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Effects of Abietic Acid Derivative Rosination on C.I. Pigment Yellow 13

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ABSTRACT

C.I. Pigment Yellow 13 was rosinated with abietic acid and the abietic acid derivative, Staybelite, at up to 40% loading. The crude pigment, recrystallised pigment and rosin coated pigment preparations were examined by solid-state NMR spectroscopy and by powder X-ray diffraction. The primary effect of the rosination procedure is to increase the crystalline order of the pigment. No evidence was found for any specific pigment–rosin interactions. © 1997 Published by Elsevier Science Ltd

Keywords: C.I. Pigment Yellow 13, solid-state NMR, powder X-ray diffraction, rosination.

INTRODUCTION

Rosination has been used commercially for many years to enhance the properties of commercial pigments without any detailed understanding of the mechanism of the action of the rosin on the pigment or the interactions involved. Pigment rosination is used to influence the surface properties of the pigment particles. The presence of rosin controls crystal growth, influencing transparency and dispersibility, reduces aggregation and agglomeration in finishing, drying and grinding, so improving dispersibility. Pigment rosination is also used to reduce interfacial tension, which positively influences the dispersibility due to the improved wetability in the application system.

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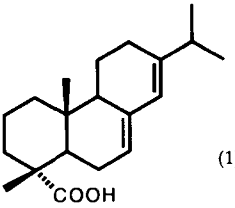
The amount of rosin used, together with the point in the synthesis at which it is added, are important factors. Addition of rosin during the early part of pigment synthesis means that the rosin is adsorbed by the crystal nuclei, thereby changing the crystal growth pattern. The resultant small particles give rise to certain improved pigment characteristics such as colour strength, gloss, transparency and purity. Other characteristics are positively influenced including dispersibility, rheology of formulations containing treated pigments and opacity.

Addition of substantial amounts of rosin (up to 40% of the pigment weight for diarylide pigments) scarcely affects the colour strength because the particles become protected from aggregation and agglomeration, are optimally coated and can contribute fully to the colour strength.

Despite the importance of rosination to pigment technology, the nature of the rosin–pigment interaction has not been experimentally investigated in detail and so the molecular details of the interactions on the pigment surface are poorly understood. Possibilities other than simple van der Waals interactions include specific functional group interactions, hydrogen bonding, dipole–dipole interactions, etc. Solid-state ^{13}C CP/MAS NMR offers a reliable method for the study of pigments and should be able to shed light on the nature of the rosin/pigment interactions. Additionally, powder X-ray diffraction (XRD) has been used extensively in investigations of pigments and should also be able to contribute to a study of these interactions.

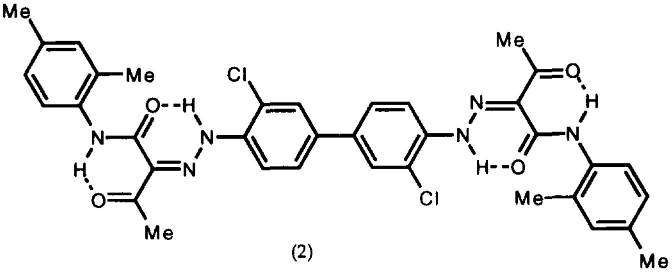
Solid-state ^{13}C CP/MAS NMR spectra of diarylide yellow pigments were studied by Cameron and Riddell, and the assignments of many of the resonances are known [1]. The spectra also allow some insights into the degree of order with which the molecules are packed in the crystallites. A highly ordered structure means a uniform distribution of neighbouring molecules around a particular carbon atom giving rise to low chemical shift dispersion and sharp lines. Disorder, on the other hand, means a non uniform neighbourhood for a particular carbon. This in turn leads to a greater chemical shift dispersion for the site and broader lines. Similar effects on line widths can be see in X-ray powder diffractograms although particle size can also cause such effects.

Many rosins used in pigment technology are derived from abietic acid (**1**) (Scheme 1) and therefore it was decided in the first instance to study abietic acid as a rosination agent. We chose to study its interaction with C.I. Pigment Yellow 13 (PY13) (**2**) (Scheme 2) because the structure of PY13 has been solved crystallographically [2], and because the ^{13}C CP/MAS spectrum of PY13 shows four good marker peaks in the three methyl resonances and the carbonyl resonance [1]. Rosination with the commercial rosin acid Staybelite, which is a partly hydrogenated abietic acid derivative with a structure that can be represented as **3** (Scheme 3), was selected for this investigation.



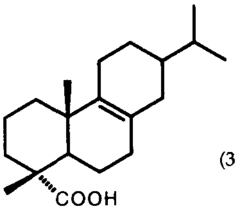
(1)

Scheme 1



(2)

Scheme 2



(3)

Scheme 3

RESULTS AND DISCUSSION

All CP/MAS NMR spectra display spinning side bands displaced from the original resonance by the spinning frequency unless this is larger than the chemical shift anisotropy. In all the spectra reported herein no spinning sidebands were observed for the aliphatic methyl resonances but appreciable spinning sidebands were observed for the aromatic, carbonyl, imine and olefinic resonances. Spinning sidebands could readily be identified by running spectra at two or more different spinning speeds. Typical spinning speeds employed were 6, 8 and 10 kHz.

The ^{13}C CP/MAS NMR spectrum of abietic acid is shown in Fig. 1. The doubling of lines apparent in the olefinic (120–150 ppm) and carbonyl (187 ppm) regions is consistent with the single crystal X-ray diffraction finding of two independent molecules in the asymmetric unit [4]. The ^{13}C

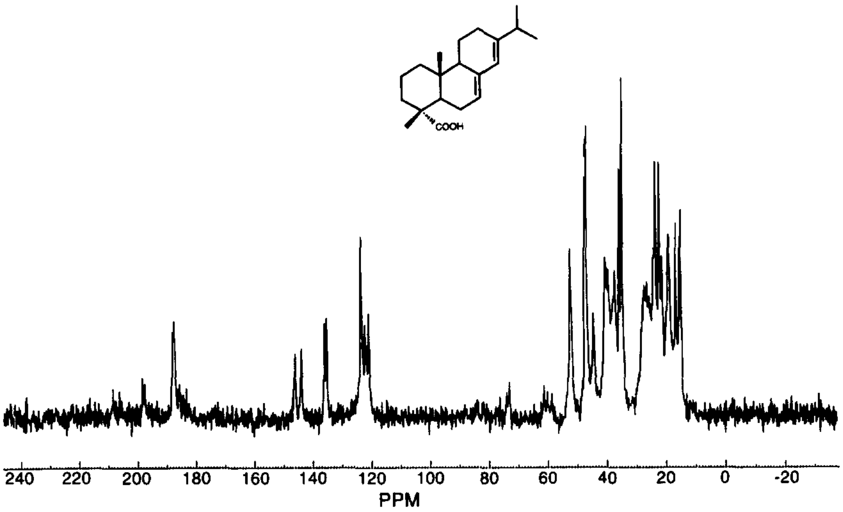


Fig. 1. ^{13}C CP/MAS NMR spectrum at 125.758 MHz of recrystallised abietic acid showing evidence of two molecules in the asymmetric unit.

CP/MAS NMR spectrum of crude PY13 and recrystallised (1,2,4-trichlorobenzene) PY13 are show as Fig. 2a and b, respectively. The dramatic line sharpening observed in the recrystallised product, in particular the methyl region (20–30 ppm) and the aromatic region (110–140 ppm), is consistent with a much greater internal ordering of the molecules in the crystals after recrystallisation.

The ^{13}C CP/MAS NMR spectrum of Staybelite rosin is shown in Fig. 3. There are two olefinic carbon resonances (120–140 ppm) consistent with one predominant molecular species, possibly **3**, and one carboxyl carbon resonance (187 ppm). The general line widths are consistent with an amorphous solid state structure for the rosin.

The crude PY13 was rosinated at high temperature (90–95°C) in an aqueous slurry to proportions of rosin of approximately 10, 20, 30 and 40 precipitated % of total weight. The rosin, which was in solution at pH 10 and high temperature, was brought onto the PY13 by the rapid addition of dilute HCl solution to pH 7.0 and the hot suspension was stirred for a further 30 min before recovery of the product. The actual proportion of rosin retained was measured gravimetrically. ^{13}C CP/MAS NMR spectra of the rosinated pigments were then obtained.

Figure 4 shows the aliphatic region of the spectra of samples of PY13 rosinated with abietic acid. Even at a loading of 10% the rosination procedure is seen to cause a dramatic increase in the crystallinity of the PY13 with the three methyl peaks from PY13 being sharply defined. As the loading

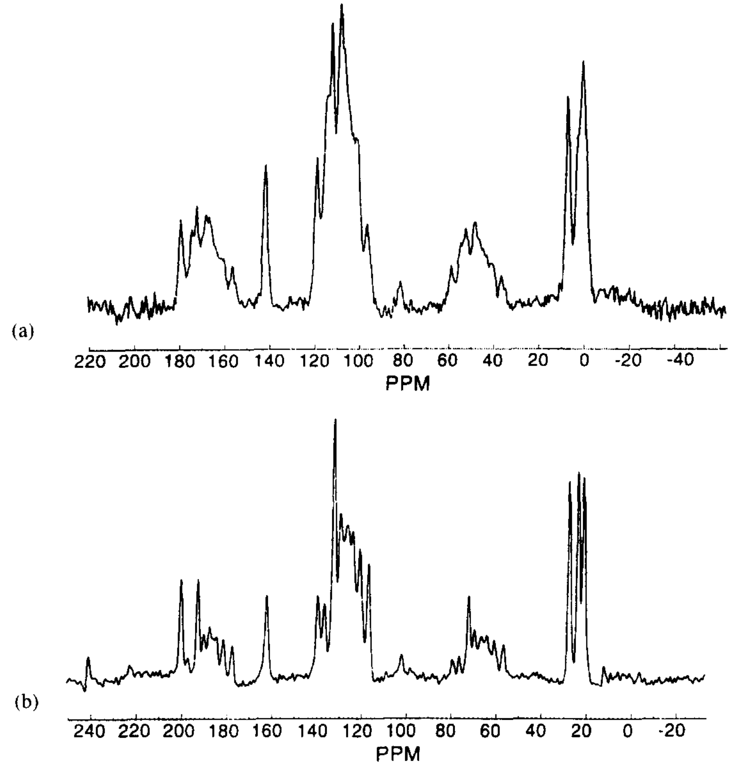


Fig. 2. ^{13}C CP/MAS NMR spectrum at 125.758 MHz of crude and recrystallised C.I. Pigment Yellow 13.

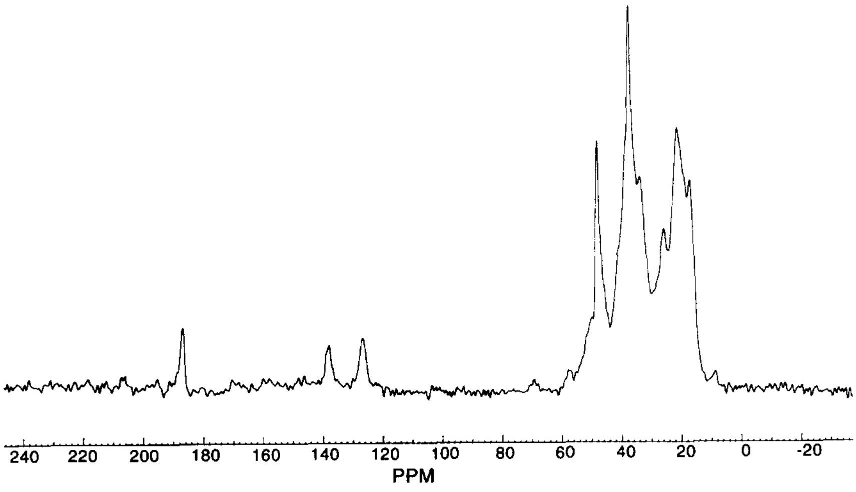


Fig. 3. ^{13}C CP/MAS NMR spectrum at 125.758 MHz of commercial grade Staybelite rosin.

increases the signals from the abietic acid begin to emerge but at loadings of 20 and 30% the signals are broad indicating an amorphous nature for the rosin coating the pigment.

A similar effect is seen for Staybelite in Fig. 5. Rosination has a dramatic effect on the crystallinity of the PY13 and the Staybelite goes onto PY13 in an amorphous form. When the rosinated Staybelite spectra were obtained at a spinning speed of 10 kHz the region 155 to 195 ppm was free from spinning side bands allowing observation of the PY13 carbonyl and Staybelite

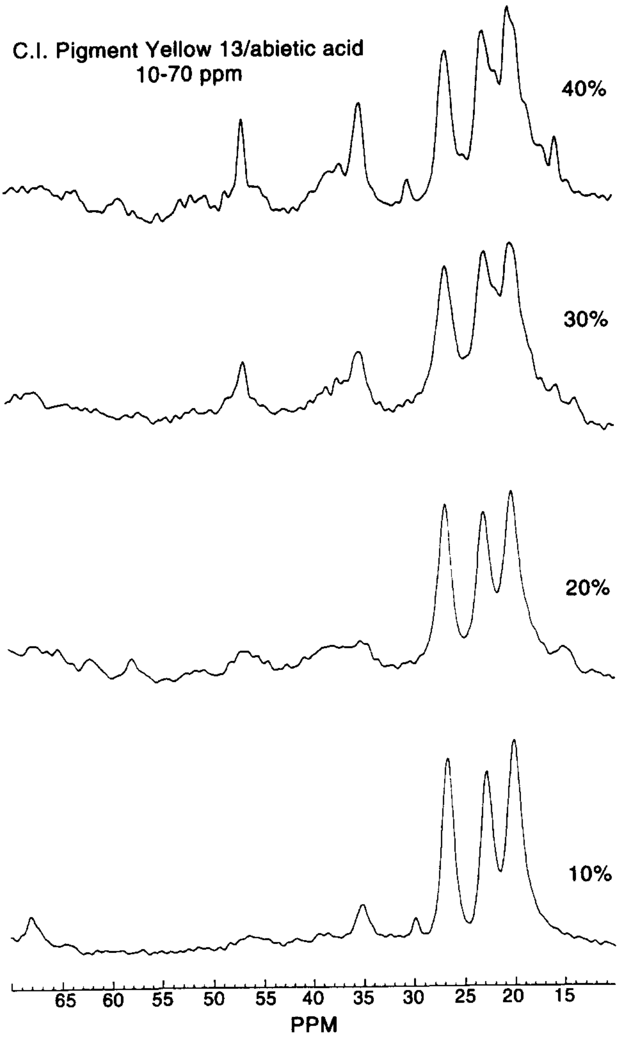


Fig. 4. ^{13}C CP/MAS NMR spectrum at 125.758 MHz in a stacked plot of C.I. Pigment Yellow 13 coated with 10–40% abietic acid (10–70 ppm region).

carboxyl resonances. These spectra are shown in Fig. 6. The carboxyl resonance is visible from 20% coating upwards at the same chemical shift. Analogously the carbonyl resonance of the PY13 does not change its chemical shift with increasing rosination. These results suggest the lack of a specific interaction between the carboxyl group of Staybelite and the rosin and also lack of any specific interaction between the carbonyl group of PY13 and Staybelite.

The improvement in crystallinity of PY13 on rosination could be due either to the presence of the rosin, or to the heat/pH treatment to which the pigment had been subjected. These hypotheses were tested by subjecting

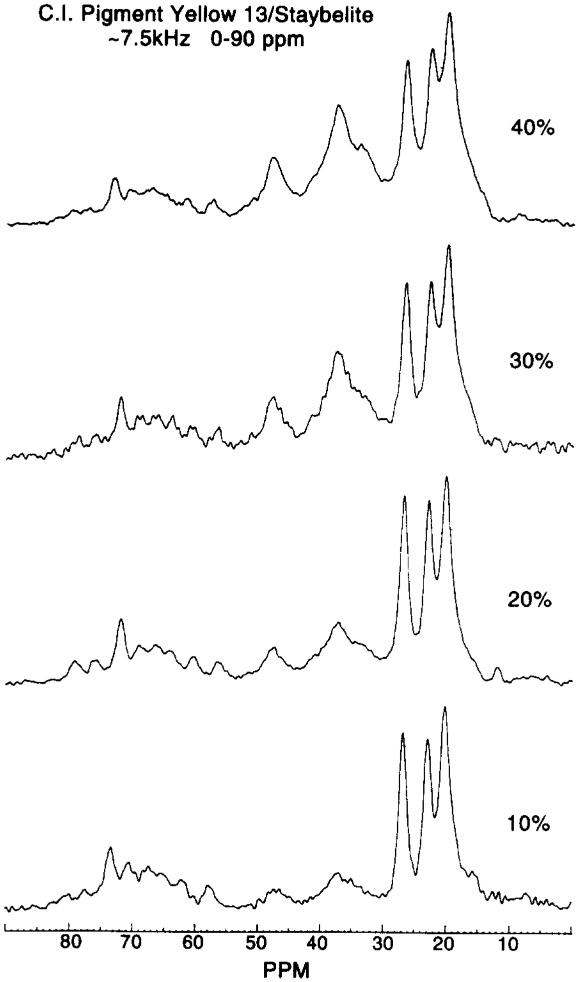


Fig. 5. ^{13}C CP/MAS NMR spectrum at 125.758 MHz in a stacked plot of C.I. Pigment Yellow 13 coated with 10–40% Staybelite rosin at *ca.* 7.5 kHz (0–90 ppm region).

crude PY13 to the entire rosination procedure in the absence of rosin. No improvement in crystallinity was observed implying that the rosin itself is responsible for the improved crystallinity and not merely the heat/pH treatment.

The samples were also studied by powder X-ray diffraction. Figure 7 shows the powder diffractograms for crude and recrystallised PY13. The improvement in internal order is dramatically illustrated. Figure 8 shows the powder diffractograms for PY13 rosinated at 40% with abietic acid and with staybelite. Lines that arise from crystalline PY13 are seen but the lines are broader than those in the recrystallised product. Interestingly no lines from crystalline abietic acid are observed confirming its amorphous nature in the rosinated product.

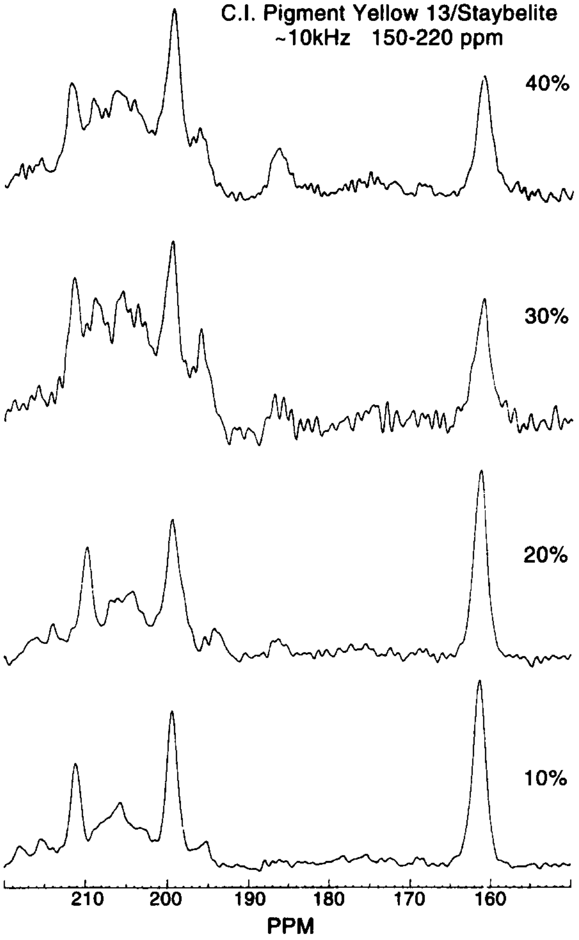


Fig. 6. ^{13}C CP/MAS NMR spectrum at 125.758 MHz in a stacked plot of C.I. Pigment Yellow 13 coated with 10–40% Staybelite rosin at *ca* 10 kHz showing the emergence of the carboxyl group resonance at 187 ppm.

Finally, to confirm that rosination confers an improvement in crystallinity to PY13 a sample of recrystallised PY13 was rosinated with 40% abietic acid. The powder diffractograms are shown in Fig. 9 and there is indeed an improvement in the line width upon rosination of the recrystallised PY13.

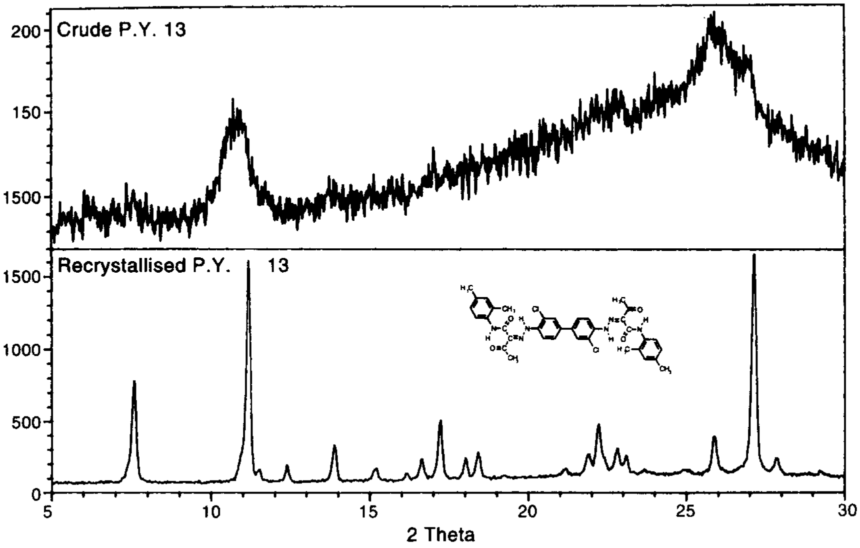


Fig. 7. Powder X-ray diffractogram of crude and recrystallised C.I. Pigment Yellow 13.

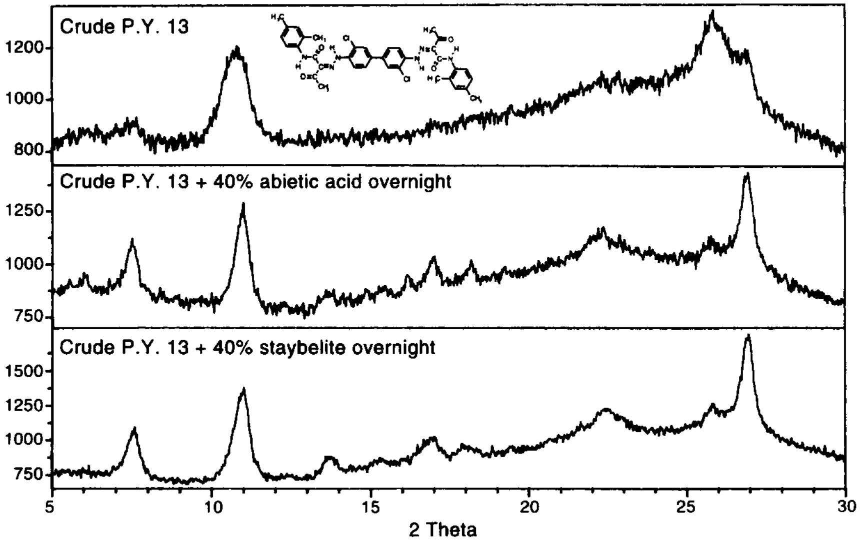


Fig. 8. Powder X-ray diffractogram of C.I. Pigment Yellow 13 coated with 40% abietic acid and 40% Staybelite rosin.

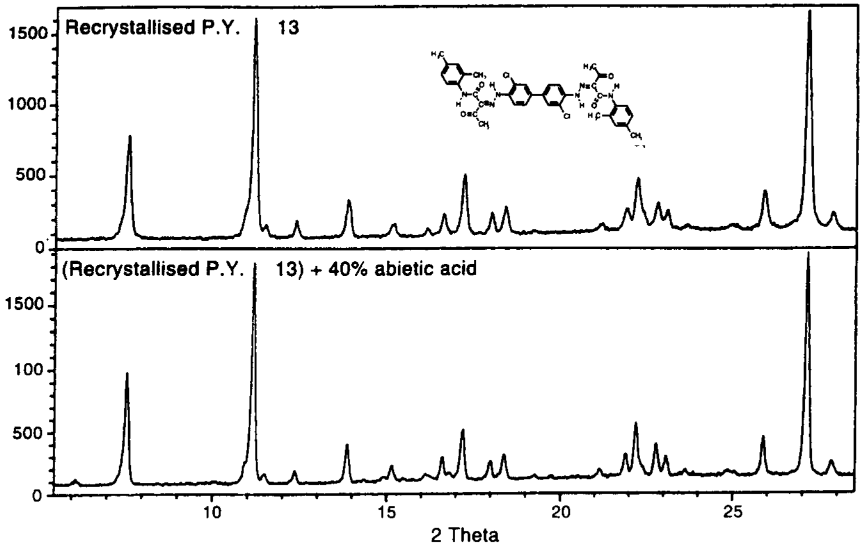


Fig. 9. Powder X-ray diffractogram crude and recrystallised C.I. Pigment Yellow 13 and recrystallised Pigment Yellow 13 coated with 40% abietic acid.

EXPERIMENTAL

Abietic acid (Aldrich technical grade), as a yellow solid, was twice recrystallised from aqueous ethanol. The recrystallised acid was a white solid and showed no traces of impurities in its ^1H and ^{13}C NMR spectra. TLC (silica gel plates with ethyl acetate–hexane, 1:1, plus a trace of acetic acid) showed very small traces of three slower running impurities. A more detailed purification procedure for abietic acid is available [3]. Staybelite®, a commercial, partly hydrogenated derivative of abietic acid, was used as supplied by Hercules Inc.

C.I. Pigment Yellow 13

A solution of acetoacet-2,4-xylidide (AAMX) (62.5 g, 0.305 mol) in 47% NaOH (27.5 g) and water (440 ml) was prepared. A solution of glacial acetic acid (23.4 g) in water (83 ml) was added dropwise to adjust the mixture to pH 6, with vigorous stirring, to re-precipitate the AAMX. The mixture was stirred for 15 min before cooling with ice to 16°C. Meanwhile, a solution of 3,3′-dichlorobenzidine tetrazonium chloride (DCB tetrazo) (ca. 11%; 361.1 g, 0.14 mol) was cooled with ice. A little sulphamic acid was added to the DCB tetrazo to eliminate residual nitrite from the diazotisation reaction. The DCB tetrazo was added to the AAMX via a peristaltic pump, maintaining the temperature at 16°C. The pH was kept at 4.8 throughout by the addition of a solution of 47% NaOH (50 g) in water (150 ml). Towards the end of the coupling reaction, the mixture was checked for excess DCB tetrazo with a solution of 'H'-acid (4-amino-5-hydroxy-2,7-naphthalene disulphonic acid). The coupling took 1 h, after which the mixture was allowed to stir for 90 min, while warming naturally to room temperature, before adjusting the pH to 6.0 with 47% NaOH. The prepared PY13 was stored as an aqueous slurry at pH 6.0. A quantitative amount of PY13 was produced (*ca* 97 g). The reaction scheme is shown in Fig. 10.

Rosinated PY13 (general procedure)

PY13 aqueous slurry (containing *ca* 9.7 g PY13) was stirred, and adjusted to pH 10 with dilute NaOH. Meanwhile, a solution of rosin acid; A 0.97 g (10% by weight of PY13); B 1.94 g (20%); C 2.91 g (30%); D 3.88 g (40%) in water (40 ml) and 47% NaOH (a few drops, sufficient to ensure solution at high temperature, *ca* 90°C) was made up with heat and stirring. The hot rosin solution was added to the PY13 slurry at pH 10, retaining the rosin in solution. Steam was applied directly to the mixture until a temperature of 95°C was reached, at which point dil. HCl was added to pH 7.0 to precipitate the rosin. Stirring was continued at 90–95°C for 30 min. After allowing to cool

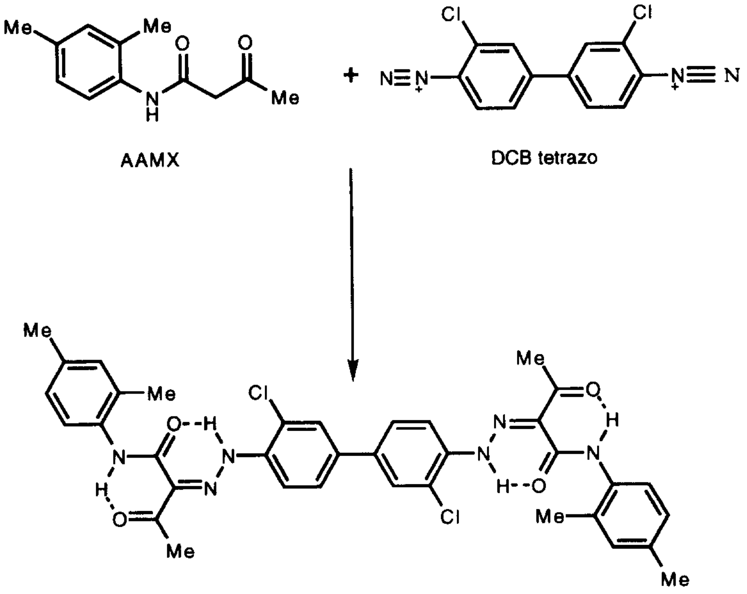


Fig. 10. The synthesis of C.I. Pigment Yellow 13.

to 70°C, the rosinated product was filtered under vacuum and washed with water until salt free (conductivity < 250 μS). The product was oven-dried at 70°C overnight. Recoveries of PY13 plus rosin were between 90 and 95% of starting materials. The text of this paper uses the % value of rosin added to the preparation. The observed retained rosin contents of the preparations are reported in Table 1.

Recrystallised PY13 rosinated with 40% abietic acid

PY13 (3.0 g), recrystallised from 1,2,4-trichlorobenzene, was added to water to make an aqueous slurry, which was adjusted to pH 10 with dilute NaOH. Meanwhile, a solution of abietic acid (1.2 g; 40% by weight of PY13) in water and 47% NaOH (few drops) was made up with heat and stirring. The hot rosin solution was added to the recrystallised PY13 slurry at pH 10, retaining the rosin in solution. The mixture was heated on an electric hot plate until a temperature of 95°C was reached, at which point dilute HCl was added to pH 7.0 to precipitate the rosin. Stirring was continued at 90–95°C for 30 min. After allowing to cool to 70°C, the rosinated product was filtered under vacuum, washed with water and oven dried at 70°C overnight. Yield 3.56 g, Total rosin 21.2%.

Solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker MSL 500 spectrometer at 125.758 MHz using 4 mm o.d. zirconia rotors. The following typical conditions were employed: contact time 1 ms, spectral width 30 000 Hz, acquisition time 17.4 ms, spin locking field frequency *ca* 60 kHz, recycle delay 5 s, spinning speeds 6 to 10 kHz. Spinning speeds were chosen such that spinning side bands did not overlap with regions of interest in the spectra. Chemical shifts were referenced to the CH_2 resonance in an external adamantane sample at 38.56 ppm. Dipolar dephased [Non Quaternary Suppressed (NQS)] spectra were obtained by a standard sequence incorporating a 50 μs dipolar dephasing delay.

Solution state ^{1}H and ^{13}C NMR spectra were obtained from $CDCl_3$ or D_2O solutions in a 5 mm tube using the high resolution probe in the MSL

TABLE 1
Rosin Contents of Rosinated PY13 Samples

	% Rosin found	
% Rosin added	*Abietic acid*	*Staybelite*
10	6.9	7.7
20	11.7	15.3
30	19.9	20.1
40	24.5	26.0

500 spectrometer or on either a Bruker AM 300 or a Varian Gemini 200 spectrometer.

Powder X-ray diffraction data were collected on a STOE Stadi diffractometer. The samples were mounted in 0.5 mm glass capillaries and the detector was programmed to collect data within a suitable scattering angle range in 0.5° increments. The detector range used and the length of time at each increment varied according to the sample.

Rosination measurements were carried out gravimetrically by Ciba Pigments using boiling ethanol/toluene (50 ml) to remove the rosin quantitatively from 3–4 g of coated pigment. The pigment was isolated by centrifugation. This procedure was repeated three times. The residual pigment was dried and weighed. The solvent fraction was evaporated and weighed.

CONCLUSIONS

The increased sharpness and resolution that are seen in the ^{13}C CP/MAS NMR spectra and the powder X-ray diffraction patterns of the rosinated PY13 are good indicators that rosination improves the crystallinity of the pigment. Even when a recrystallised C.I. Pigment Yellow 13 sample is rosinated, a further increase in pigment crystal order is observed in the rosinated sample. The NMR and XRD results show that the rosin coating the pigment is in an amorphous state. The mechanism of this improved crystal order is uncertain, although a physical phenomenon could be responsible, where the rosin layer applies a degree of pressure on the pigment crystals to reduce volume and so increase order.

There is no evidence from this work of any specific functional group interactions being important in these rosinations.

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