Improved dispersion and stability of natural hybrid pigments

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Introduction

Pigments are fundamental in the composition of paints and inks. Synthetic and natural pigments differ by their performances, their costs and their opportunities to be used. Synthetic pigments offer high chroma and high color strength, but more and more synthetic pigments are now controversial because of their toxicity and the urge to reduce companies' carbon footprint. To find a solution, the paint companies evolve to replacing these synthetic pigments with natural ones. However, natural pigments still face many obstacles if they want to achieve the same performance as synthetic pigments. Indeed, natural pigments have certain obstacles that must be overcome: the shade must be improved for all applications, the range of colors is limited, and the light fastness is weak.
An innovative technology inspired by the Mayan civilization offers a solution to remove all these locks [1]. This patented technology developed by PIGM'Azur can be summarized in one sentence: "the protection of organic coloring molecules by a controlled natural encapsulation with a sepiolite clay". This innovation makes it possible to obtain a range of pigments up to 100% natural with many advantages: a wide range of colors, a better resistance to external aggressions (UV, chemical, thermal...) and a dispersibility in all medias (water, oils, polymers, solvents ...). However, this dispersion is obtained with high energy, whatever the media, and the presence of clay increases viscosity. These parameters are very important for paint formulation.

The project focuses on natural clay-based pigments characterization and dispersion, in different medias. The aim of the project is to find an efficient technique to disperse the pigments in water and in oil by varying the percentages, stirring time and speed. The objective is to observe the behavior of the pigments and to determine what strategies and parameters are to consider in order to obtain an effective dispersion while conserving a low viscosity.
The study then moved on to the evaluation of different dispersants that are over 70% biodegradable, to optimize viscosity (<2000 mPa.s) and stability in water and oil. The effectiveness of the dispersants was tested using four pigments and by monitoring viscosity trends at room temperature and at 50°C.
Among the dispersants tested, a polysorbate (dispersant 1) and a polyglyceryl-6 caprylate/caprate (and) sodium caproyl lauryl lactylate (dispersant 2) emerged as the most effective. Dispersant 1 produced fluid, stable dispersions, while dispersant 2 showed thixotropic behavior with a stable viscosity below 2000 mPa.s under shear. Microscopic and colorimetric analyses confirmed the quality and stability of the dispersions. In addition, the impact of pH was explored, showing that alkaline state improves the dispersion of pigment particles due to increased negative charges on clay particles. This encouraging result leaded to conduct additional trials on alkaline dispersions that concluded on the stability of pigments in an alkaline environment.

Dispersion of sepiolite-based pigment

Sepiolite has a fibrous texture whose structural formula is based on the Brauner and Preisinger model. It is a hydrated magnesium pseudo-phyllosilicate, whose cell formula is $Mg_8Si_{12}O_{30}(OH)_4$-$(H_2O)_4$-$8H_2O$ [2].
Efficient dispersion of the clay pigment in a preferentially water-based medium is essential to achieve superior, quality properties. However, the individual acicular particles of fibrous clays, such as sepiolite, tend to aggregate easily in water due to hydrogen bonding and Van der Waals interactions, forming clusters and aggregates that limit the quality of clay dispersion. In addition, the specific crystalline structure of fibrous clays prevents their delamination (or exfoliation), as is the case with platelet clays. In order to improve the dispersibility of sepiolite-based pigment, several approaches can be evaluated, among which the most common strategies include mechanical treatment, addition of dispersants and chemical modification of the mineral surface [3]. In this study, mechanical treatment and dispersant addition will be evaluated.

To achieve effective dispersion of pigment particles in a liquid medium, a certain amount of energy is required to ensure that the particles are completely surrounded by the liquid, avoiding any permanent contact between them. In order to guarantee the success of end applications, it is crucial to obtain pigment dispersions featuring small particle size and high stability [4]. Mechanical processing offers various methods such as the use of high-speed shear, ball milling, or ultrasound, among others. These processes are capable of disaggregating the bundles into smaller structures or individual rods, without compromising the crystal structure and length of the nanoparticles [3].

Materials and methods

Four pigments were tested, including two blues and two yellows in different medias, water and oils, and the results will focus on one blue, NC63 Blue, in water.

To determine the optimum energy to disperse the pigment in water, various tests were carried out using several agitation techniques, including magnetic agitation, the Rayneri or deflocculator (high speed mixer) and the Speed Mixer or ball mill. The aim was to obtain the highest possible quantity of pigment while ensuring good particle size distribution. To prepare for these tests, 10% pigment powder is added to water, then stirred with a magnetic stirrer, a deflocculator at 3000 rpm, and a ball mill at 2500 rpm for 15 minutes.

After comparing these three dispersion techniques and selecting the most efficient one, an improvement was made to the latter by using two dispersants, designated dispersant 1 and dispersant 2. The aim of this improvement is to achieve better dispersion and optimized viscosity, while maintaining a high percentage of pigment.

Finally, an alkaline dispersion method was implemented. The aim of this approach is to optimize pigment dispersion with reduced energy consumption, taking advantage of high pH conditions to improve particle stability and distribution. This method not only maintains a homogeneous dispersion, but also reduces overall viscosity, facilitating the integration of pigments into various formulations.

Results and discussion

1. Comparison of the different dispersion methods

The results of the three blue pigment dispersion techniques are shown in Figure 1. The analysis will identify the advantages and limitations of each method in terms of dispersion quality and pigment distribution, providing crucial information for future decisions on selecting the most appropriate dispersion method.

A	B	C

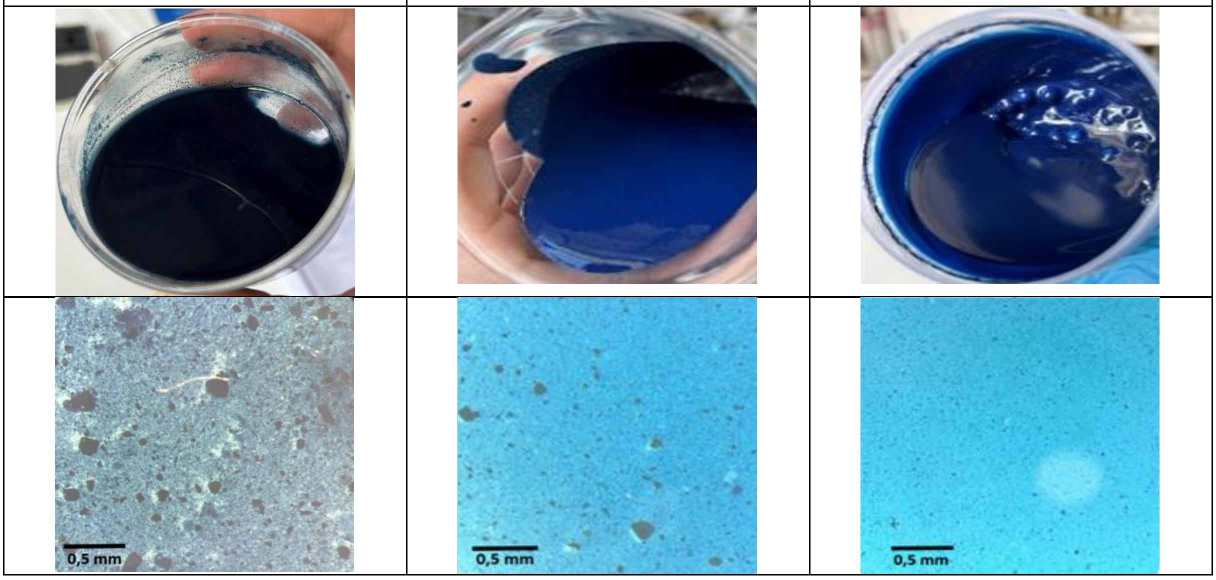


Figure 1. From left to right: Images of the pigment dispersions obtained with the different dispersing methods; (A) magnetic agitation, (B) deflocculator and (C) ball mill

	(A) Magnetic agitation	(B) Deflocculator	(C) Ball mill
Viscosity (mPa.s)	64	1364	4585

Table 1. Viscosity obtained with the different dispersing methods; (A) magnetic agitation, (B) deflocculator and (C) ball mill

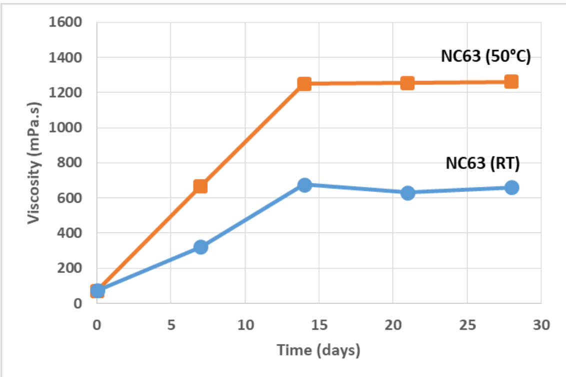
In this study, the Speed Mixer emerged as a crucial tool for conducting a comparative evaluation of dispersion techniques, specifically when compared to magnetic agitation and the deflocculator. Detailed analysis of the results revealed notable differences between the three methods, both at the macroscopic and microscopic levels.

On a macroscopic scale, the dispersions exhibited considerable variations in appearance and viscosity. Notably, the dispersion achieved with the ball mill showed the highest viscosity among the methods tested (Table 1). This finding indicates that as shear energy increases, the viscosity of the dispersion also rises, highlighting the direct correlation between the intensity of the shear force applied and the resulting physical properties of the pigment dispersion. At microscopic level, observations show a clear improvement in the quality of pigment pastes generated by the Speed Mixer in terms of dispersion and particle size distribution (Figure 1). This microscopic difference underlines the Speed Mixer's superior efficiency in producing more homogeneous, better-dispersed pigment dispersions. This could have positive implications for end-use pigment applications in various industrial fields. The higher the energy, the better the pigment dispersion, but the viscosity also increases. This is because applying higher energy during the dispersion process breaks up pigment agglomerates more effectively, resulting in a more uniform distribution and smaller particle size. However, this improvement in dispersion is often accompanied by an increase in suspension viscosity. This relationship is due to the fact that better dispersed pigment particles interact more with the surrounding medium, creating a more viscous suspension. Consequently, while increasing energy brings benefits in terms of dispersion quality, it also requires careful management of viscosity to maintain the desired properties of the final product. However, the problem lies in the high viscosity of the dispersion obtained by this method. It is therefore necessary to reduce this viscosity while maintaining a high percentage of pigment, in order to avoid an excessively fluid consistency and preserve the coloring power of the pigment paste, hence the use of dispersants.

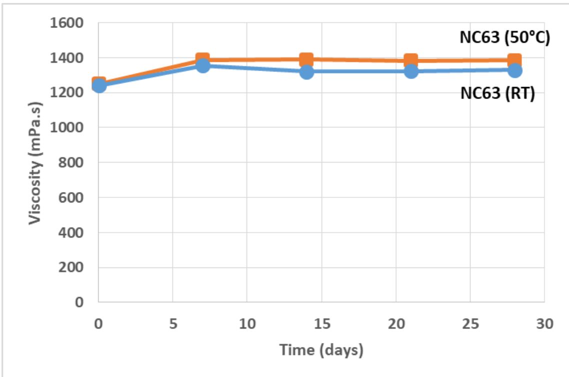
2. Use of dispersing agents

In pigment application, the dispersant plays an essential role in the stability of the pigment dispersion. Dispersants prevent pigment aggregation during grinding and long-term storage, which is very important for obtaining quality pigment dispersions. They stabilize pigments by creating repulsive forces between individual pigment particles through anchoring groups with a high affinity for the pigment surface [4].

Further experiments focused on the use of the Speed Mixer, given its proven effectiveness in the preparation of pigment pastes. The graphs below have been plotted to represent the temporal evolution of the viscosity of NC152 Blue dispersions with the use of dispersant 1 and dispersant 2, at both room temperature (RT) and 50°C.



Viscosity comparison at RT and 50°C for dispersant 1



Viscosity comparison at RT and 50°C for dispersant 2

Figure 2. Evolution of viscosity over time in presence of dispersant 1 (on the left) and dispersant 2 (on the right) at RT and 50°C

In particular, dispersant 1 produced an initial dispersion with Newtonian behavior, where viscosity remains very low at D0, but begins to increase before stabilizing from D+14 (Figure 2). On the other hand, the dispersion obtained with dispersant 2, which exhibits thixotropic behavior, maintains an almost constant viscosity throughout the 28-day period. It is important to note that thixotropy differs from rheofluidification, the latter being linked to a decrease in

viscosity as a function of applied stress, whereas thixotropy implies a decrease in apparent viscosity over time, under constant stress.
Results obtained at room temperature show viscosity values slightly lower than those measured at 50°C. Interestingly, both dispersants maintained a stable viscosity over time, remaining below the 2000 mPa.s threshold, with thixotropic behavior for dispersant 2.

Dispersant 1, polysorbate 85 can reduce the surface tension of water, facilitating the wettability and dispersion of sepiolite particles in water. It also has emulsifying and stabilizing properties, which help to keep sepiolite particles dispersed in water and prevent their agglomeration or sedimentation. By creating a surface barrier around sepiolite particles, it reduces the attraction between them and prevents their aggregation.
The performance of dispersant 2 is comparable to that of standard PEG solubilizers on the market. Polyglyceryl-6 caprylate/caprate is derived from polyglycerin-6 (a component of vegetable oil) mixed with caprylic and capric acids (saturated fatty acids from coconut/palm). It is used in many products for its solubilizing properties, helping ingredients to dissolve more easily. On the other hand, sodium caproyl lauryl lactylate is a lactyl ester (derived from lactic acid) with caproic and lauric fatty acids. It helps reduce the surface tension and contributes to the even distribution of the product during use, which explains the results obtained with dispersant 2.

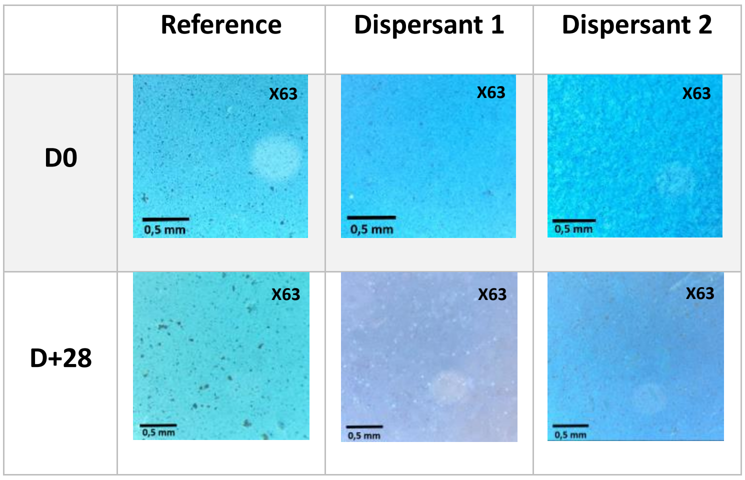


Figure 3. Microscopic images of the reference, dispersant 1 dispersion and dispersant 2 dispersion, at D0 and after 28 days

At a concentration of 10% NC63 Blue pigment, significant variations are observed in the microscopic images of the different dispersions (Figure 3), both in terms of particle size distribution and dispersion quality. Pigment pastes made with the pigment alone (the reference) are characterized by a greater presence of aggregates and a non-uniform particle size distribution. The two dispersants, clearly stand out as effective, generating high-quality, aggregate-free dispersions over the 28-day period. This observation explains the stability of the dispersions obtained with these two dispersants, as well as the maintenance of an appropriate viscosity.

3. Alcalin pH effect

The optimum pH is between 8 and 8.5, corresponding to the point at which sepiolite acts as a buffer in the aqueous medium. This buffering capacity of sepiolite can be attributed in part to the release of Mg ions from the octahedral sheet of its structure. At a pH above 9, viscosity decreases considerably, and rheological behavior becomes Newtonian [5].

To corroborate the data extracted from Alvarez's 1984 study concerning the optimum pH for best sepiolite dispersion, final tests were carried out with NC63 Blue in water, at a concentration of 10%. The pH was adjusted above 9 using a 10% sodium hydroxide solution.

The results obtained (Table 2) conclusively confirm the findings of Alvarez's study. Above a pH of 9, the dispersion adopts a Newtonian behavior with a viscosity of around 55 mPa.s. Increasing the pH of the suspension seems to improve the dispersibility and colloidal stability of the sepiolite particles, due to the increase in the negative charge of the clay particles. This increase in negative surface charge is due to the presence of hydroxyl groups or the breaking of M-O-M bonds (M = Si or Mg) at very alkaline pH. This increase in surface charge promotes particle disaggregation and stabilization, thus preventing reaggregation, which induces instability in systems. It has also been established that a very low absolute zeta potential, below ±5 mV, encourages flocculation and particle instability in solution, and that stability tends to occur only above a value of ±30 mV [4].

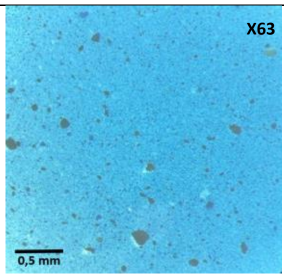
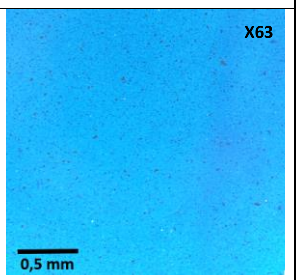
Conditions	Speed Mixer (15 min – 2500 RPM)	
	Neutral pH	pH > 9
J0		
pH	pH = 7,71	pH = 11,39
Viscosity (mPa.S)	4585	55
Microscope		

Table 2. Results of the dispersions at neutral pH and alkaline pH

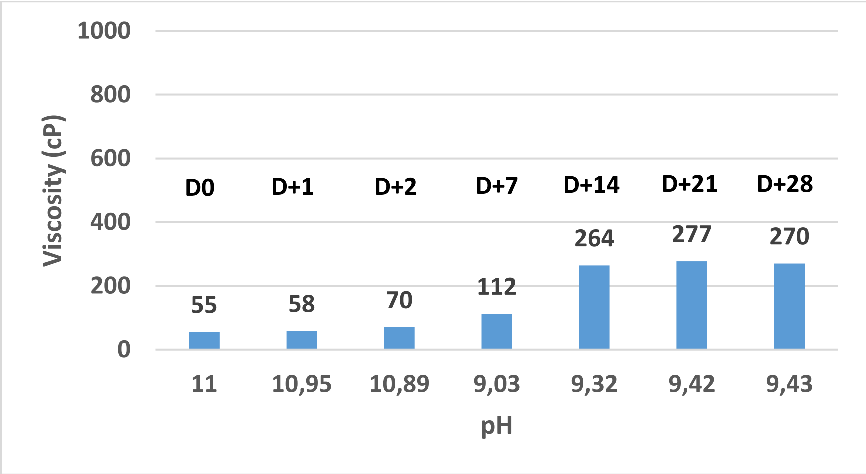


Figure 4. Evolution of viscosity over time at alkaline pH

From the graph above, it is clear that alkaline pH has a significant impact on dispersion viscosity (Figure 4). Although pH gradually decreases over time, viscosity remains low throughout the 28-day period, stabilizing from day 14 onwards. Taking this observation a step further, we can note that maintaining an alkaline pH promotes a more homogeneous dispersion of pigments, reducing interactions between particles that might otherwise increase viscosity. This stability of viscosity, despite the drop in pH, suggests that the initial alkaline environment creates favorable conditions for efficient, long-lasting pigment dispersion. This is particularly important for industrial applications where stable viscosity is crucial to ensure consistent, high-quality performance of pigmented products.

Conclusion

This research project was successfully carried out within PIGM'Azur, with the aim of studying the dispersion of sepiolite-based pigments in water, using dispersing agents. The results obtained provided valuable information on the optimum conditions for the dispersion technique, the choice of dispersants and their effectiveness, and the influence of factors such as stirring speed, temperature and pH. The rigorous methodological approach, combining microscopic and rheological analyses, enabled the dispersions obtained to be thoroughly characterized.

The central objective of the project was to determine the optimum approaches and parameters for achieving efficient pigment dispersions, with a uniform particle size distribution. In addition, it aimed to achieve a viscosity below 2000 mPa.s while maintaining a high pigment concentration. This was achieved by using dispersants that were at least 70% biodegradable. The results showed that using the Speed Mixer with a rotation speed of 2500 RPM for 15 minutes proved to be the most effective method for obtaining efficient dispersions.

Furthermore, it has been shown that the choice of dispersant plays a crucial role in the quality and stability of dispersions, with promising results for both dispersants. Dispersant 2 is advantageously distinguished from Dispersant 1 by its all-natural provenance and COSMOS approval, making it an environmentally friendly choice. A notable feature of dispersant 2 is its ability to generate dispersions with thixotropic behavior, while maintaining a stable viscosity below 2000 mPa.s under shear. In contrast, dispersant 1 has the advantage of rapidly creating fluid, stable dispersions, reaching this state as early as D+14 for NC63 Blue. As a result, the final choice between these two dispersants is left to the customer's discretion, depending on the objective and quality requirements for the desired pre-dispersion. The unique features and benefits of each dispersant must be carefully evaluated in relation to the needs and criteria of the final product.

Further experiments were carried out on NC63 Blue to assess the impact of pH on sepiolite dispersibility. In line with the literature, a pH above 9 induces a significant drop in viscosity, transforming rheological behavior into Newtonian, and this observation was confirmed with NC63 Blue at a concentration of 10%. Thus, in an alkaline environment, the dispersion of sepiolite particles is optimized thanks to the accentuation of negative charges on the clay particles, reinforcing their repulsive force and inhibiting their aggregation. These results may be of considerable interest to both the customer and the manufacturer, given the simplicity of dispersion in the absence of any dispersant.

Ultimately, this project offers a valuable contribution to the industry by providing innovative solutions for the dispersion of clay-based pigments, paving the way for more stable and higher quality formulations in various products such as paints and inks.

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