Exploring the potential of natural clays as dispersants for organic pigments

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Abstract: Dispersions consisting of various clays (smectite, mica, and kaolinite) and Pigment Yellow 138 (PY138), a yellow organic pigment were prepared through an in-situ grinding process at low concentrations (0.1% w/w) and at high concentrations (0.5% to 5% w/w) where smectite were observed to exhibit better colloidal stability over the control. Preliminary studies investigating the capabilities of the above clay as possible dispersing agents for PY138 had been conducted using UV-Vis spectroscopy. Among the clays used, smectite resulted in the most stable dispersions at low concentrations. At higher pigment concentration, a critical concentration was observed around 1.0% w/w smectite.

Key Words: clay, pigment dispersion, organic pigments, dispersant

1. INTRODUCTION

The ability of natural clays to suspend particles makes them as alternative to conventional dispersing agents, particularly in pigment dispersion applications (Dong et al., 2009; Lan et al., 2010; Lan and Lin, 2011). Unlike conventional dispersing agents, which rely on adsorption for stability, clays achieve particle suspension by forming a 3D network structure due to their charged surfaces.

Lan and Lin (2011) showed that using a certain type of clay called fluorinated mica clay (FMC) helps stabilize organic pigments. They found that increasing the amount of clay improves the stability of the pigment dispersion, possibly because the clay's shape is different from the pigment's, making it harder for the pigment particles to clump together. On the other hand, Cullari et al. (2021) found that when they mixed graphene sheets with a clay called fibrous sepiolite clay, the clay's fibrous structure trapped the graphene, preventing it from clumping together. This suggests that clays can play a crucial role in keeping nanomaterials dispersed evenly.

While clay has shown success in dispersing nanoparticles, its potential as a pigment dispersant remains largely unexplored. In the paint and coating industries, clay is widely used because of its adaptable surface and rheological properties. However, its main role is as a viscosity modifier, ensuring that paint and coating formulations maintain the desired consistency and finish upon application.

The potential of clays as dispersing agents has not been thoroughly investigated. This presents an opportunity for the coatings industry due to clay's cost-effectiveness and low toxicity compared to conventional dispersants like alkylphenol ethoxylates (APEs), which face strict regulations. Our study investigates clay as a dispersing agent for organic pigments, highlighting its potential as an environmentally friendly alternative in paint and coating formulations.

2. METHODOLOGY

2.1 Materials

Pigment Yellow 138 (PY138) (CAS No.30125-47-4) and four types of clay: smectite, mica, and kaolinite were provided by Chemrez Technologies, Inc. These were used as received. Distilled water was used as a solvent for dispersion.

2.2 Sample preparation

The preparation of the clay-assisted pigment dispersions was based on a modified technique by Lan and Lin (2011). Distilled water, pigment, and a particular type of clay (as dispersants) were pre-weighed and placed on separate areas on the glass pan. Overall, four types of clay as dispersing agents were used: smectite, mica, and kaolinite. A few drops of water were slowly added to the clay to initiate gelation, followed by thorough grinding using a glass muller (Kremer Pigmente GmbH & Co. KG.). Once the desired paste consistency was achieved, PY138 was incorporated, and continuous grinding was performed while slowly adding distilled water. The dispersions were stirred using a magnetic stirrer at 1500 rpm for 30 minutes, followed by 15 minutes of sonication.

2.3 UV-Vis spectroscopic measurements

Accelerated sedimentation was performed to simulate the effects of long-term storage of the dispersions. Previously prepared samples were poured into a conical flask and stirred using a magnetic stirrer at 1500 rpm. Then, 15 mL of the samples were transferred into another conical flask and centrifuged for 5 minutes. The middle portion of the aqueous-rich layer was collected and analyzed spectroscopically (300-800 nm range with a 2 nm resolution).

Dispersions with an absorbance significantly 1.0 underwent serial dilution for further measurements.

For dispersions at the middle concentration (0.5% to 5.0% w/w pigment), a value referred to as the apparent absorptivity was used as a measure of stability and calculated using the dilution factor. The formula for apparent absorptivity was as follows:

$$\epsilon_{Apparent} = \frac{A}{\mu_{F_{dil}} c l}$$

where:

$\epsilon_{Apparent}$	=	apparent absorptivity
A	=	absorbance
$\mu_{F_{dil}}$	=	dilution factor
c	=	concentration
l	=	path length

3. RESULTS AND DISCUSSION

Figure 1 compiles the digital images of the pigment dispersion at a concentration of 0.1% w/w PY138 pigment using various clays at concentrations of 0.1% w/w and 0.3% w/w clay. The visual examination of the images reveals a notable reduction in sedimentation within the dispersion upon the addition of clay dispersing agents, with the exception of kaolinite clay.

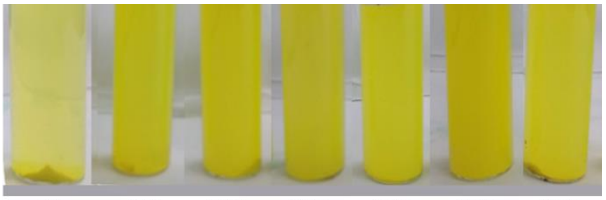

Fig. 1. Photographs of clay-assisted dispersions of 0.1 and 0.3%w/w PY138

Sedimentation means particles sinking to the bottom of a liquid. How fast this happens shows how stable the mix is. As sedimentation is a time-dependent process, a standardized centrifugation was performed to simulate long-term ambient storage conditions. This helped us check how stable different samples were. The absorbance of the aqueous phases of the clay-assisted dispersions were measured after conducting standardized centrifugation and dilution to 1/5 of the starting concentration, as recorded in Figure 2. A significant increase in absorbance was observed for pigments dispersed in clay compared to the control (pigment + water only). Among the clay-assisted dispersions, those added with smectite exhibited the highest absorbance at 0.69 at 0.1% w/w clay and 0.8 at 0.3% w/w clay.

However, the absorbance of PY138 added with mica and kaolinite, respectively, did not show any significant improvement compared to the control. This lack of improvement in kaolinite-dispersed PY138 can be attributed to its inferior surface charge properties compared to the former two.

Due to its higher degree of enhancement in measured absorbance, the pigment dispersion with smectite was chosen for further investigation at higher PY138 pigment concentrations.

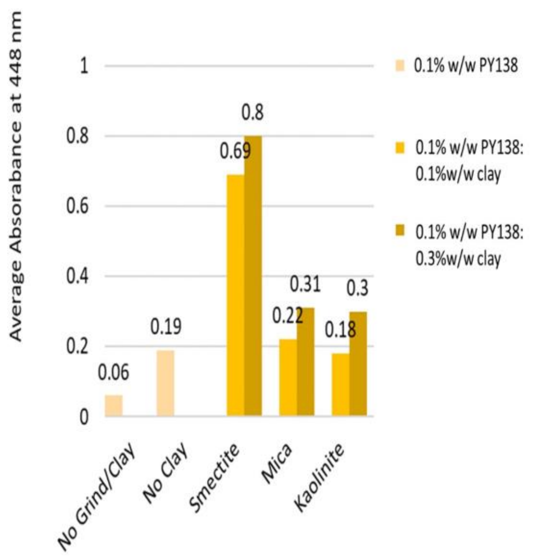

Fig. 2. UV-Vis absorbance of clay-assisted dispersion at 0.1%w/w PY138 at 448 nm diluted to 1/5 of its starting concentration.

Figure 3 illustrates the measured apparent absorptivity, calculated using equation 1. The apparent absorptivity represents the quantity of dispersed organic pigment remaining in the system following standardized centrifugation. The results demonstrate that as the clay concentration increases up to 1.0% w/w, there is a corresponding increase in the amount of organic pigments suspended in the water phase. However, beyond 1.0% w/w clay, the apparent absorptivity starts to decrease. This suggests that the critical concentration of smectite for optimal dispersal of PG-454 is approximately 0.5% to 5.0% w/w PG-454 in combination with 1.0% w/w clay.

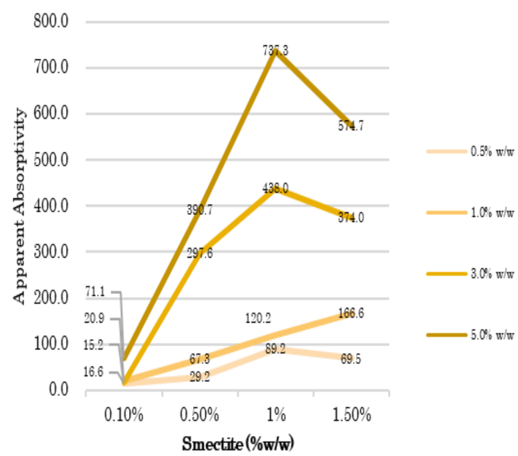

Fig. 3. Average relative absorptivity of smectite-assisted pigment dispersions at 0.5% to 5% w/w PY138 concentration

As shown in Figure 3, the observation of a critical concentration on clay-assisted dispersions is evident. This is also previously reported in oil-in-water Pickering emulsions using clays and cationic layered double hydroxide (LDH) (Machado et al., 2019).

4. CONCLUSIONS

In conclusion, results of our study underscore the potential of clays as effective dispersing agents for pigment dispersions. Among the clay-assisted dispersions of Pigment Yellow 138 (PY138), the smectite-assisted dispersion showed remarkable stability. The optimal concentration of smectite was noted at 1.0% w/w as evidenced by their apparent absorptivity measurements. Various concentrations of PY138 pigment dispersions from 0.5% to 5% w/w were prepared.

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