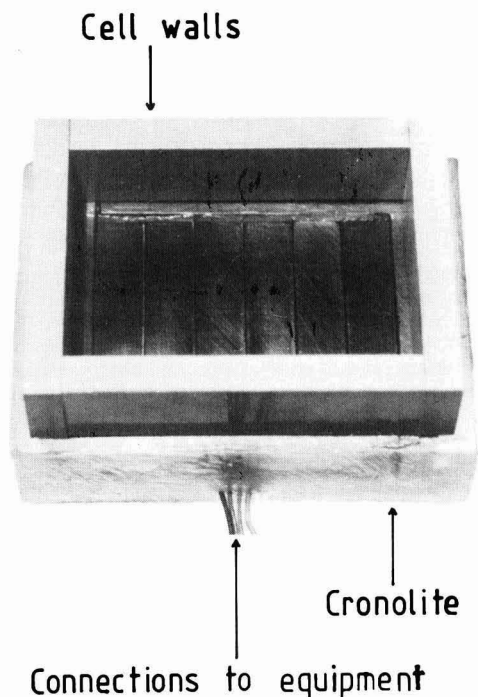
Figure 5. Photograph of the multi-layer sandwich cell ready for corrosion monitoring of painted steel

made. Normally, the terminals of segments 1-3-5 are connected to each other, and the same applies to segments 2-4-6. Measurements can also be made between two adjacent segments (as anode and cathode).

To immerse the test surface in electrolyte a plastic enclosure (25 mm high) is mounted on the four sides of the cell. This is achieved by fixing four (PVC) plastic walls to the sides of the metallic frame of the cell using silicone rubber adhesive (Figure 5).

4. Principal advantages of the "multi-layer sandwich" cell

The multi-layer sandwich cell possesses the following qualities for the study of protective coatings of metal surfaces.

#### 4.1 The cell is useful in monitoring corrosion rates at the interface of metal/lacquer system

Figure 6 shows the behaviour of an acrylic lacquer 400 μm thick applied to the multi-layer sandwich cell and immersed in distilled water for four days. Before applying the lacquer to the test surface, this was contaminated with 2,500 mg/m² NaCl. Plot (A) shows the values of corrosion rate under the film, measured between segments 2-4-6 connected together, and segments 1-3-5 also connected together. Plot (B) is for measurements across the lacquer film carried out with the help of a 25 cm² platinized titanium counter electrode. The impedance of the counter electrode is negligible compared to that of the working electrode.
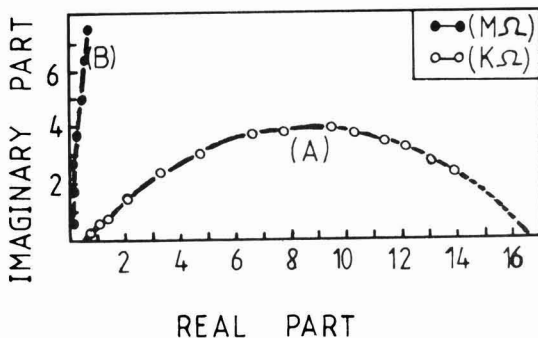
Figure 6. Impedance diagrams obtained with coated multi-layer sandwich cell. (A) Measurements under lacquer film, between segments 2-4-6 and 1-3-5. (B) Across the lacquer film

Curve (B) shows a behaviour comparable to that of a capacitor. The phase angles are close to 90° and the impedance moduli for similar frequencies are higher than those in curve (A).

In curve (A) the impedance plot is a semi-circle, which can be related to the eletrochemical activity (corrosion) on the metal/lacquer interface[4]. In curve (B) the strong ohmic resistance across the lacquer prevents the development of this semi-circular shape.

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Experimental conditions	Frequency (Hz)								
	5	10	30	100	300	1000	3000	10000	30000
44 hours contact between electrolyte and lacquer film	2	1.8	1.5	1.4	1.2	1.1	1	0.98	0.91
Immediately after removing the electrolyte and drying the surface	2	1.8	1.5	1.3	1.2	1.1	1	0.93	0.89
5 hours later in the laboratory atmosphere	25	23	20	18	17	16	15	14	14
24 hours later	105	104	100	90	86	44	43	37	31

The multi-layer sandwich cell was contaminated with 500 mg/m² NaCl and later covered by an acrylic lacquer 80 μm thick. The electrolyte was distilled water.

4.2 The cell is useful to determine the integrity of protective layers

Electrochemical measurements between adjacent segments will permit the comparison between different regions of the painted surface. From this it is possible to obtain information relating to the integrity of protective layers.

Figure 7 shows the behaviour of an acrylic lacquer 65 μm thick immersed in distilled water for three hours; before applying the lacquer on the test surface, this was contaminated with 1,000 mg/m² SO_2. The corrosion rate is higher in the 5-6 pair compared to the 3-4 pair, in which the behaviour of metal/lacquer system is almost purely capacitive.

If there is a pore or flaw in the lacquer film, in a classical test cell (Figure 1) the measurements will give information about that flaw and not about the general behaviour of the film. In the multi-layer sandwich cell this problem can be avoided, since different areas of the test surface can be studied separately, by connecting together different pairs of segments.

4.3 The cell is useful in tests in natural environments

The multi-layer sandwich cell does not require an external counter electrode. Thus, it can be used with thin electrolyte layers (e.g. in the atmosphere), where the traditional three-electrode method is not feasible. The multi-layer sandwich cell is useful to obtain measurements between adjacent segments, with an insignificant amount of electrolyte in the metal/lacquer system. Table 1 shows measurements, first after 44 hours of contact between lacquer and distilled water, and then at different times of exposure in the laboratory atmosphere, after drying the test surface.

5. Conclusions

The previous results show that it is possible to measure electrochemical activity under a paint film, by means of a multi-layer sandwich cell. The use of this type of cell can also help solve some of the problems that arise with classical cells, such as monitoring corrosion rates in thin electrolyte layers.

Figure 7. Impedance diagrams showing the behaviour of different segment pairs

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Rheological parameters of red iron oxide-alkyd paints: their dependence of pigment content and on solubility parameters of solvents

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Abstract

The rheological properties of synthetic red iron oxide paints in 66 per cent linseed oil-pentaerythritol-phthalate alkyd have been studied by conducting viscosity measurements at different shear rates. The analysis of viscosity data for paints containing the pigment in concentrations ranging from 30 to 65 per cent PVC's provided information about the dependence of rheological parameters on the pigment content and on the solubility parameters of the solvents. The data are also used for determining the critical pigment volume concentration of iron oxide in alkyd and the dependence of CPVC on the nature of solvents. The dependence of the CPVC on the nature of the solvents is attributed to solvent-resin interactions and to the affinity of solvents to the pigment. The analysis of data by using Casson's equation indicates that sag resistance of these paints is least affected by pigment content and the nature of solvents used, however, their brushability properties are found to depend on these parameters. The rheological parameters also provide quantitative information about compatability of solvents with binder and the pigment.

Introduction

In practice, a single point viscosity measurement by flow cup is used for specific mode of application of paints. However, the flow characteristics of paints so determined do not remain the same under the shearing stresses of different methods of application. The flow behaviour of paints depends mostly on their rheological properties which are governed by the forces of interaction among pigment, binder and solvent[1]. The rheological properties of dispersed system depend mainly on viscosity of dispersing phase, concentration, shape and size of dispersed particles and the forces of interaction[2]. The rheological behaviour of paint systems from fundamental and application point of view has been studied by several workers[3,4].

The effect of binders like epoxies, phenolics, and polyvinyl butyral on rheological properties of iron oxide suspensions[5], the flocculation behaviour and intrinsic viscosity as function of the concentration of the same pigment[6] and the effect of surfactants on these properties[7] are also reported. Some workers[3,4,8] have correlated their findings with the physico-chemical and interaction parameters of dispersed systems and others[3,4,9] used the data for defining the properties such as levelling, spreading, wet edge, brushability and ease of application of pigment dispersions. Only a few have interpreted the results in terms of pigment content and the effect of solvents and additives used in paint formulations[10,11].

Apart from oil absorption and the recent binder absorption[12], the changes in the properties of paint coatings and their free films with increasing PVC have been used for determining the CPVC and at least 15 such methods are reported[3]. In the literature the possible variation in the CPVC value of a pigment in a binder in the presence of different types of solvents has not been reported. The interactions among pigment, binder and solvent may alter the limiting concentration of a pigment (CPVC) in the dispersion. Taking this feature into consideration the effect of pigment content and the nature of solvents on the rheological properties of red iron oxide-alkyd paints has been studied and reported in this paper.

The alkyd used earlier[13] was pigmented with synthetic red iron oxide and apparent viscosities of pigmented dispersions were determined at different shear rates using a Brookfield RVT Viscometer. The results were analysed using the mathematical equations, and interpreted in terms of: (1) per cent pigment volume concentration, (2) shear dependence of paints, (3) pigment-resin-solvent interactions, and (4) solubility parameter of solvents.

Mathematical Equations

The apparent viscosity data for paints at different shear rates were converted into parameters required for using in (1) Power Law[14] and (2) Casson's[15] Equations.

The flow behaviour (n) and consistency index (k) were determined by using the relationship between shear stress (τ) and shear rate ($\dot{\gamma}$):

$$\log \tau = n \log \dot{\gamma} + \log k \dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

The yield stress (τ_0) and viscosity at infinite shear rate ($\eta\infty$) were determined by using the relation:

$$\tau^{1/2} = \tau_0^{1/2} + \eta\infty\dot{\gamma}^{1/2}\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

The procedures for calculating spindle constants, shear stress and shear rate data are described elsewhere[13].

Experimental

Materials

- Pigment grade synthetic red iron oxide; found to be α-Fe_2O_3 in X-ray analysis.
- Commercial grade 66 per cent linseed oil-pentaphthalate alkyd[13].
- Laboratory grade moderately and poorly hydrogen bonded solvents[13].

Paints

Paints having different pigment volume concentrations (PVC's) ranging from 30 to 65 per cent with an increment of 5 PVC were prepared with each of the solvents i.e., (i) Xylene and white spirit mixture, (ii) Cyclohexane, (iii) Ethyl acetate, and (iv) Butyl cellosolve. The paints were ground in Steele-Cowlishaw high speed planetary ball mill to the fineness of 7-8 on Hegman guage. The solvent

Alkyd solutions[13]					Paint formulations				
Weight fraction of alkyd in solution	Apparent viscosity in poise in different solvents				Pigment volume concentration in paints	Apparent viscosity in poise in different solvents			
	Cyclo-hexane	Xylene and white spirit	Ethyl acetate	Butyl cello-solve		Cyclo-hexane	Xylene and white spirit	Ethyl acetate	Butyl cello-solve
I (0.4931)	2.15	1.50	0.60	2.00	I (30%)	4.0	22.0	5.2	4.8
II (0.4538)	1.85	1.10	0.45	1.45	II (35%)	6.0	38.0	6.0	6.0
III (0.4150)	0.95	0.70	0.35	1.10	III (40%)	7.0	40.0	18.5	19.0
IV (0.3763)	0.50	0.45	0.25	0.75	IV (45%)	11.2	54.0	24.0	32.0
V (0.3389)	0.30	0.30	0.20	0.55	V (50%)	6.8	192.0	24.5	6.0

content in each formulation was maintained at 25 per cent of the total weight of the dispersion.

Viscosity Measurements

The viscosity measurements were conducted with Brookfield RVT Viscometer, in a room conditioned at 26± 1°C, at 8 shear rates corresponding to 0.5, 1.0, 2.5, 5, 10, 20, 50 and 100 rpm speeds of spindles[16].

Results

For each paint, the shear stress corresponding to respective shear rate was calculated from the apparent viscosity data. A selected set of data is presented in tables 1-3 and also illustrated in figures 1-14.

Discussion

Apparent Viscosity

The apparent viscosity of paints in a specific solvent, measured at 5 and 50 rpm, is plotted as function of pigment content in figures 1-4. These plots pass through a maximum value with an increase in PVC from 30 to 65 per cent. The fall in apparent viscosity beyond a certain PVC is because of the absence of sufficient binder to hold the pigment particles together and less resistance by the dispersed flocs to the mobility of the spindle. In other words, the PVC at which the dispersed flocs exert maximum resistance leading to maximum apparent viscosity could be considered related to the critical pigment volume concentration (CPVC) of the dispersion.

The viscosity of paint dispersions at 50 rpm is found to be lower than that at 5 rpm because of their pseudo-plastic behaviour. The reduction in the size of the flocs at higher rpm also results in the reduction of apparent viscosity[17].

The viscosity data in Table 1 show the differences in viscosities of iron oxide dispersions and those of alkyd solutions with respect to solvents used. For example, at 5 rpm, the viscosity of unpigmented alkyd solution (concentration used in paint formulation No. 1) is 0.60P in ethyl acetate, 1.50P in xylene and white spirit, 2.0P in butyl cellosolve and 2.15P in cyclohexane. When the same alkyd solution is pigmented at 30 PVC level the viscosity of paint in ethyl acetate is 5.2P, in xylene and white spirit is 22.0P,

in butyl cellosolve is 4.8P and in cyclohexane is 4.0P. The difference in the viscosities of alkyd solution and the paint formulated with it indicate the difference in the level of interactions among pigment, binder and solvent.

Effects of solvents on CPVC

The PVC values corresponding to the mid point of maxima of apparent viscosity plots (figures 1-4) have been considered to be related to the critical pigment volume concentration of red iron oxide in alkyd and will be referred as CPVC in further discussion. The CPVC's so obtained are found to differ from each other with respect to the solvents used in the formulation. For example, the CPVC of red iron oxide in 66 per cent linseed alkyd is around 53 per cent when ethyl acetate is used as a solvent and it is 45 per cent when cyclohexane is used.

There are several factors which affect the pigment-binder-solvent interactions and consequently the CPVC of the formulation. In an earlier study on rheological properties of alkyd solutions, it was found that ethyl acetate had maximum interaction with the alkyd whereas cyclohexane had the least[13]. Apart from this, in a separate study on the interaction of pigment with solvents, it was observed that red iron oxide in ethyl acetate remained suspended for over 24 hours and the same pigment settled down within 30 minutes of suspension in cyclohexane[18]. The high CPVC value of iron oxide in in alkyd medium when ethyl acetate is used as solvent can be explained in the light of above observations. In the case of ethyl acetate on account of its structural similarity, the alkyd molecular chains uncoil to a greater extent and provide larger surface area. And also iron oxide pigment having relatively more affinity towards ethyl acetate gets solvated better in alkyd solutions in ethyl acetate. The factors, like covering of relatively large surface area by alkyd molecules as well as the pigment particles getting solvated in ethyl acetate facilitate the paint formulation to accommodate greater amount of iron oxide in the medium of dispersion. On the other hand in the case of solvents which have poor structural similarity to the binder and low affinity towards the pigment, push more binder on to the surface of the pigment and the CPVC of pigment in the medium of dispersion is likely to be low.

The CPVC values of red iron oxide in alkyd medium in presence of solvents, xylene and white spirit mixture and

Table 2
Critical Pigment Volume Concentrations of Red Iron Oxide in Alkyd in Presence of Different Solvents.

Method of calculating CPVC values	Cyclohexane	Xylene and white spirit	Ethyl acetate	Butyl cello-solve
1. Apparent viscosity plots (Figures 1-4)	45	50	53.5	45
2. log k vs. PVC plots (Figure 7)	44.5	50	52	45.5
3. log (k/w) vs. W plots (Figures 8-9)	42.8	53.5	55	43.6
4. $\dfrac{1}{\log (\eta\infty/\eta o)}$ vs. $\dfrac{1}{\varnothing}$ (Figure 12)	40-45	45-50	55	40-45

Table 3
Slope n̄ and Intercept log k from Power Law Plots for Iron Oxide Paints in Different Solvents

PVC of red iron oxide in paints (%)	Cyclohexane		Xylene and White spirit		Ethyl acetate		Butyl cellosolve	
	n	log k	n	log k	n	log k	n	log k
30	0.8983	1.0036	0.8822	1.7363	0.9199	1.0064	0.8819	0.9835
35	0.8857	1.2023	0.9147	1.9639	0.8197	1.1435	0.9166	1.1714
40	0.8985	1.2739	0.8204	2.1770	0.9519	1.6833	0.7967	1.5958
45	0.9376	1.3426	0.8412	2.2692	0.9487	1.7753	0.8429	1.9328
50	0.9342	1.1255	0.8788	2.8691	0.9121	1.7793	0.8056	1.1717
55	0.9077	0.8979	0.7705	2.4445	0.8257	2.0754	0.7574	1.0812
60	0.8403	0.7912	0.7574	2.0698	0.8654	1.7952	0.7884	0.9019
65	0.8886	0.7461	0.7567	2.0034	0.6810	1.7000	0.8390	0.7701
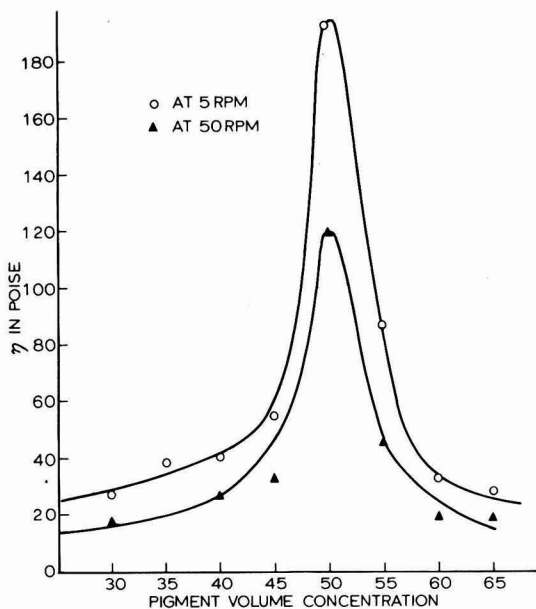
Figure 1. Dependence of apparent viscosity of alkyd paints in xylene and white spirit mixture on PVC of red iron oxide
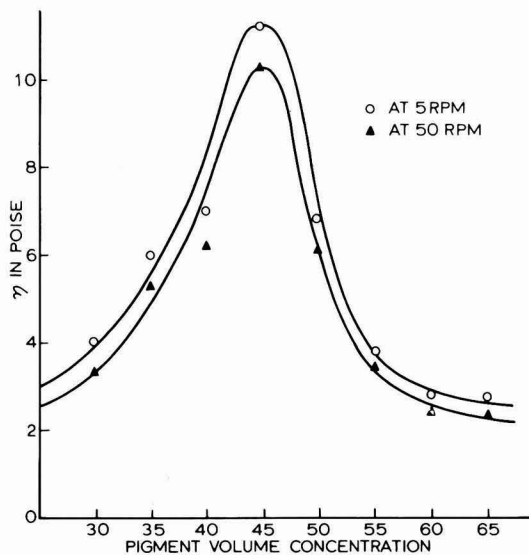
Figure 2. Dependence of apparent viscosity of alkyd paints in cyclohexane on PVC of red iron oxide
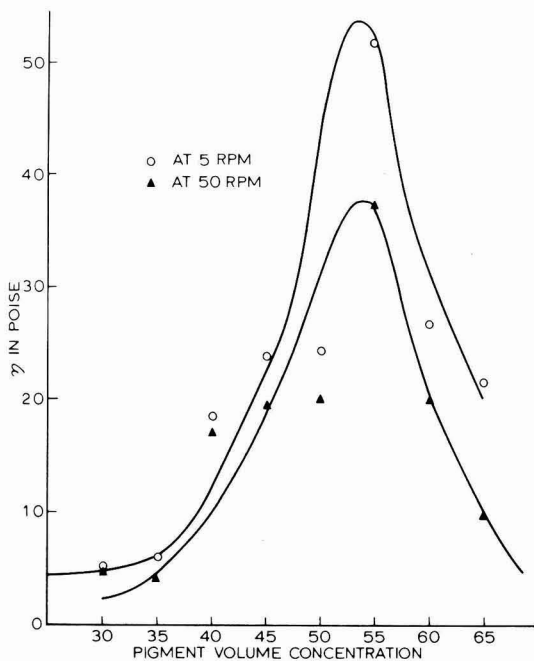
Figure 3. Dependence of apparent viscosity of alkyd paints in ethyl acetate on PVC of red iron oxide

Figure 4. Dependence of apparent viscosity of alkyd paints in butyl cellosolve on PVC of red iron oxide

butyl cellosolve are also found to be in the range of 45 to 55 per cent (Table 2).

Usually the CPVC of a pigment in a binder is determined by oil absorption or other methods. However, the effect of solvents on CPVC is not considered while conducting such determinations. The observations reported here illustrate the differences in the CPVC values of red iron oxide pigment in alkyd with respect to solvents used in the formulations. Hence, it would be better if CPVC of a system is determined by taking into consideration the physico-chemical properties of pigment, binder, solvent and other additives used in the paint formulation. The determination of CPVC value of a pigment in liquid state of a paint formulation is of more practical importance than the one conducted on hard paste or on dried coating films. The use of data obtained from rheological properties of paint dispersions for determining the CPVC is simple, quantitative and informative, and even the effect of additives can also be estimated.

Shear dependence of paints

a) Power Law Equation

The power law equation is usually used for analysing the data relating to the rheological properties of polymer solutions. It has also been used for studying the flow behaviour of some pigmented dispersions[19].

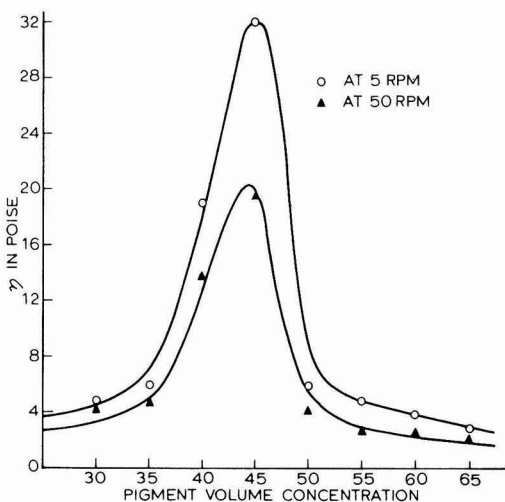This viscosity data for paint dispersions has been analysed with the help of the power law equation. By way of illustration, two sets of plots for paints in poorly and moderately hydrogen bonded solvents, are respectively given in figures 5 and 6. The plots of data expressed by the

equation, $\log \tau = n\log\bar{\gamma} + \log k$ for individual paint systems are found to be linear (figures 5 and 6). The values of rheological parameter 'n' (obtained from the slopes of these plots) being less than unity, show pseudoplastic type of flow behaviour for all the paints. In an earlier study it was found that the flow behaviour of alkyd solutions changed from pseudoplastic to dilatant at higher shear rates[13]. When the same alkyd solutions are pigmented, they exhibit only pseudoplastic flow behaviour (Table 3).

The values of n do not hold any relationship with the content of pigment and binder or the nature of solvent used in the paint formulation except showing the nature of flow under shear stresses (Table 3).

On the other hand, log k, the intercept of power law plots, is found to hold a relationship with the pigment content in the formulations and also to depend on the interactions among pigment, binder and solvent (Table 3).

A gradual increase in log k values is observed up to a certain PVC and then a decrease when the PVC is further increased (Figure 7). The maxima of the plots could be related to the limiting pigment content or in other words the CPVC. The CPVC values obtained from power law −log k plots are in fairly good agreement with those from apparent viscosity plots (Table 2).

Log k and 'W'

The following equation, proposed earlier[13], expressed the relation between log k and W the weight fraction of resin in the solution:

$$\log (k/W) = k_2W + C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Here, the constant k_2 a rheological parameter depends on the interactions among the constituents and 'C' is the limiting shear stress. This equation has been used for establishing a relationship between log k and the content of pigment in the paints, by considering W as the weight fraction of pigment and the homogeneous alkyd solution as the dispersing medium.
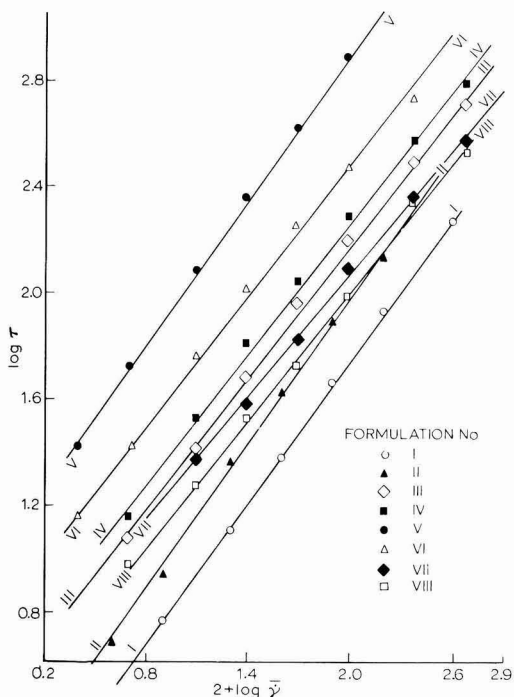
Figure 5. Shear stress vs. shear rate for red iron oxide paints in xylene and white spirit mixture. RVT spindle used for formulations I and II is No. 3 and for III-VIII is No. 5
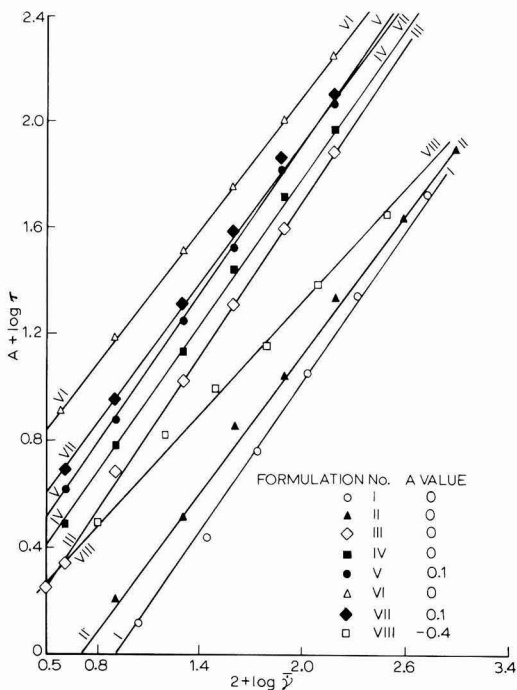
Figure 6. Shear stress vs. shear rate for red iron oxide paints in ethyl acetate. RVT spindle used for formulations I is No. 2 and for II-VIII is No. 3. A is an arbitrary constant used to displace the lines vertically for clarity
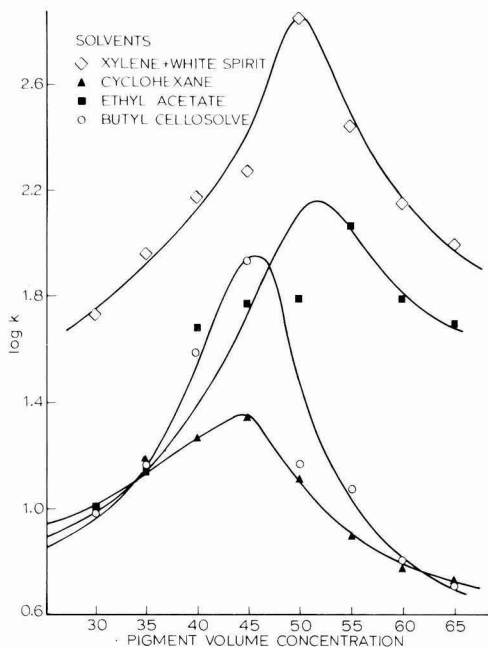
Figure 7. log k [intercept, equation (1)] vs. PVC of red iron oxide

It is observed that the log (k/W) versus W plots for paints in a specific solvent are linear up to a certain value of W and then change their course with reverse slopes (Figures 8 and 9). The two plots intersect at a point which could be considered to correspond to the critical weight fraction of pigment in the dispersion. The critical weight fractions of iron oxide in alkyd obtained from the plots are 0.588, 0.636, 0.6417 and 0.592 and the CPVC values calculated from them are 42.8 per cent, 53.5 per cent, 55 per cent and 43.6 per cent when cyclohexane, xylene and white spirit, ethyl acetate and butyl cellosolve are used as solvents, respectively.

b) Casson's Equation

This equation is reported to provide useful knowledge about the rheological properties of dispersions, especially, paints[3,4,20,21]. While making use of this equation the data for paints in different solvents are plotted in terms of $\tau^{1/2}$ versus $\bar{\gamma}^{1/2}$. The plots for paints having different PVC's are found to be linear and to converge at one point on the ordinate. For illustration, a few plots are given in figures 10a, 10b, 11a and 11b. The convergence of the plots at one point indicates that the intercept τ_0, the yield stress, is independent of the content of pigment in the formulation. Even the nature and type of solvents used do not have any significant influence on τ_0 as its values in different solvents do not differ much from each other. τ_0, the yield stress, is considered to be a measure of sag resistance of paints. It can be inferred from these observations that the sag resistance of red iron oxide paints in long oil alkyd is least influenced by pigment content and the nature of solvents used in the present study.

The increase in the slopes (η_∞) up to a certain PVC and then decrease on further increase in PVC indicate the dependence of η_∞ on PVC. Similarly the difference in η_∞

Figure 8. log (k/W) vs. weight fraction 'W' of pigment [equation (3)]

Figure 10a. Relation between sheer stress and sheer rate [equation (2)] for paints in cyclohexane
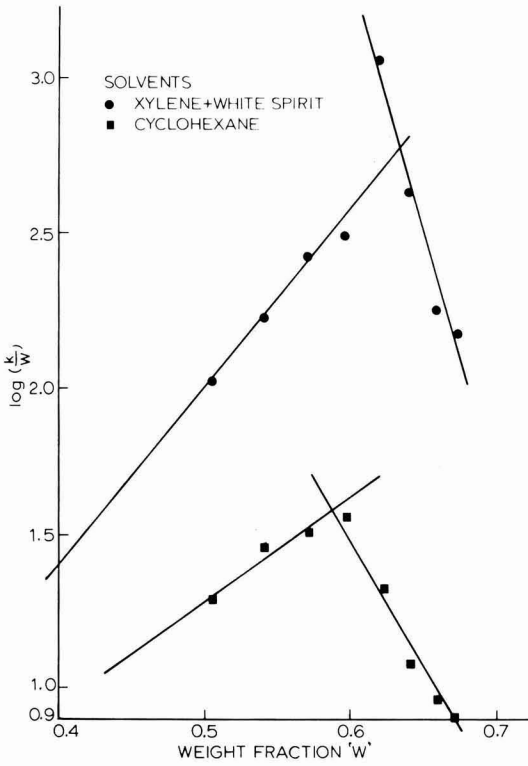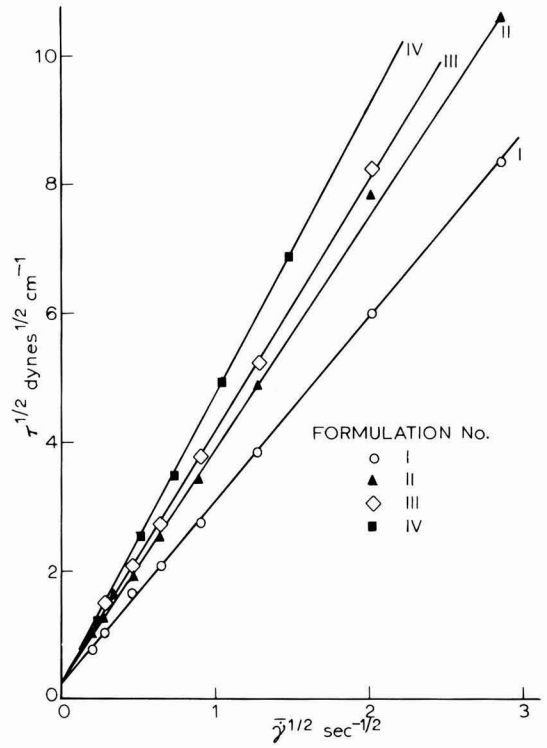

Figure 9. log (k/W) vs. weight fraction 'W' of pigment [equation (3)]

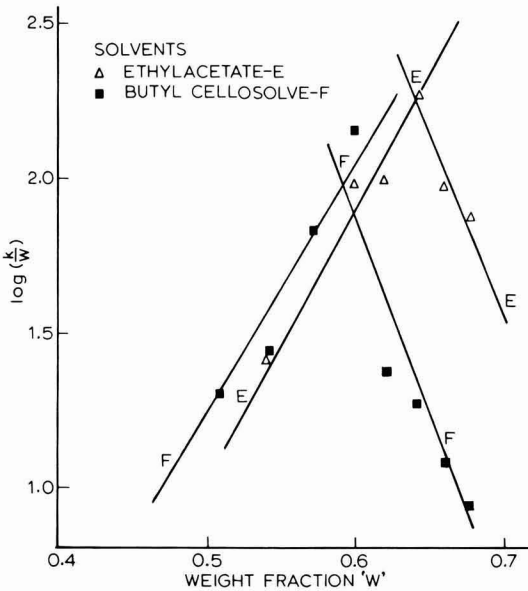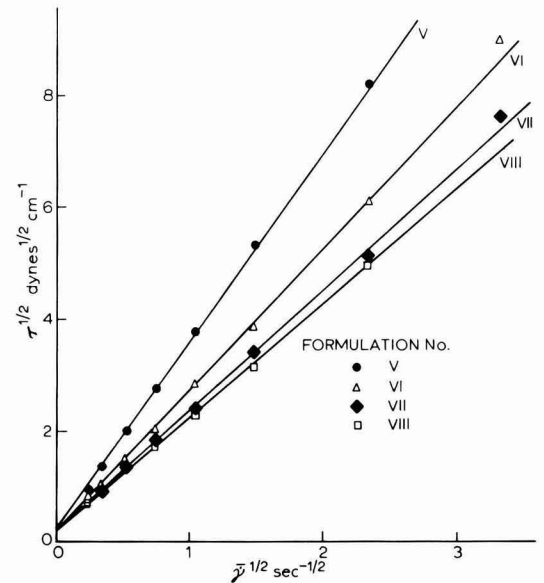Figure 10b. Relation between shear stress and shear rate [equation (2)] for paints in cyclohexane
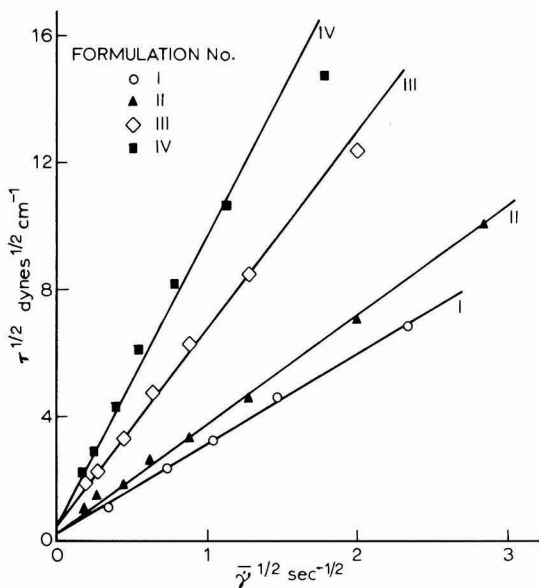
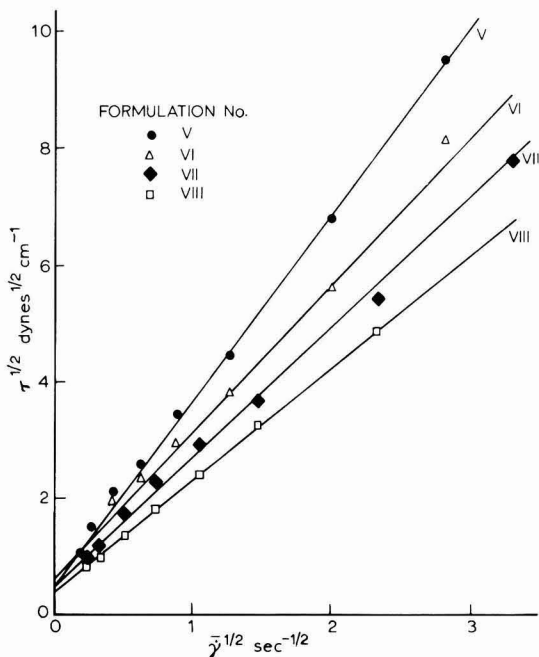Figure 11a. Relation between shear stress and shear rate [equation (2)] for paints in butyl cellosolve

Figure 11b. Relation between shear stress and shear rate [equation (2)] for paints in butyl cellosolve

values for paints at a particular PVC show the influence of solvents on them. η_∞ is a measure of ease of brushability and is expected to depend on pigment content as well as on the nature of solvents used in the formulations. The above observations support this view. The further analysis of η_∞ data is described below:

In his book, Patton[22] has reported the following equation, which correlates η_∞ with volume fraction $\varnothing$ of pigment in the paint formulations:

$$\frac{1}{\log(\eta_\infty/\eta_0)} = \frac{1}{K\varnothing} - \frac{1}{KU} \quad \ldots\ldots\ldots(4)$$

Where

η_∞ = infinite shear rate viscosity, and
η_0 = viscosity of liquid medium (binder and solvent)
K = a constant being function of pigment-binder-solvent interactions; and
U = the ultimate pigment volume content

This equation was derived by Asbeck, Schrerer and Vanloo[23] by converting the equations of Vand[24] and Brailey[25] into a simple hyperbolic form. They suggested that this equation can be used for determining the ultimate pigment volume content in a paint formulation by extrapolating the plot of $1/\log(\eta_\infty/\eta_0)$ versus $1/\varnothing$.

In his studies, Brailey[25] found this equation to follow linearity, for volume fractions from 0.05 to 0.5. Asbeck, Schrerer and Vanloo[23], who studied the dispersion of titanium dioxide and magnesium silicate, respectively in bodied linseed oil in the concentration range 10 per cent to 35 per cent, calculated the ultimate pigment volume content U, by extrapolating the plots. However, they have not used this equation for paints containing higher level of pigmentation as well as in presence of solvents.

This equation is found to have certain limitations in its applicability to the present data. It holds good for plots of $1/\log(\eta_\infty/\eta_0)$ versus $1/\varnothing$ for paints having low pigment content. At higher PVC's the plots are linear but with reverse slopes (Figure 12). In other words, the plots of equation (4) in the present study cannot be extrapolated to the limiting point for calculating the values of U[23-25]. However, the point of intersection of two plots could be equated to the critical pigment volume fraction. The CPVC values obtained from the plots of equation (4) (figure 12) for paints in various solvents are: 40-45 per cent (cyclohexane), 45-50 per cent (xylene and white spirit mixture), 55 per cent (ethyl acetate) and 40-45 per cent (butyl cellosolve). These values compare fairly well with the values compare fairly well with the values of CPVC obtained from other methods (Table 2).

Correlation of data with solubility parameters of solvents

1. Rheological parameters

The rheological parameter k_2 obtained from the slopes of equation 3, indicates the level of interaction among pigment, resin and solvent. The plot of k_2 versus solubility parameter (δ) of solvents (Figure 13) passes through a minimum. This indicates the optimum compatibility of binder and pigment with the solvents having δ-values corresponding to the maximum of the plot.

144
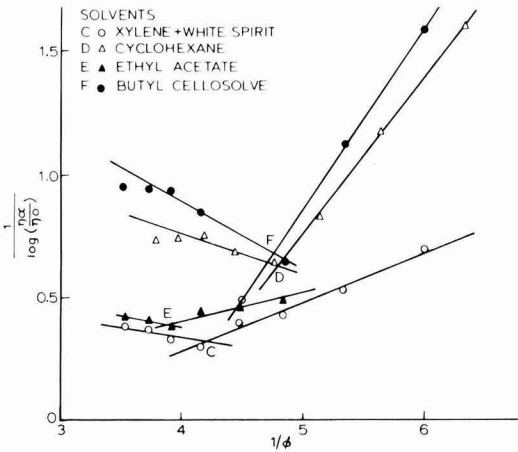
Figure 12. Plots of $1/\log(\eta\infty/\eta_0)$ as function of $1/\emptyset$ [equation (4)] for paints in different solvents

Figure 13. Rheological parameter k_2 (slopes of plots in figures 8 and 9) vs. solubility parameter of solvents

2. Limiting Shear Stress

The plot of limiting shear stress versus the solubility parameters of solvents (Figure 14) also indicates a range of δ-values where the compatibility among the ingredients of paint formulation is at an optimum. Solvents having their solubility parameters in this range are likely to be the good solvents for red iron oxide paints in alkyd medium.

Summary

1. The critical pigment volume concentration (CPVC) of red iron oxide alkyd paints is determined by using apparent viscosity data and found to depend on the nature of solvents used in the formulation.

2. The CPVC of the paints have also been determined by using the data obtained from standard and proposed equations.

3. The dependence of CPVC on solvents is attributed to the factors such as the interaction between solvent and binder as well as the affinity of the solvent for the pigment.

4. The paints exhibit pseudoplastic type of flow behaviour at shear rates corresponding 0.5 to 100 rpm speeds of Brookfield viscometer.

5. The intercept log k of the Power Law equation is found to depend on the content pigment of the paints as well as on the solubility parameter of solvents.

6. The equation proposed earlier for alkyd solutions is also found to hold good for paint dispersions.

7. The analysis of data by using Casson's equation indicates that the sag resistance of paints is least affected by changing the PVC or solvents but the brushability of paints is found to depend on these parameters.

8. The findings provide quantitative information about the degree of compatibility of solvents with binder and pigment in the formulations.

Figure 14. Limiting shear stress function "C" (intercepts of plots in figures 8 and 9) vs. solubility parameter of solvents

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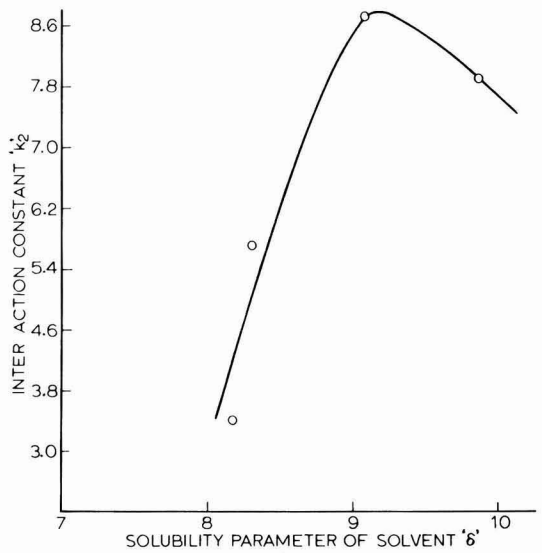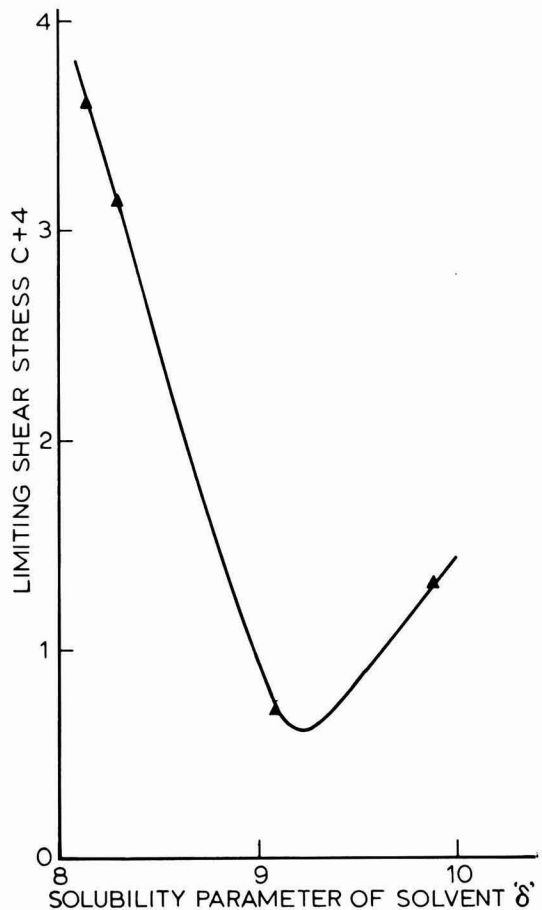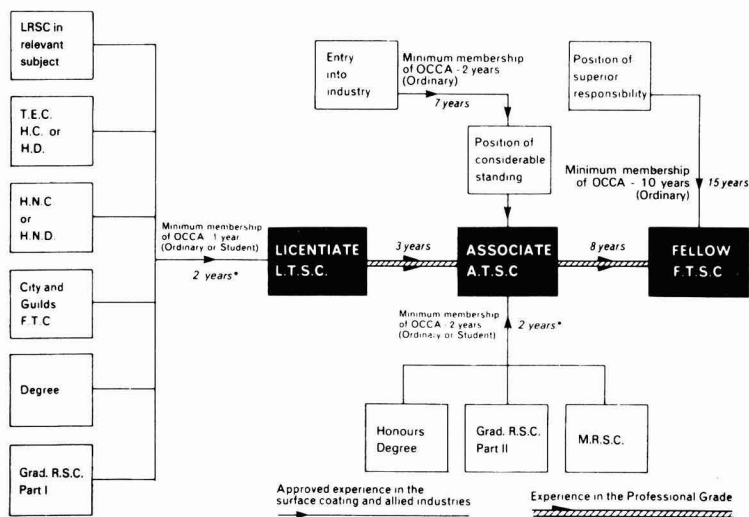
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Maleinization of rosin and isolation of maleopimaric acid

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Abstract

The reaction of the maleinization of rosin was optimized with respect to various reaction parameters such as temperature, time, and content of maleic anhydride. Rosin-maleic adducts were also prepared from the raw oleo-resin and its characteristics compared with that prepared from rosin. Maleopimaric acid was isolated from the rosin-maleic adduct by extraction and crystallization. The purity of maleopimaric acid was checked by determination of melting point, acid value, optical rotation, IR, NMR and mass spectra and modern analytical techniques like TLC, GLC and HPLC.

Introduction

Rosin is obtained by distillation of raw oleoresin. It consists of 90 per cent resin acids and 10 per cent non-acidic material. During distillation of oleoresin, the naturally present levopimaric acid isomerizes to other resin acids such as abietic, neoabietic and palustric acids[1-3]. All these acids react with maleic anhydride through Diels-Alder reaction mechanism under vigorous conditions to form maleopimaric acid[4 9].

Halbrook and Lawrence[10] studied the preparation of maleopimaric acid and fumaropimaric acid from pure abietic type acids and rosin and isolated maleopimaric acid by column chromatography. Harris[11] studied the conversion of the Diels-Alder adduct of rosin with maleic anhydride directly to fumaropimaric acid under the influence of alkali, high temperature and pressure. Kalnins and Dobelis[12] studied the reaction between resin acids and dienophiles at different temperatures in the presence of various catalysts like H_2SO_4, HCl, $ZnCl_2$ and $AlCl_3$ and reported that the differences due to the catalysts were most marked at lower temperatures. Smirnova and Paderin[13] prepared the adduct of levopimaric acid with maleic anhydride from 50 per cent turpentine solution of pine oleoresin using equimolar proportions of levopimaric acid and maleic anhydride. The adduct was purified by washing with turpentine oil and then with gasoline.

The main drawbacks with using the above methods have been the cumbersome techniques coupled with the uneconomical yields. In the present work various parameters of the reaction between maleic anhydride and rosin, such as temperature, time, and maleic anhydride content were studied. A simple technique for the isolation of maleopimaric acid from rosin-maleic adduct in economical yields has also been suggested. The method is much more convenient than the methods already reported.

Experimental

Materials

Rosin: N grade, acid value 166.0, softening point 90°C,

volatile matter 1.1 per cent, matter insoluable in toluene 0.1 per cent, and ash content 0.02 per cent.
Raw oleoresin: Comprising of 89.0 per cent rosin, 9.4 per cent turpentine oil, and 1.6 per cent water.
Maleic anhydride: Riedal, AR grade.
Toluene: BDH, LR grade.
Mineral turpentine oil (MTO): Commercial, distilled between 150 to 180°C.

Preparation of rosin-maleic adduct

From Rosin

Rosin (5 kg) was melted under an inert atmosphere in a three-necked flask fitted with a stirrer, themometer, and gas inlet tube. Maleic anhydride (1.45 kg) was added to the molten mass under continuous stirring. The temperature was then raised to 190°C and maintained for 2.5 hours.

From raw oleoresin

Raw oleoresin (1 kg) was taken in a four-necked flask fitted with a stirrer, condenser, thermometer, and gas inlet tube. It was heated to 100°C and maleic anhydride (258 g) was added slowly. The reaction mixture was refluxed at 175°C for 6 hours. Thereafter, turpentine oil was removed by distillation under a current of nitrogen gas.

The prepared rosin-maleic adduct was studied for acid value, free maleic anhydride content and softening point. The results are give in Table 3. The conventional method for the acid value determination was not found suitable in the case of the rosin-maleic adduct as it gave lower values. An indirect method was, therefore, used for acid value determination in which 1-2 g sample of the adduct was refluxed with 0.5 N alcoholic KOH solution for 1.5 hours and the contents titrated with 0.5 N HCl solution. A blank determination was also carried out simultaneously. Free maleic anhydride content was determined by titrating the aqueous extract of known weight of material with standard alkali. The softening point was determined by the ball and ring method.

Isolation of maleopimaric acid

The rosin-maleic adduct prepared as above was extracted in a Soxhlet apparatus with a solvent mixture of M.T.O. and toluene (10:1) for 8 hours. The extract was concentrated to about 40 per cent solids and allowed to stand at 20°C overnight when crude maleopimaric acid crystallized out. This was purified by repeated crystallization (3 times) from the same solvent mixture. The final yield of maleopimaric acid was 52 per cent of the theoretical.

The Isolated maleopimaric acid was characterized by determining the acid value, melting point, optical rotation

Time (hrs)	150°C		170°C		180°C		190°C		210°C	
	AV	FMA(%)	AV	FMA(%)	AV	FMA(%)	AV	FMA(%)	AV	FMA(%)
1.0	343.4	3.1	358.0	2.4	362.0	2.4	368.0	2.4	369.0	0.9
2.0	359.0	2.4	363.0	1.9	366.4	1.8	376.6	1.7	378.7	0.4
2.5	359.6	1.9	366.4	1.5	369.5	1.5	380.0	1.6	380.4	0.2
3.0	361.4	1.6	369.0	1.3	371.4	1.3	380.6	1.4	380.6	0.2
4.0	365.6	1.4	370.2	1.1	374.0	1.1	380.2	0.9	375.0	0.1
5.0	366.0	1.3	370.4	0.9	376.0	0.9	380.3	0.8	374.0	0.1

AV   = Acid value determined after removing free maleic anhydride.
FMA = Free maleic anhydride.

Maleic anhydride (% by weight of rosin)	Acid value* of the adduct	Free maleic anhydride in the adduct	Softening point of the adduct (ball and ring) (°C)
32	380.4	2.14	112-113
30	380.0	1.60	112-113
29	380.0	0.60	112-113
28	373.6	0.26	110-111
25	354.8	0.22	109-110

*Acid value determined after removing free maleic anhydridge.

(3.3 per cent solution in methanol), IR (in KBr disc), NMR (in deuterated acetone on varian T-60A NMR spectrophotometer) and mass spectroscopy. The purity of the maleopimaric acid was further established by TLC, GLC of the methyl and silyl esters on 1.5 m × 4 mm glass column packed with 3 per cent SE-30 supported on chromosorb W (80-100 mesh), and run isothermally at 275°C using nitrogen gas as carrier gas at a flow rate of 50 ml/min, and HPLC of maleopimaric acid as well as its methyl ester on μ-Bondapak C_{18} column using ethyl acetate as solvent.

Results and Discussion

Rosin-maleic adduct

Table 1 shows the reaction parameters, viz. temperature and time, required for the formation of rosin-maleic adduct. The rate of formation of adduct increases as the reaction temperature is increased up to a maximum of 190°C at which the adduct formation is complete in 2.5 hours which is measured by the rise in the acid value of the product. Further increase in temperature brings no significant improvement in the reaction rate. Figure 1 shows the relationship of temperature and reaction time with the rise in acid value of the product during maleinization. The reaction rate, as stated above, can be distinctly seen to be improving with the rise in temperature up to 190°C. A fall in the acid value of the product is observed at 210°C after 3 hours, indicating a possibility of decarboxylation at higher temperatures. The same
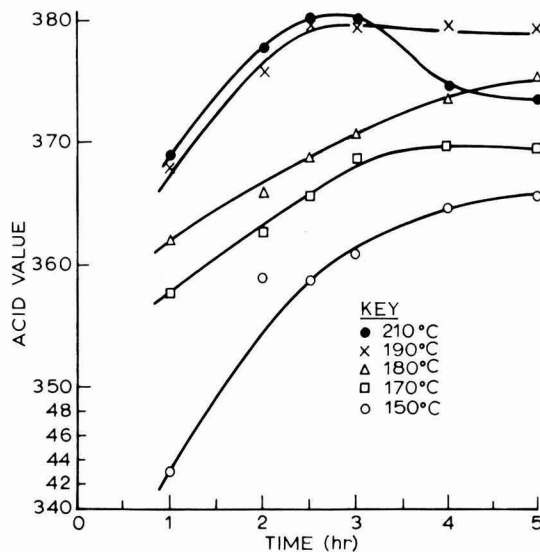

Figure. 1. Maleinisation of rosin (30%) at different temperatures and timings.

phenomenon has also been observed by Halbrook and Lawrence[10] and Vassiliev[14] at 200°C and above. Therefore, 190°C temperature at 2.5 hours reaction time is the optimum for the maleinization reaction.

Table 2 shows the results of experimental runs of maleinization of rosin at 190°C for 2.5 hours using varying quantities of maleic anhydride. The data shows the optimum quantity required is 20 per cent by weight of rosin since the acid value and the softening point of the product remain constant even with higher amounts of maleic anhydride. At the same time, with 28 per cent and lower maleic anhydride contents complete maleinisation of rosin is not achieved as is indicated by low acid values and softening points of the resulting adducts.

Table 3 shows the characteristics of rosin-maleic adduct samples prepared from rosin and raw oleoresin. It is observed that the adduct prepared from rosin gave higher acid value and softening point than the adduct obtained from oleoresin. This can be explained from the fact that the turpentine oil present in raw oleoresin contains some conjugated terpenes which may simultaneously react with maleic anhydride to give a hydrocarbon adduct having a much lower softening point. Therefore, the adduct prepared from rosin only was taken for further studies for the isolation of maleopimaric acid.

Figure 3. NMR spectrum of maleopimaric acid (in $(CD_3)_2CO$).

The NMR spectrum (Figure 3) is characteristic of maleo-pimaric acid:

δ0.7(3H)	angular − CH_3
δ0.9(3H)	$-\overset{\overset{\displaystyle COOH}{\displaystyle \mid}}{\underset{\displaystyle \mid}{C}}-$ CH_3
δ1.0 − 1.2(6H)	$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{-CH}}$ (doublet)
δ5.6 (1H)	$-\overset{\mid}{C}=\overset{\mid}{C}-H$
δ7.6 − 7.8(1H)	$-COOH$ (D_2O−exchangeable)
δ3.0 (2H)	$\overset{\displaystyle CH-\overset{\overset{O}{\|\|}}{C}}{\underset{\displaystyle CH-\underset{\underset{O}{\|\|}}{C}}{}}$ O (multiplet)
δ2.2 − 2.4(1H)	$\underset{/}{\overset{\mid\,\mid}{}}$ CH (Allylic methine)

The purity of this acid is further evident as single entity from TLC, GLC (Figure 4) and HPLC (Figure 5). The Mass Spectrum (Figure 6) of the acid indicates M 400 analysed for $C_{24}H_{32}O_5$. The fragmentation pattern also conforms to its structure

$M^+ 400; M^+ -28 (C=O) 372; M^+ -72(\overset{-C}{\underset{-C}{}}O)328; M^+ -98 (\overset{CH-C}{\underset{CH-C}{}}O)302$

which is the molecular weight of levopimaric acid, confined by base peak of mass spectrum.

Table 3
Characteristics of rosin-maleic adduct samples prepared with rosin and raw oleoresin

Characteristics	Maleic adduct prepared with	
	Rosin	Raw-oleoresin
Acid value (Maleic anhydride free adduct)	380.0	352.0
Free maleic anhydride (%)	0.6	nil
Softening point, (*C)	112-113	105-106

Maleopimaric acid

The maleopimaric acid isolated from the adduct had an acid value of 420 which is in agreement with its theoretical value. It had a melting point of 228.5°C and optical rotation as $[\alpha]D^{26.5 \text{ C}} - 32.10$ which is in agreement with the values reported by Loeblich et al[8].

The IR spectrum (Figure 2) of the product shows bands at 1840 and 1775 cm^{-1} attributed to anhydride groups. Another medium band appears at 1685 cm^{-1} due to cyclic olefins. Normal bands at 2800 to 2500 cm^{-1} (OH stretching of free carboxylic groups and 1440 cm^{-1} (carboxylate) are also present in the spectrum.
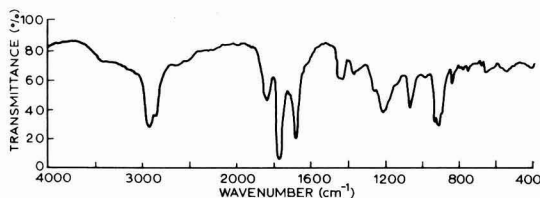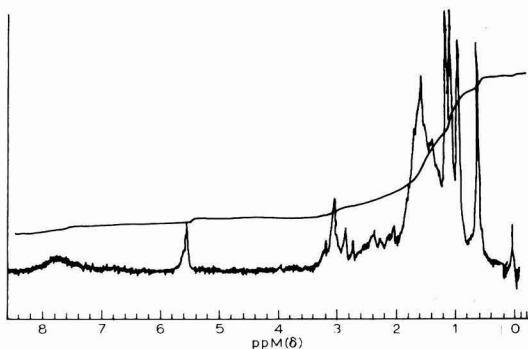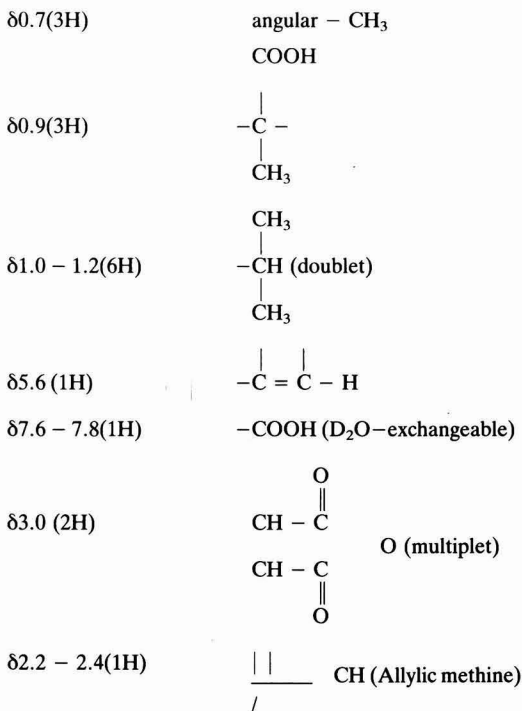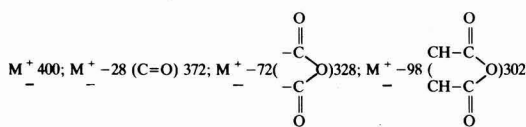

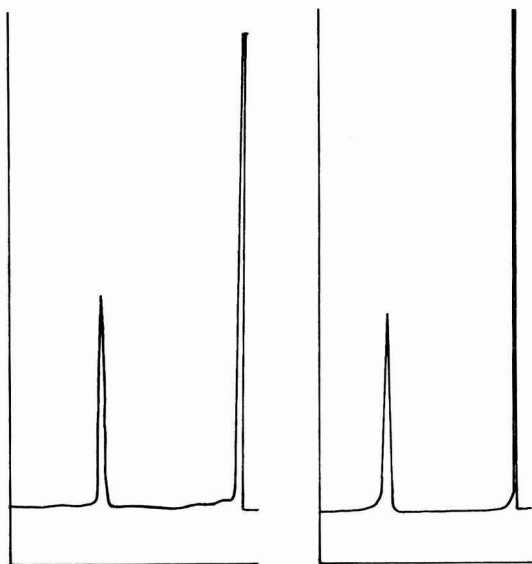Figure 2. IR Spectrum of maleopimaric acid (KBr disc).

Figure 4. Shown left GLC of silance derivative of maleopimaric acid (Tri-sil, 1.0ul and 275°C; column 3% SE-30). Shown right GLC of methyl ester of maleopimaric acid (3% SE-30, 0.6ul and 275°C).
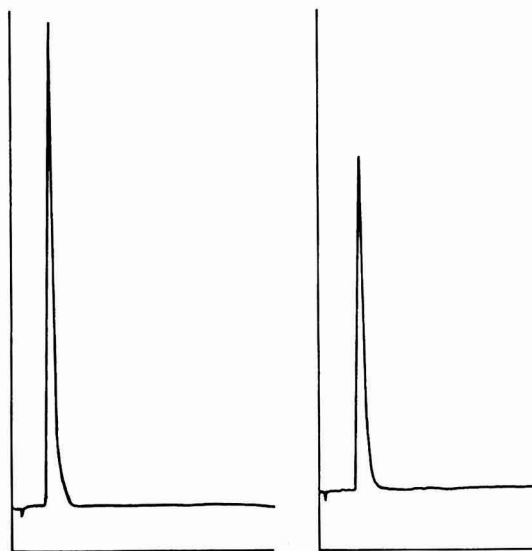

Figure 5. Shown left HPLC of maleopimaric acid (1.0 ml/min.). Shown right HPLC of methyl ester of maleopimaric acid (1.0 ml/min.).

The present acid value 420 was obtained by reflux method adopted in the present work. With the conventional method the acid value came to be only 280, accounting for only two carboxylic groups. It is, therefore, quite evident that the third carboxylic group is somewhat sterically protected after maleinization and does not react with alkali under ordinary conditions.
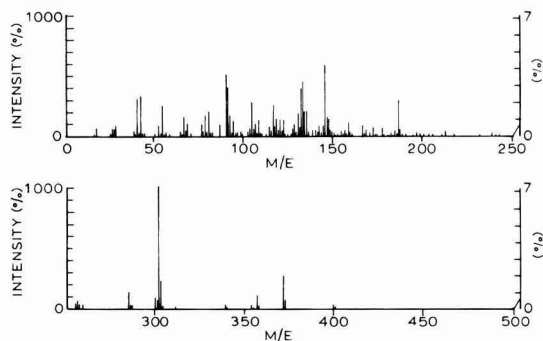

Figure 6. Mass spectrum of maleopimaric acid.

Conclusions

The optimum reaction parameters for maximum degree of maleinization of rosin are a temperature of 190°C and time period of 2.5 hours with 29 per cent maleic anhydride. Maleopimaric acid was obtained in good yield using a simple extraction and crystallization method. Maleopimaric acid being a polybasic acid can definitely have better utilization in surface coatings, printing inks, polymers and adhesives industries.

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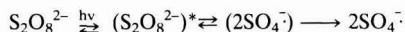
next month's issue

corrigendum

The photochemistry of the peroxodisulphate ion in aqueous alcohol solutions by C. G. Roffey (*JOCCA*, 1985, 68 (5), 116).

On page 117, column 1, paragraph 1, third line:
($e = 460$ M^{-1}cm^{-1}) should read ($\epsilon = 460$ m^{-1}cm^{-1}).
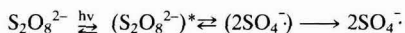
On the same page, paragraph 3, line 4; hydrogen ions should read hydroxide ions.

On page 119, column 2

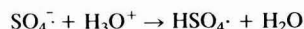Equation 1 should read

$$S_2O_8^{2-} \underset{\rightleftarrows}{\overset{h\nu}{}} (S_2O_8^{2-})^* \rightleftarrows (2SO_4^{-\cdot}) \longrightarrow 2SO_4^{-\cdot}$$

Equation 6 should read

$$S_2O_8^{2-} \underset{\rightleftarrows}{\overset{h\nu}{}} (S_2O_8^{2-})^* \rightleftarrows (2SO_4^{-\cdot}) \longrightarrow 2SO_4^{-\cdot}$$

Equation 7, HSO$_4\cdot$ formation, should read

$$SO_4^{-\cdot} + H_3O^+ \rightarrow HSO_4\cdot + H_2O$$

On the same page, the quantum yield for cerium (IV) formation, should be 1.05 ± 0.14.

The ISBN number in Figure 1 and Reference 16 should read 0471 10063 3.

Unfortunately the author did not receive his proofs on time to make the above corrections. We apologise for any inconvenience caused.

occa meetings

London Section

Hyperdispersant technology

The fifth technical meeting of the 1984/85 season was held on Thursday 28 February 1985, at the Pearly King, Bromley High Street, Bow, London, E3.

As a token of remembrance to Mr F. D. H. Sharp, the late Chairman of the London Section, who died suddenly and unexpectedly recently, a minute's silence was observed before the meeting started.

Then, a very informative talk was given by Dr J. Toole, of ICI Organics Division, on the subject of Hyperdispersant technology.

Dr Toole explained that Hyperdispersants was a generic name to a new class of pigment dispersing aids. They were different from Surfactants, which were usually used in aqueous media. Hyperdispersants were designed to operate in solvent media.

The mechanisms by which the Hyperdispersants attached themselves to the surface of pigment particles was discussed, also the continued effect as pigment particles were fractured to smaller units.

These new Hyperdispersants are now being sold under the trade name of Solsperse in a series numbered from 3,000 to 20,000.

The choice of Solsperse to be used depended on the type of pigments to be dispersed, examples of inorganic pigments and extenders specific pigment dyestaffs such as phthalocyanine blues and greens, carbon blacks, azo dyes, and the types of solvents to be used, i.e. low polarity hydrocarbons and esters and polar solvents, e.g. alcohols, ketones, etc.

The effects of dispersing pigments using Hyperdispersants using triple roll mills, Ball mills and modern dispersing machinery to effect energy saving, higher pigment concentrations, intensification of colour strength developed was demonstrated through a series of well prepared colour slides.

Dr Toole explained that these new materials had first

been introduced to the printing ink industry and had been well received.

Hyperdispersants were now being introduced to pigment manufacturers, the paint, plastics and other allied industries.

Reference was made to the physical characteristics of Solsperse Hyperdispersants, also their solubility and compatability with various solvents and how these affected their use for different applications.

The talk was followed by a question period, and it became apparent that much work was being done in several industries; experiences were shared. Several questions remained unanswered because of work still in hand.

The vote of thanks was proposed by Norman Locke for a very informative, well prepared talk with slides. He felt there was little he could add to the discussion because of its admirable presentation and the frankness of the discussion which followed.

Mr Ken Arbuckle closed the evening with thanks to ICI for their hospitality in sponsoring the evening. The attendance of nearly 100 represented the largest attendance for a technical meeting this session.

J. H. Tooth

The glass transition temperature and internal strain of paint fumes

At the final technical meeting of the 1984/85 session held at the Pearly King, Bow, on 21 March 1985, Mr John Prosser and Mr Tom Bullett of the Paint Research Association, Teddington, gave a paper on "The glass transition temperature and internal strain of paint films". The meeting was chaired by Mr K. H. Arbuckle, and there were 20 members and guests present.

Mr Prosser first discussed the measurement of glass transition temperatures (Tg), favouring differential thermal analysis. When measuring Tg the rate of testing should be specified, as rapid changes give different values from slow changes—some relaxation of internal strain occuring when conditions change slowly. Pigmented films generally have a Tg value about 5°C higher than the corresponding unpigmented films. The concept of "free volume" in a film was considered, being essentially the spaces between the macromolecular polymer chains. The free volume is increased by the presence of solvent, plasticiser or low molecular weight species—the latter present initially or produced by degradation during ageing, and may be water soluble. Ageing, more particularly outside exposure or accelerated weathering, leads to loss of these components of the film and hence to an increase in Tg.

The internal stress of films is related to the Tg. It may be measured by applying films to thin steel shims; stresses set up during drying or curing cause the shims to bend, and the force required to straighten them is a measure of the internal stress. The value is affected by solvent content, temperature and humidity, also by the film thickness.

Mr Prosser suggested that when measuring changes in physical properties of paint films to assess their durability the films should first be subjected to a week's accelerated weathering, and that the measurements then made should be regarded as the initial values.

Mr Prosser and Mr Bullett replied jointly to questions raised in the discussion, and a vote of thanks was proposed by Dr H. Hamburg.

T. A. B.

Bristol Section

Lectures given in the second half of the 1984/85 session

The lectures given in the second half of the session were again of much interest and the attendance in general was, as expected, greater when a buffet was available. The meetings were chaired by Mr R. Saunders and the interest in the subject matters discussed was clearly evident by the number of questions asked at the end of the lecture.

The lecture given on 29 January 1985 on Hazard Labelling and European Legislation entitled "Hanging on" by Mrs D. Cornelius of Cray Valley Products was exceptionally well attended since it was a joint lecture with the BPVL Club. A large number of members travelled from Birmingham to hear the lecturer. The legislation both British and EEC on the labelling of products in the paint and printing ink industries was clearly described, including the difficulties of being able to find the space available to print all the necessary data on small volume containers. The controversial points at issue such as TLV versus Occupational Exposure Limits were highlighted and the ever increasing number of additional requests necessary to comply with the law. Difficulties which small companies were experiencing such as the obligations of the "Manufacturers or Suppliers" were discussed. The interest in the topic which becomes law in 1986 was evident by the large numbers of questions asked at the end of the lecture. Mr Fowkes proposed a vote of thanks to the lecturer.

The second lecture of 1985 took place on the 26 February 1985 when the original speaker was unfortunately unable to attend. However his place was taken at short notice by three of his colleagues Messrs. Musgrim, Nichols and Tew, who jointly gave an excellent account of the preparation, properties and performance of "Newer Organic Silicone Resins" manufactured by Croda Resins Ltd. The manufacture of the extensive range of these resins was described and the properties of the particular range of resins discussed. The effect of silicone addition to the polymer with regard to heat resistance and general physical properties was explained by a slide presentation and

commentary and use of a overhead projector. The properties of the Plastokyd Resins described during the lecture was made available to those requiring this data from a useful selection of technical information sheets.

The final lecture of the series was given on 19 March, when Mr Peter Gallagher of Cabot Carbon Ltd., gave a lecture on "The Selection of Carbon Blacks for Inks and Paints". This was a most interesting lecture, giving, as it did, details of the modern manufacturing methods to obtain the large range of carbon black pigments now available. The manufacturing techniques of obtaining carbon blacks with different particle sizes was described including pelletization. The need for careful selection of the oil feed stock to insure the quality of the pigment was stressed. However the adventitious of contamination of a feed stock with sea water led to products with structure. Technical data on all the products in the range was made available to those present.

Question time was, as usual, well supported and included questions on the role of carbon black in motor tyres.

The vote of thanks was given by the Chairman.

J. R. Taylor

Midlands Section

Hyperdispersant technology

The Fourth Technical Meeting of the Midlands Section was held on the 21 February 1985 at the Clarendon Suite, Stirling Road, Edgbaston, Birmingham.

Members and guests heard Dr J. Toole of I.C.I. Organics Division speak on: "Hyperdispersant Technology". Dr Toole said that the term "Hyperdispersant" had been devised by I.C.I. Organics Division to describe a novel class of dispersing aids. These dispersants are very effective in the dispersion, deflocculation and stabilisation of solids in organic liquids. The hyperdispersant molecule is made up of two parts, one part is a polymeric chain having a strong affinity for the solvent while the other part, the anchor group, is strongly absorbed by the pigment surface, because of the complexity of the pigment and extender surfaces a small range of hyperdispersants have been produced.

The speaker outlined some of the advantages that had been found by using these dispersants. Energy savings can be made by increasing the mill charge also by higher pigment concentrations leading to greater productivity. By carrying out the dispersion in solvent or weak resin solution a number of paints can be made from one mill-base.

The dispersants were produced initially for the ink industry where they have been well received. The next development was air-drying systems including chlorinated rubber paints. Q.U.V. testing was carried out on these systems and proved to be satisfactory. Dispersants for

stoving systems have been tried with some success but the work is not yet fully completed. The final stage will be the automotive paints.

Dr Toole amply illustrated his talk with numerous slides and in conclusion outlined some of the dispersants that had been produced. He gave lists of some of the pigment types and their recommended dispersant that had been successfully dispersed in the laboratory.

The interest shown in the talk was reflected by numerous questions asked and Mr R. Devenish finally brought the meeting to a close with the vote of thanks to the speaker.

B. E. Myatt

Manchester Section

Gel-permeation chromatography

On Monday 1 April 1985, Dr R. A. Ellis of Crown Paints gave a most interesting talk entitled "Gel-permeation Chromatography" to a large audience at Crown Paints, Darwen. The lecture was followed by a sumptuous buffet meal in the canteen at Crown House, provided most generously by Crown Paints.

Liquid chromatography can be divided into four major classes:

- Liquid – Liquid
- Liquid – Solid
- Ion exchange
- Gel-permeation

Early work on chromatography went largely unheeded and it was not until the '40's that Martin and Sink developed the procedure and eventually showed that the eluting substance could be a gas, which led to the development of commercial GLC apparatus.

In the early days of gel-permeation chromatography it was realised that this is a size rather species separation technique, smaller species moving into the pores in the column material. The original name for the technique was Gel-filtration.

Until 1984 gel-permeation was only applicable to aqueous systems but then the development of new base materials allowed the use of organic solvents.

Column packings are divided into three types; materials suitable for aqueous systems, materials for organic systems and a few materials such as porous silica and glass which are suitable for both systems.

Packings can also be divided by their structural strength into hard and soft gels. Modern methods involve elution

under high external pressure which causes the collapse of soft gels.

Hard gels are produced from macro-reticulate polystyrene or porous glass.

The polystyrene is produced by solution polymerisation in a mixture of toluene and dodecane. The balance between solvent and diluent affects the final pore size, increase in the toluene content of the mixture produces smaller pores.

Porous glasses are produced by thermal treatment of borosilicate glass followed by chemical leaching. The resulting structure is highly polar and can lead to adsorption of the sample. It is essential to de-activate the surface, especially with aqueous media.

A further development in this field is hydrodynamic liquid chromatography. A liquid solvent flows through a column packed with non-porous spheres with coated surfaces. The flow rate of the sample through the column varies with the attraction of the species to the sphere

surface and the size of particles in the stream. Large particles will only experience rapid flow rate in the centre of the stream, small particles will approach the sphere surface in the slower part of the stream thus achieving separation.
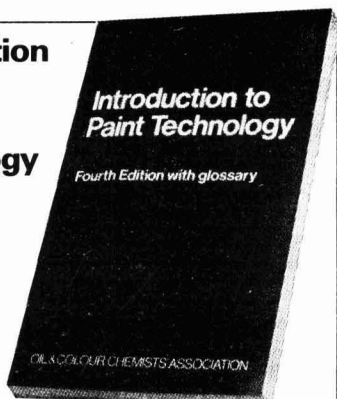
Dr Ellis gave details of the system as set up in practice with the separated sample components being identified by the use of a differential refractometer linked to a recorder.

By the use of such apparatus in the field of resin chemistry it is possible to follow the reaction in an alkyd cook, compare laboratory and commercial resins, compare binder systems, follow drying processes and observe the adsorption of resins onto pigments.

After the well-illustrated talk Dr Ellis answered a series of questions from the audience. A vote of thanks was offered by Mr Mike Nixon.

R. G. Handley

reviews

This is a comprehensive treatise on paint technology written by academics and a number of widely experienced members of the staff of BASF Farben + Fasern AG. In seven major sections it covers raw materials and paint manufacture, properties and testing of liquid paints and paint films, application methods, the coating of metals and organic substrates, decorative paints including emulsion paints and paint systems for timber and plastics, industrial hygiene and environmental protection related to German legislation. DIN standards and a glossary of terms followed by an extensive bibliography complete the volume. Fifteen years have passed since the 10th edition and the book has been completely rewritten and reorganised and in spite of its title one finds, in contrast to the earlier edition, very few, if any, references to specific products of BASF. It is an excellent introduction for technicians and a useful reference work. One small criticism by this reviewer is its arrangement whereby the index of contents precedes each of the seven chapters instead of appearing as a whole at the beginning of the book. However, the book boasts a good subject index.

Reader Enquiry No. 30

This is a practical handbook for technicians working in painting shops and concerned with application of all types of surface coatings. It covers not only all methods of applying industrial paints and the relevant equipment, but also types of paint preparation, quality control, safety measures and a host of other information. The book appears annually so that information is regularly updated and the introductory chapter relates to current trends and developments. It is bound in durable flexible plastic and its size (10.5×15 cm) enables the user to slip it into his pocket for handy reference. The last 40 pages or so serve as a register of sources of supply for equipment and materials.

*Reader Enquiry Service No. 31*

H. R. Hamburg

company visits

Contraves launch Contalab

Contraves Industrial Products Ltd, Ruislip, a division of the Oerlikon-Bührle group, Zurich, are best known in the paint and ink industries for their range of precision Viscometers. In April they introduced their new "CONTALAB" system to UK customers, demonstrating this fully automated computer-controlled laboratory reactor system in operation.

Contalab consists basically of a jacketed l-litre reaction vessel fitted with a reflux condenser and a stirrer; all parts in contact with the reactants are of glass or PTFE. Temperatures in the jacket and in the reaction vessel can be controlled with an accuracy of $\pm 0.5°C$ within the range $-30°C$ to $200°C$. The pH in the reaction vessel can be controlled within ± 0.1 pH. The internal pressure in the reaction vessel can be controlled within ± 1.5 mbar, up to atmospheric pressure. Inert gas purging may be used if required. Up to five different liquid reagents may be pumped into the reaction vessel in weighed amounts up to 800g, accurate to ± 0.1g, alternatively an optional attachment permits additions of pourable solids. For safety the system incorporates alarm limits for the various measurements—when these are exceeded an alarm is sounded and/or the reaction stopped.

To operate, the timing and details of each successive stage in the complete chemical process are fed into the computer via a keyboard, using a simple question-and-
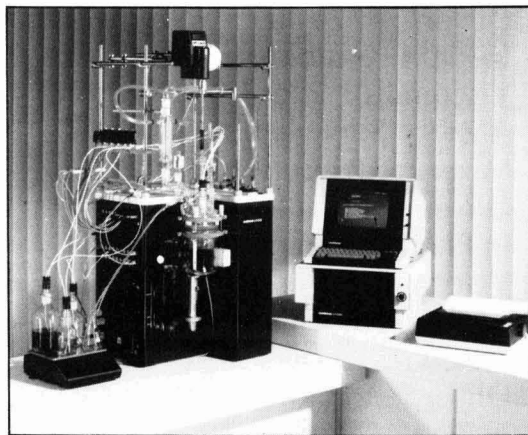
Contalab

answer procedure; the computer then controls the process, compiles the data and records the results. The process details measurements at the various stages and the final results are stored on discs from which they can be retrieved as a visual display or as a print-out. For repeat runs the process details can be modified if required without re-entering the complete programme.

The Contalab permits complex chemical reactions to be

undertaken more accurately than by manual control, saves laboratory staff time and, because of the in-built safety limits, can be used 24 hours a day. Practical laboratory experience is that with the same staff the number of experiments per week is increased by a factor of two or three and that the results are more reproducible than with manual control.

T.A.B.

PPG buys into the UK paint industry.

On 29 March 1985, International Paints automotive division at Ladywood, Birmingham became a wholly owned subsidiary of PPG Industries of Pittsburg, USA. The new company will be known as PPG Industries (UK) Ltd.

The plant specialises in supplying the automotive and aircraft industries, and has been a licensee of PPG Technology for many years.

After the takeover the vice president of the Coatings & Resins Group, Malcolm Slaney, talked to every one of the 400 employees on the site, and explained to them that the company intended to expand existing research and production facilities with the objective of securing a larger share of the UK market and thus ensure a long term future for the company.

The entire management of the plant has been retained, with Austin O'Malley a former director of International Paints as chief executive of the company.

PPG technology is now applied to over two/thirds of all Free World car production, and Ladywood supplies all the British car manufacturers as well as the car refinishing industry. It has a major share in the aircraft speciality coating industry.

The two comments by Malcolm Slaney and by Austin O'Malley sum up PPG (UK)'s philosophy better than any transcription can do:

"The acquisition of the International Paint business and factory at Ladywood completed our plan to service, through local manufacture, the entire European car industry. Motor car production, especially in Europe, is a trans-national business: PPG is the only Automotive Coatings supplier capable of matching this spread".

"We at Ladywood are delighted at the prospects this acquisition opens up. The combination of PPG's technological resource and the professional skills of the workforce at Ladywood will create an even more powerful force in the automotive paint business".

D. S. Newton

Raw material cost increases threaten UK paint margins

Figures released by the Paintmakers' Association of Great Britain are said to reveal that rising raw material costs used in the manufacture of paint are now reaching a point where the profitability of the industry as a whole is under considerable threat.

Raw material costs for the first three months of 1985 rose by 9.7 per cent, more than twice the equivalent rise in sales prices of 4.1 per cent, and well above the current rate of inflation. During March alone, raw material costs rose by 11 per cent.

A particularly disturbing trend to emerge recently has been the sharp increase in the cost of titanium dioxide and aromatic solvents. Raw material costs currently account for approximately half the manufacturing costs of a tin of paint. The increases in their costs have been consistently higher than equivalent sales price increases over a period of some two years. Since mid-1984 the discrepancy has grown from 8.0 per cent to the current 9.7 per cent, and is putting the industry under considerable pressure.

Export sales of paint remain buoyant and although only increasing by 0.6 per cent this quarter remain at record levels—up to 6.9 per cent year on year. Building paint sales volume rose by 1.0 per cent but only because of higher retail sales, since trade paints were down by 3.5 per cent.

In the beleaguered industrial sector, where along with the rest of the economy paintmakers have experienced the worst effects of the recession, 1985's first quarter was down by 1.3 per cent.

Overall, paint sales have stood still during this quarter compared to the same period in 1984, and hardly above the similar 1983 period, but up by 2.8 per cent on a year on year basis.

Michael Levete, Director of the Paintmakers' Association, commented: "The most worrying problem for the industry as a whole is the continuing acceleration in the cost of raw materials essential for paint manufacture".

Reader Enquiry Service No. 32

Consortium sets up colloid technology service

A new industrial colloid technology service is being set up by the Harwell Laboratory (UKAEA) and the University of Bristol. The new venture—The Colloid Technology Consortium—is being launched with initial financial assistance from the Department of Trade and Industry.

The consortium will help companies make effective use of the latest developments in colloid science and technology. Aimed at industry generally, but at small and medium sized firms in particular, it will provide both consultancy and research and development services.

A wide range of organisations manufacture, employ or need to dispose of, colloid materials. Users of the new service will be drawn from the chemical, oil, food, dye-stuffs, paint, printing and coating, adhesive, detergent, cosmetic, textile, ceramics, mineral processing, agrochemical, pharmaceutical and bio-technology industries.

The consortium brings together the expertise of Harwell, Bristol University's Department of Physical Chemistry, and the Industrial Colloid Advisory Group (INDCOLLAG), which has been providing a colloid consultancy service for small companies since 1972. It also combines the analytical and research facilities of Harwell and Bristol, and the consortium will undertake research and development on new materials and products, advanced methods of materials characterisation, and on process and instrument development.

Reader Enquiry Service No. 33

New distributors for Paraplex plasticisers

Croxton & Garry Ltd have recently been appointed as the new distributors covering UK and Eire for the Paraplex G series and Monoplex range of plasticisers, taking over this distributorship from Rohm & Haas (UK) Ltd. The Paraplex G range consists largely of polymeric plasticiser grades based on different molecular weight polyesters, offering good durability, low volatility with absence of migration and hydrocarbon extraction. These properties find applications particularly in surface coatings, rubbers and thermoplastics. Within the Paraplex G range, epoxidised soya bean oil is also offered as a general plasticiser and a heat and light stabiliser for PVC.

Reader Enquiry Service No. 34

New pigment grinding medium

Capricorn Chemicals Ltd., have announced the introduction of Lanco Disperse 10 UN, a new pigment grinding medium from the range of G. M. Langer and Co. KG, of Bremen. Based upon a low viscosity acrylic resin, it is said to be designed for the manufacture of concentrates with high pigment loadings.

Lanco Disperse 10 UN is said to display excellent compatability characteristics with a wide range of resins (including polyesters and polyurethanes), solvents such as esters, ketones, alcohols, aromatic and aliphatic hydrocarbons, and plasticisers. It can be considered for use in air drying, stoving or two pack systems without detrimental effects on the cured film.

The product can be used to produce high quality pigment concentrates with good viscosity stability, uniform particle size and resistance to flocculation, on triple roll, sand, pearl or ball mills, even when using "difficult" pigments.

Reader Enquiry Service No. 35

New computer programme for labelling

In January 1986 the Health and Safety 1984 Regulations regarding the labelling of substances which may be regarded as dangerous, toxic etc. becomes obligatory under the act "The Classification, Packaging and Labelling of Dangerous Substances Regulations 1984".

It will then be necessary to print the correct labels showing any of the listed substances which may be present in the formulation together with the symbols and essential phases and hazard warning signs for the dangerous substances present including lead compounds, etc.

A user-friendly computer programme is now available from Ault & Wiborg Paints Ltd., which is said to cover a wide range of substances used in the paint, varnish, polymer, printing ink and adhesive industries. This programme can it is claimed be enlarged if necessary to cover other industries which come under the above regulations.

It is simple and quick to use and is a necessary adjunct to both the laboratory and works to ensure that a product complies with the regulations.

A printout can also be obtained which can be used as a hazard data sheet for supply to customers, or as the basis for provising shop floor information.

Reader Enquiry Service No. 36

Newcastle Section

Annual Ladies Night

The Annual Ladies Night was once again held at the Five Bridges Hotel, Gateshead, on Friday 15th February 1985. The function was attended by 185 people and included the President and Chairman from the Manchester, Scottish, Midlands and West Riding Sections and their Ladies. The Director and Secretary Mr R. H. Hamblin was also in attendance.

After an excellent meal, the Newcastle Section Chairman, Mr Ion B. Bolam proposed a toast to the Ladies and Guests and the President, Mr. C. N. Finlay, proposed a toast to the Newcastle Section.

Music was provided by the George Rowell Orchestra who catered for all tastes in a very professional way.

H. B. Fuller

Shown (from left to right) at the Newcastle Ladies night are, in the back row: Mr H. Fuller, Mr A. McKendrick, Mr I. B. Bolam, Mr C. N. Finlay, Mr H. Young, Mr G. Robson, Mr E. C. Wallace and Mr R. H. Hamblin; in the front row, Mrs J. G. N. Smith, Mrs McKendrick, Mrs Bolam, Mrs Finlay, Mrs Young, Mrs Robson and Mrs Wallace.

Investigative Technologist

Coates Brothers Inks Ltd. require an Investigative Technologist currently employed in the surface coating industry and using instrumental separative and identification techniques.

The successful candidate will join a small team of chemists who are involved in a wide range of investigations providing a service to our Research and Development Departments. These investigations will involve all types of inks and related products.

The job will provide:-

1. Opportunities for the individual to clearly demonstrate interpretive and innovative skills, associated with analytical and surface coating problems and formulations.
2. Scope for career advancement not only in analysis but in many functions within a technically based organisation.

It is expected that suitable candidates will be between 25-40 years and be fully familiar with modern industrial techniques and the raw materials used in the surface coating industry.

The salary is negotiable, the usual fringe benefits apply.

Applications should be in writing with full personal and career details to: **Mrs. C. M. Clark, Personnel Officer, Coates Brothers plc, Cray Avenue, St. Mary Cray, Orpington, Kent BR5 3PP.**

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SURFACE COATINGS

VOL 2–PAINTS AND THEIR APPLICATIONS

Prepared by OCCA Australia

Surface Coatings was first published in 1974. Since then the industry has undergone dramatic and rapid changes. For the second edition the book has been split into two volumes, the first covering raw materials and their usage, the second paints and their applications. Volume 1 was published in the autumn of 1983.

Volume 2 gives a comprehensive overview of decorative and industrial paints. Cross references to appropriate chapters in *Volume 1* are provided and the index covers both volumes. Revised and rewritten by over 80 expert contributors from industry, research institutes and universities, the books represent the most up-to-date reference available on paint technology.

Volume 2 is available in December by placing orders now (prepayment only) through the Oil & Colour Chemists' Association at £32.50 (inc. p&p in the UK) plus £3.00 for orders sent overseas by surface mail.

Volume 2 – Hardback – 480 pp.

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