Selection of dispersants for the dispersion of C.I. Pigment Violet 23 in organic medium

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Abstract

The dispersion of the organic carbazole violet pigment (C.I. Pigment Violet 23) in organic solvent requires the use of dispersant additives. Three carboxylic dispersants have been investigated regarding this purpose. Their adsorption behaviour has been evaluated by means of adsorption isotherms and the molecular interactions taking place at the surface have been inferred from ^{13}C NMR spectroscopy. The rheological behaviour of the dispersions has considerably been improved by the presence of the dispersants. In particular, the copolymer dispersant that adsorbs the most strongly reduces the suspension viscosity and allows to increase the pigment loading by 50% keeping the rheological properties. The consequences of deflocculation of the suspension on the colorimetric properties are an enhanced tinting strength and an improved colour stability.
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1. Introduction

In the domain of organic coatings where dispersions of the pigments and resins are spread on the surfaces and dried, the dispersion state of the pigment in the dry film controls its properties. A fine and homogeneous dispersion is needed and dispersant additives are often used for that purpose. The interaction between dispersant and pigment (dye) in the painting is of major importance and its optimization permits to ensure a good quality of the finished product. In particular, the presence of the dispersant allows avoiding anomalies susceptible to generate flocculation, sedimentation, fall of gloss … The literature is rich in works dealing with this alliance of pigments with dispersants [1,2]. The stability of the dispersion and the final properties of the films depend on the nature of the various components and their mutual interactions.

The dispersability of the pigment in the solvent and the compatibility of the pigments and resin have to be optimized with the help of an adequate dispersant.

In the domain of the organic pigment family to which belongs the C.I. Pigment Violet 23 of the present investigation, most works concern phthalocyanines and carbon blacks [3−5]. In particular, interesting results in industrial applications have been obtained with dispersants bearing carboxylic functions [6−8].

The carbazole pigment Violet 23 (C.I. Pigment Violet 23) is the most important and the most used commercial form of dioxazine derivatives [9]. Its violet colour has a blue-redden hue that cannot be reproduced with a mixture of pigments. The crystallographic analyses have shown an angular structure of the molecule [10] (Fig. 1).

Because of its high chemical resistance that is similar to the phthalocyanine blues, the C.I. Pigment Violet 23 is frequently used in tinting paints. It can also be used to mask the yellowish aspect in white solvent coatings. To fulfil this role, the pigment must be well dispersed.

Unfortunately, it is difficult to prepare a stable and fine dispersion of the C.I. Pigment Violet 23 by means of grinding in

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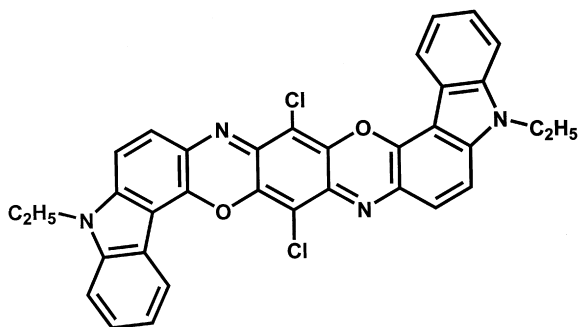*E-mail address:* naceur.ayed@insat.rnu.tn (N. Ayed).

Fig. 1. Molecular structure of the C.I. Pigment Violet 23.

an organic medium. Additives are always used to solve problems related to bad pigment dispersion, viscosity increase on storage and thixotropy. Indeed, the experience shows that C.I. Pigment Violet 23 concentrates have a high tendency to gel on storage if an adequate dispersant is not used or when its dose is not optimized. The consequences are usually low tinting strength that requires consumption of larger amounts for tinting. On the other hand, the increase in viscosity causes big troubles in automatic tinting.

Thus, the polymer dispersants are added to obtain homogeneous dispersion of the pigment in the liquid phase that leads to weak viscosity and allows high pigment loading and high tinting strength. The stabilization of the dispersed state is also ensured [11–14].

In organic media, polymer dispersants usually adsorb by means of hydrogen bonding, ionic interactions, van der Waals forces and acid–base interactions [15,16]. After adsorption onto the surface of the particles, the polymer dispersant can create repulsive forces between the particles. These forces are essentially of a steric nature in non-polar medium [17–19].

The polymers can be divided into three major classes: homopolymers or random copolymers, terminally attached polymers and block copolymers. Homopolymers or random copolymers take a coiled configuration when they are adsorbed onto the solid surface; trains, loops and tails can also be observed [20]. The configuration of terminally attached polymers is somewhat different; they have little affinity for the surface except at the terminal group that may be bound by a chemical reaction or by another strong attraction to the solid. The situation for block copolymers is similar to that of terminally attached polymers provided one of the blocks has strong affinity for the surface and the other block has little affinity for it. The length of the adsorbing segment in block copolymers dictates the distance between the adsorbed polymers and the length of the non-adsorbing block controls the thickness of the adsorbed layer. "Mushroom" and "brush" structures are expected for the copolymers on the surface [21,22].

In the present work, the dispersion of the C.I. Pigment Violet 23 in non-aqueous medium in the presence of three dispersants having carboxylic functions has been studied. The conditions of dispersion and stabilization of this pigment in relation to the three tested dispersants have been studied and optimized. In the first part, the adsorption of such dispersants has been compared and the adsorption mechanism of the most

efficient dispersant has been investigated by spectroscopic measurements. Rheological studies allowed optimization of the formulation and lastly, the consequences of the improved dispersion on the colour properties were evaluated.

2. Experimental

2.1. Materials

The C.I. Pigment Violet 23 in powder form was supplied by Clariant. This powder was characterized by an average diameter of 40 nm and a specific surface (BET) of 86 m^2 g^{-1} according to the data provided by the supplier.

Three dispersants with carboxylic functions commercialised by BYK Chemie have been used in this work. Their characteristics are shown in Table 1. A medium oil alkyd Setal 196 supplied by Akzo Nobel resins has been used as a grinding resin and xylene has been used as a solvent.

2.2. Rheological measurements

For the rheological measurements, the suspensions have been prepared by adding 8 wt% of the violet pigment to a solution containing the solvent, the grinding resin (65 wt%) and the needed quantity of the dispersant. The mixture was grinded for 2 h in a Red Devil disperser.

The rheological measurements were realized at 20 °C with a Brookfield RVT and a Krebs Stormer type viscometers. The first one allows measuring viscosities at low shear rates (speed < 100 rpm) and characterizes the resistance of the suspensions against sedimentation. The latter gives an apparent viscosity at a higher shear rate (spindle speed 200 rpm) which is expressed in Krebs units (KU) and describes how easy is the manipulation of the pigment concentrates. The Krebs units have been converted into mPa s units using tables provided by the supplier.

2.3. Colorimetric measurements

The pigment tinting strength is its ability to colour a white paint. The tinting strength measures the Kubelka–Munk K/S with respect to that of a reference sample. The reference used has the same composition as that of the studied samples, but contains a standard commercial dispersant. Thus, mixtures of 8 wt% violet pigment concentrate and a 28 wt% TiO$_2$ alkyd

Table 1
Characteristics of the dispersants

Dispersant type	Nature	Abbreviation	wt%	Molar mass
Homopolymer	Alkylammonium salt of polycarboxylic acid	AAAC	50	Low
Homopolymer	Ester of hydroxy-carboxylic acid	EACH	98	Low
Block copolymer	Alkyl ester of polycaprolactone	CP	45	High

white paint were realized in such a way that the ratio of the amount of TiO_2 to that of violet pigment was equal to 9. The same mixtures were used in the "rub out" test which consists in rubbing one zone of the paint film and comparing the colour difference ΔE^* with an intact zone. All colorimetric measurements were realized with a Spectraflash 300 spectro-colorimeter supplied by Datacolor.

2.4. Adsorption measurements

The adsorption isotherms were determined using the depletion method. Suspensions containing the dispersant dissolved in xylene and 1 wt% of C.I. Pigment Violet 23 were prepared in an ultrasonic bath for 15 min and left under magnetic stirring for 24 h. After, centrifugation, the supernatant was analysed by UV/vis spectroscopy to determine the concentration of dispersant with the help of a calibration plot measured from reference solutions. The adsorbed amount per unit area, Γ, was calculated from the difference of the total mass of the dispersant, m_{total}, and the mass in solution, $m_{solution}$, the mass and specific area of Violet 23 (M_{solid} and A_{sp}) as:

$$\Gamma = \frac{m_{total} - m_{solution}}{A_{sp} M_{solid}}$$

The UV/vis spectrophotometer was of the type Shimadzu, model UV-2401 PC. Typical absorption spectra of the studied dispersants are shown in Fig. 2.

2.5. ^{13}C solid-state NMR

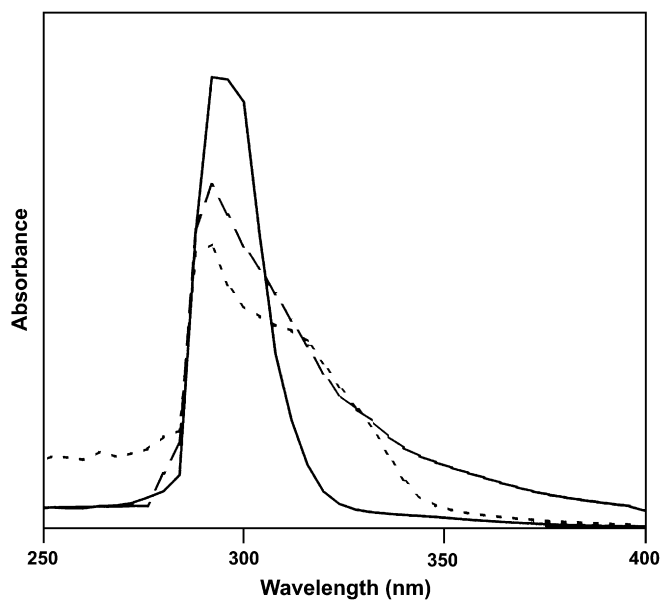The CP/MAS ^{13}C NMR spectra were obtained using a Bruker ultra shield TM type instrument operating at 75 MHz.

3. Results and discussion

3.1. Adsorption study

3.1.1. Adsorption isotherms

The adsorption isotherms of the three dispersants have been determined by the depletion method. The curves in Fig. 3 are type-I isotherms of the Langmuir classification.

In all the cases, the adsorbed quantity increased with the increase in the polymer concentration in the solution till an adsorption plateau was reached. The shape of the isotherms showed that, independently of the mass and the chemical composition of the dispersant, the adsorption was of a monolayer type. The solid surface reached saturation during the monolayer filling. A medium affinity of the three dispersants towards the surface of the C.I. Pigment Violet 23 was noted. The slopes of the isotherms at low equilibrium concentrations are quite high but the isotherms are not typical of a high affinity where significant adsorption takes place at nearly zero equilibrium concentrations (quasi-infinite slope). Significant amounts of dispersants were maintained in the solution even for the low concentrations. According to its molecular structure, the C.I. Pigment Violet 23 has no structural acidity at its surface. Therefore, the hydrogen bonding formation and the electron donor−acceptor complex mechanisms were not favoured. Consequently, the adsorption driving forces would be due to π−π dispersion interactions between the aromatic rings of the carbazole molecule and the π-electron of the carbonyl oxygen of the polymer. Such mechanism was also suggested for the adsorption of aromatic compounds on carbons [23]. The polymeric dispersants ensured a stable adsorption because the large number of anchoring groups per molecule made the total adsorption energy high, even if individual contacts were weak [11,12].

The adsorbed dispersant quantity on the pigment surface increased with the molar mass. In fact, these amounts were of the order of 0.30, 1.10 and 2.05 mg m^{-2} for AAAC, EACH and CP, respectively. This result was characteristic of a
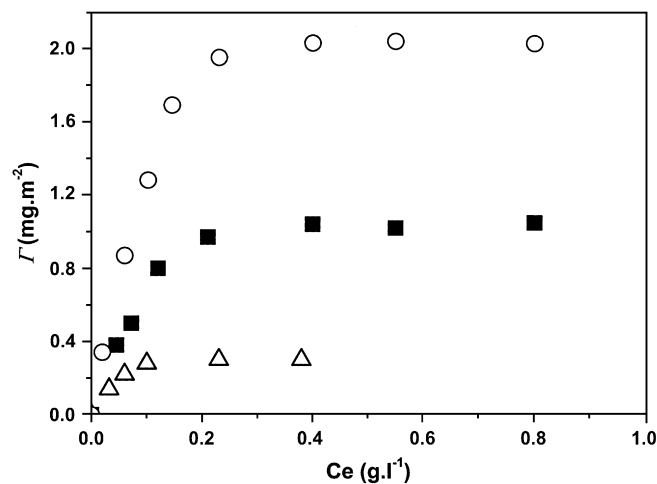

Fig. 2. UV/vis absorption spectra of the three studied dispersants. CP (full line), EACH (dash-dot), and AAAC (dotted).

Fig. 3. Adsorption isotherms of the various dispersants onto C.I. Pigment Violet 23. (△) AAAC, (■) EACH, and (○) CP.

non-porous surface; the possible micropores have sizes smaller than those of the polymer dispersants (radius of the pores < 20 Å) [24].

Because of the Langmuir-like shape of the isotherms, the Langmuir model has been used in order to quantitatively characterize the dispersants' adsorption towards the violet pigment. The Langmuir isotherm reads:

$$\Gamma = \Gamma_{max} \frac{KC_e}{1 + KC_e}$$

where C_e is the equilibrium concentration of the polymer in solution (g 1^{-1}), Γ_{max} the amount of adsorbed polymer for a full monolayer coverage (mg m^{-2}) and K is the equilibrium adsorption constant in Langmuir model. The linearized form of the Langmuir equation is as follows:

$$\frac{C_e}{\Gamma} = \frac{C_e}{\Gamma_{max}} + \frac{1}{K\Gamma_{max}}$$

and allows an easy check of its validity by a plot of C_e/Γ as a function of C_e.

Although this approach allows to predict the polymer adsorption at a given concentration, one must bear in mind that the Langmuir model has no theoretical basis for the adsorption of polymers at the solid/liquid interface, especially when a polydisperse polymer is used.

A linearity of the C_e/Γ variation against the quantity of the dispersant in the solution C_e (Fig. 4) proves that the Langmuir model is a judicious choice. The slopes of the straight lines represent the reciprocal of the adsorbed amount of dispersant in the monolayer. The values of maximum adsorbed density as given from the adsorption isotherms (Γ_{max}) and as calculated from the Langmuir model (Γ_{max}^*) and the adsorption equilibrium constants K are given in Table 2.

The agreement of the adsorption characteristics with the predictions made from the Langmuir model suggests a monolayer adsorption. Adsorption isotherms pertaining to multilayer adsorption such as the Freundlich model do not fit to
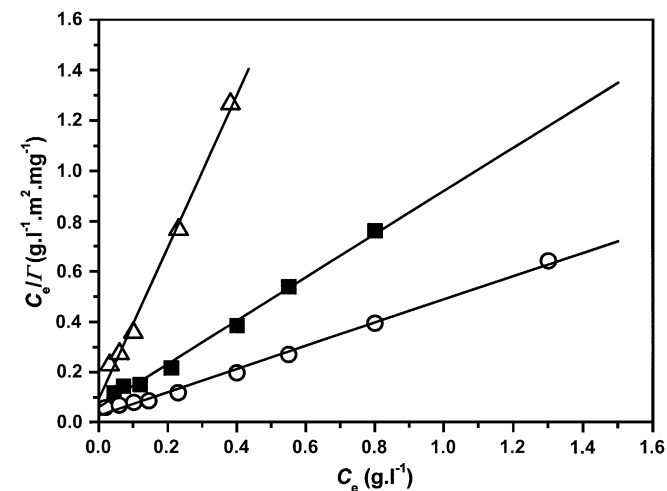
the experimental data. The monolayer is thicker with the high molar mass dispersant (CP). The AAAC and EACH dispersants are homopolymers that may adsorb in a flat conformation. On the contrary the CP dispersant is a block copolymer that may adsorb as isolated coils (mushroom) in dilute solution and as radially stretched coils (brush) in concentrated regime. The higher adsorption of the copolymer may originate either from its higher molar mass or due to its block copolymer structure. A thicker polymer layer allows a better steric stabilization of the particles. The minimum thickness for a good stabilization is of the order 100 Å [12], this can justify the best results obtained with the copolymer dispersant compared to the two other low molar mass dispersants.

3.1.2. Solid-state nuclear magnetic resonance (NMR)

The results obtained from the adsorption isotherms allowed us to conclude on the efficiency of the carboxylic copolymer CP as a dispersant of the C.I. Pigment Violet 23 in organic medium. ^{13}C NMR spectroscopy was used in order to investigate the interactions with the surface at a molecular level. Spectrum was recorded at the maximum of adsorption (2.1 mg m^{-2}).

The adsorption of the copolymer dispersant onto the Violet 23 was confirmed by ^{13}C NMR. Indeed, the spectrum of the pigment (Fig. 5) was modified after contact with the copolymer. New peaks were observed which corresponded to those of the copolymer: the ester group at 173 ppm and the peaks corresponding to the CH$_2$ of the polycaprolactone backbone between 20 and 35 ppm. The line of the carbonyl at 173 ppm appeared much sharper than the other lines of the polycaprolactone, which strongly suggested that the ester groups of polycaprolactone were less mobile than the remaining parts of the polymer backbone. The groups that were observed as sharp lines were immobilized at the pigment surface and, consequently, behaved as "trains". The methylenes of the polycaprolactone that appeared as broad lines formed loops in the adsorbed layer. The low spectral resolution may be due to the overlap of slightly shifted lines [25], suggesting a gradient of molecular motion away from the solid surface. The alkyl chains of the copolymer could not be observed in the spectrum of the adsorbed polymer. Although the corresponding lines were weak, the line of the terminal methyl group at 15 ppm should have been detected. Presumably the corresponding lines were too broad, suggesting a high mobility of these groups which were involved in the tails.

3.2. Rheological investigation

3.2.1. Dispersant demand

The dispersant demand is the minimum amount of dispersant required for reaching a low and constant viscosity. This

Fig. 4. Linearized Langmuir adsorption isotherms of polymers onto C.I. Pigment Violet 23. (△) AAAC, (■) EACH, and (○) CP.

Table 2
Adsorption results

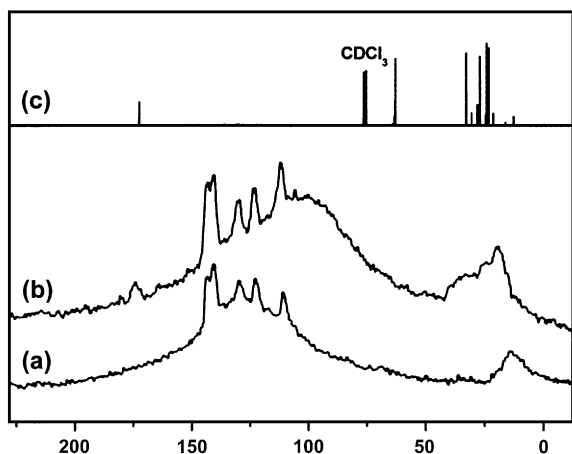| Dispersant	Γ_{max} (mg m^{-2})	Γ_{max}^* (mg m^{-2})	K (l g^{-1})
AAAC	0.30	0.33	33
EACH	1.10	1.16	14
CP	2.05	2.16	17

Fig. 5. ^{13}C solid-state NMR spectra of (a) carbazole violet pigment, (b) C.I. Pigment Violet 23 with adsorbed CP, and (c) liquid NMR spectrum of the co-polymer in solution in CDCl$_3$.

Fig. 7. Rheological behaviour of C.I. Pigment Violet 23 dispersions in the presence of the various dispersants: (×) 0%, (Δ) AAAC 0.5 wt%, (■) EACH 0.8 wt%, and (○) CP 3.5 wt%.

is measured by incorporating increasing amounts of dispersants into the pigment base. The viscosities were measured at 50 rpm using a spindle no. 4. The results are shown in Fig. 6a and b.

The viscosity minimums were obtained for weight concentrations equal to 0.5% for AAAC and 0.8% for EACH corresponding to 6% and 10% of the pigment quantity, respectively. For these optimal concentrations, the viscosity decreases were 650 mPa s for EACH and only 510 mPa s for AAAC.

The optimal concentration of the CP is much larger. Indeed, it was 3.5% which corresponded to 44% of the pigment quantity. The viscosity lowering at this optimal concentration was larger than those obtained with the two other dispersants and corresponded to 1100 mPa s.
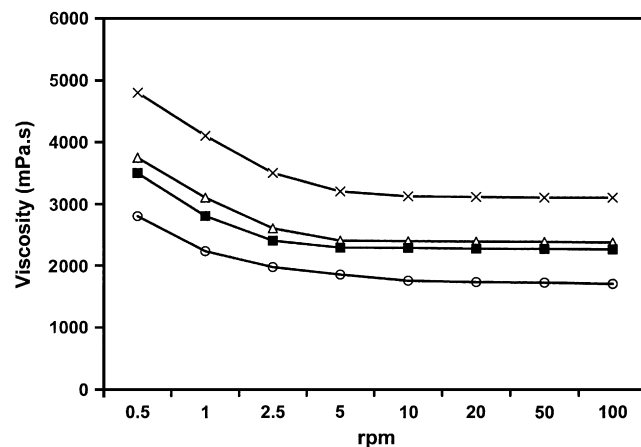
The ratio of the copolymer dispersant to the pigment was clearly superior to those of the low molar mass dispersants. Such higher dispersant demand might be due to the adsorption as a thick layer requiring larger quantities [26]. On the contrary, the AAAC and EACH dispersants adopted a flat conformation.

The required amounts of dispersants were much larger than those usually required for inorganic pigments [11]. This is simply related to the high specific area of the violet pigment for which a high amount of polymers are required to fully cover the pigment particles. If we consider that the adsorption isotherms as determined at 1 wt% weight fraction of pigment are still valid at 8 wt%, then the adsorbed quantities at the dispersant demand can be calculated from the Langmuir equation. Thus, it was found that the pigment particles were 100% covered at the minimum of the viscosity. The maximum
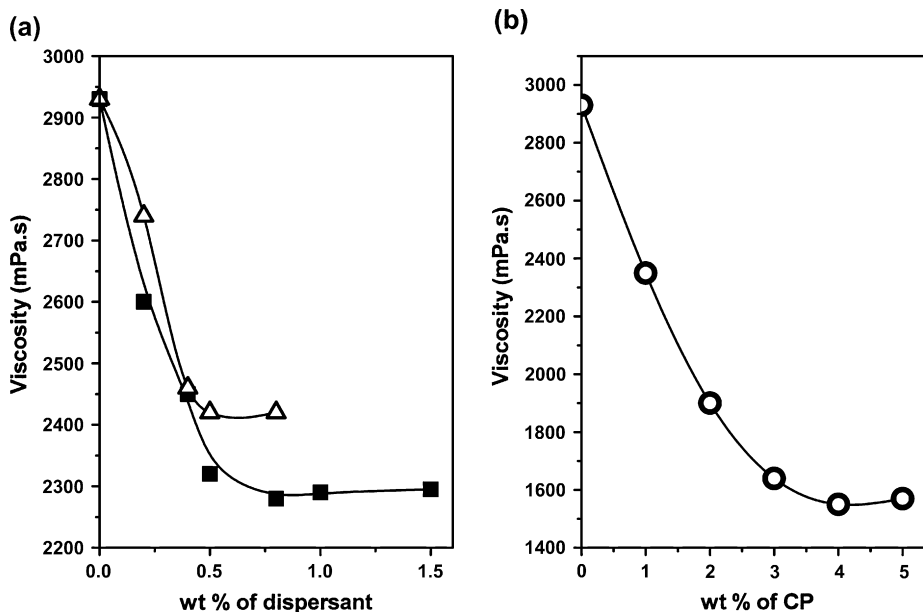

Fig. 6. The viscosity plotted against the dispersant concentration. (Δ) AAAC, (■) EACH, and (○) CP.

Table 3
Viscosity values measured with the Krebs Stormer rheometer in Krebs units and its equivalents in mPa s

	η (KU)	η (mPa s)
Without dispersant	95	1401
0.5 wt% AAAC	90	1172
0.8 wt% EACH	89	1129
3.5 wt% CP	82	858

fluidization of the slurries was attained at the kink of the adsorption isotherm where the plateau started.

3.2.2. Rheological behaviour

The rheological profiles plotted in the absence and in the presence of different dispersants are shown in Fig. 7. The dispersant amounts were those corresponding to the dispersant demand.

In every instance, a shear thinning behaviour was observed. At a low rotation rate (0.5 rpm), the decrease in the viscosity was of the order of 2000 mPa s in the presence of the copolymer CP, and only about 1000 mPa s when EACH or AAAC was used. At a higher rotation rate, the viscosity drops were equal to about 1400 mPa s and 800 mPa s.

The shear thinning profiles obtained in the presence of each of the low molar mass dispersants showed that their deflocculating action on the C.I. Pigment Violet 23 was limited. Such behaviour was dependent on the thickness of the adsorbed layer of the polymer [27].

The rheological behaviour was closer to Newtonian especially in the presence of the CP dispersant of higher molar mass. This dispersant with high affinity towards the violet pigment formed a thick layer around the particles leading to an efficient dispersion and to a large reduction in viscosity.

The viscosity measurements at a higher shear stress with a Krebs Stormer viscometer (Table 3) showed the same viscosity decrease upon addition of the dispersant. The dispersion based on the C.I. Pigment Violet 23 pigment and the copolymer dispersant was the easiest to flow at the high shear rates of usual industrials operations such as homogenization, pumping, …

3.2.3. Long time stability of the dispersions

The viscosity evolution of the C.I. Pigment Violet 23 bases upon storage in the oven was followed at a slow and fast rotor rate. The results are shown in Fig. 8.

In the absence of the dispersants, a viscosity increase reflecting an instability on storage was observed. A large increase in viscosity has been observed during storage and the pigment base finally became a gel for which the viscosity could not be measured.

The copolymer dispersant gave the best rheological stability to the C.I. Pigment Violet 23 base because the viscosity variations were lower than 300 mPa s. On the contrary, the viscosity increase was 600 mPa s for the two low molar mass dispersants, thus, the stability was also not correctly ensured.

These phenomena were also confirmed by Krebs Stormer viscosity measurements (Table 4). Thus, the dispersant-free suspensions turned into a gel after two weeks, while the viscosity increase was 5–6 KU for the low molar mass dispersants and only 2 KU for the high molar mass copolymer.

3.2.4. Pigment loading

Because of their high specific areas, organic pigments have high demands in binder and in wetting-dispersant additives. As a consequence, this limits the incorporation of these pigments into the colorant bases. This is a difference with respect to inorganic pigments. The use of an adequate dispersant at an optimum dosage permits to increase this ratio keeping similar rheological behaviour.

Starting from the rheological behaviour of the dispersant-free dispersion at the initial concentration of 8 wt% of pigment, an addition of dispersant at the optimal dispersant demand allowed an increase in the pigment loading in such a way that the rheological behaviour remained very close to that of the reference dispersion. The successful attempts presented in Fig. 9 show that the rheological behaviour was not perfectly superimposed because the shear thinning behaviour was slightly different.

A C.I. Pigment Violet 23 load of 12.5% can be achieved by using the high molar mass copolymer. However, the use of
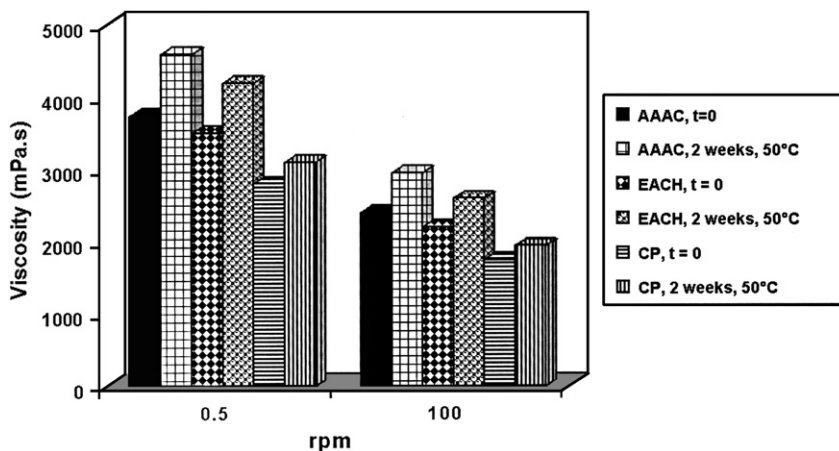

Fig. 8. The effect of two-week storage at 50 °C on the rheology of the violet pigment bases.

Table 4
Effect of two-week storage at 50 °C on the viscosity of the violet pigment dispersions in Krebs units

	Initial viscosity	Viscosity (KU) after two weeks at 50 °C
Without dispersant	95	Gel
0.5 wt% AAAC	90	95
0.8 wt% EACH	89	95
3.5 wt% CP	82	84

AAAC or EACH has increased the pigment load only by 2%, which indicated a limited deflocculating action of these two dispersants.

When the colorant bases were prepared at the optimum ratios, their Krebs Stormer viscosities (Table 5) essentially showed that we can benefit from an increase in the pigment loading without loosing the flow properties.

3.3. Colour properties

The consequences of good dispersion state of the pigment on the development of the tinting strength during the grinding process and colour stability on storage have been investigated. Thus, it is known that the tinting strength of a pigment is improved in case of very homogeneous dispersion inside the grinding medium (resin). On another hand, the slow aggregation of the pigment particles causes a change in colour. The dispersion of the pigment particles inside the resin matrix is ensured by the various dispersants studied. The ability of the dispersants to prevent pigment aggregation both during grinding and on long time storage has been evaluated by means of the tinting strength measurements and the "rub out test".

3.3.1. Development of the tinting strength

Tinting strengths were measured after mixing 8 wt% violet pigment concentrate with 28 wt% TiO$_2$ alkyd white paint in such a way that ratio TiO$_2$/violet pigment was equal to 9. In

Table 5
Viscosities at optimum pigment ratios in Krebs units

Pigment ratio (wt%)	Dispersant	Viscosity (KU)
12.5	CP	92
10	EACH	94
10	AAAC	96

the presence of each of the three dispersants, the tinting strength of the C.I. Pigment Violet 23 developed linearly during the first 20 min of grinding. Thereafter, the kinetic slowed down until a maximum tinting strength was reached. This three-step behaviour was theoretically and experimentally described by Völtz [28,29]. After 80 min, the copolymer dispersant allowed the achievement of a tinting strength equal to 100%. This value was obtained only after 120 min in the presence of EACH. Contrarily, AAAC was of poorest performance since the obtained tinting strengths were lower than 100% during the measurement duration (Fig. 10).

Thanks to its good dispersion state, the C.I. Pigment Violet 23 has achieved the largest tinting strength in the presence of the high molar mass copolymer. Indeed, the large number of anchoring groups contained in its long molecular chain and its block chemical structure allowed the formation of a thick layer around the particles and their efficient stabilization against aggregation.

3.3.2. Colour stability

The colour change is usually due to a non-homogeneous repartition of the pigment particles which can result from a local accumulation like that in the case of the flocculation or sedimentation. A "rub out" test consists in measurements of the chromatic deviation ΔE^* between an intact region of the sample and a part of its surface that has been made homogeneous by rubbing it. This test was realized in order to judge the efficiency of the studied dispersants. Measurements were realized
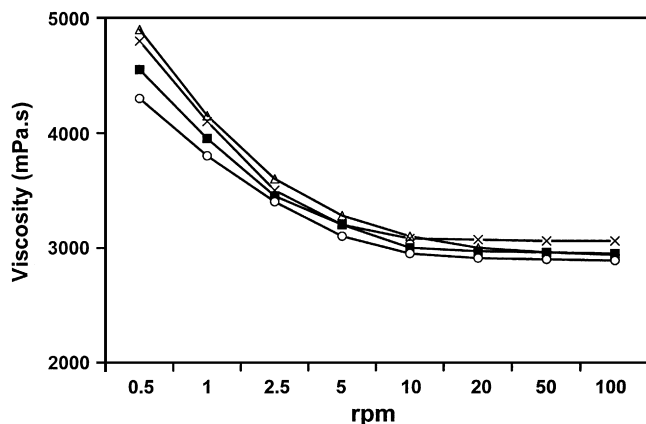

Fig. 9. Effect of the various dispersants for increasing pigment loadings at minor modification of the viscosity. (×) 8 wt% pigment and 0% dispersant, (Δ) 10 wt% pigment and 0.6 wt% AAAC, (■) 10 wt% pigment and 1.0 wt% EACH, and (○) 12.5 wt% pigment and 5.4 wt% CP.
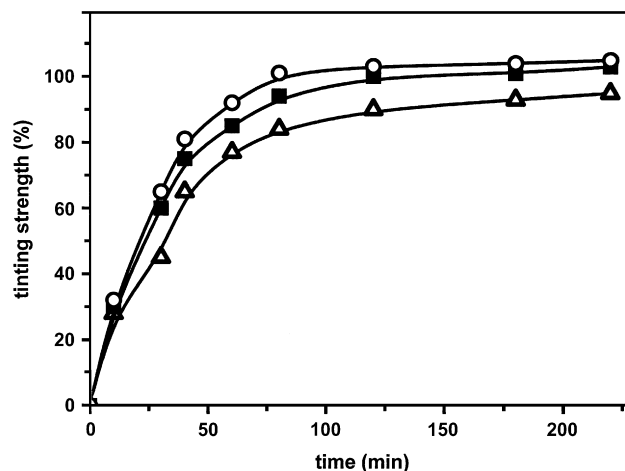

Fig. 10. Development of the tinting strength of the violet pigment in the presence of the various dispersants. (Δ) AAAC 0.5 wt%, (■) EACH 0.8 wt%, and (○) CP 3.5 wt%.
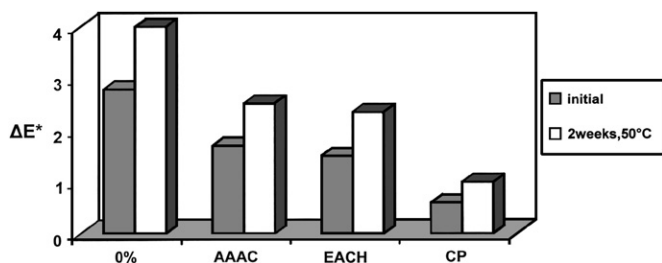
Fig. 11. The effect of two-week storage at 50 °C on the results of the rub out test for the violet pigment concentrate without and in the presence of the various dispersants.

after the sample preparation and after two weeks ageing at 50 °C (Fig. 11).

The colour differences observed between the rubbed and the intact zones were obviously larger in the absence of the dispersants ($\Delta E^* = 4$). This is related to the instability of the dispersion and the high tendency to the flocculated state. The use of a low molar mass dispersant such as AAAC and EACH has allowed the reduction of these differences, but their performances were limited. Indeed, the ΔE^* obtained in the presence of these two dispersants was around 2.5 after storage in the oven. This value reflected a more or less extensive flocculation.

The copolymer type dispersant (CP) is a better stabilizer for the C.I. Pigment Violet 23 concentrate. The consequence was a small difference in colour that did not go beyond unity even after the two-week storage. The thick layer of adsorbed copolymer stays at the pigment surface for a long time and keeps its dispersing ability on storage.

4. Conclusion

The carboxylic block copolymer dispersant of a high molar mass is an efficient dispersant for the C.I. Pigment Violet 23 in non-polar medium. The preparation of the concentrate suspensions of this pigment was optimized. The adsorbed amount was found to be equal to 2.10 mg m^{-2}, which resulted in a thick adsorbed layer as compared to carboxylic homopolymers.

The copolymer adsorption as studied with NMR technique took place basically via the carboxylic groups. The adsorption driving forces would be essentially due to $\pi−\pi$ dispersion interactions between the aromatic rings of the carbazole molecule and the π-electron of the carbonyl oxygen of the polymer. The dispersant conformation of the copolymer on the C.I. Pigment Violet 23 surface was mainly made of loops and tails.

The addition of the block copolymer dispersant allowed the increase in the pigment loading from 8% to 12.5% keeping the viscosity profile constant. The consequences of the presence of an efficient dispersant were a higher tinting strength and a better colorimetric stability as revealed by the ''rub out'' test.

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