The utilisation of natural clays as dispersing aids in aqueous pigment dispersions

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Abstract

The ability of natural clays to suspend particles makes them a promising candidate for use as dispersants, with potential applications in pigment dispersions. Unlike conventional dispersing agents that stabilise particles through adsorption, clays can maintain particle suspension by forming a three-dimensional network structure due to their charged surfaces. While there are reports of clays effectively dispersing various nanoparticles, to the best of our knowledge, their use as dispersing agents for pigments has not yet been explored.

Clay-assisted dispersion presents a valuable opportunity for the coatings industry due to the low cost and minimal toxicity of clays. In contrast, conventional dispersants such as alkylphenol ethoxylates (APEs) are subject to increasing restrictions and scrutiny due to their high toxicity and long-term environmental persistence.

Here, we report the use of clays as dispersing agents for an organic pigment. Dispersions comprising various clay specimens (smectite, mica, and kaolinite) and Pigment Yellow 138 (PY138), a yellow organic pigment, were prepared via an *in-situ* grinding process at both low (0.1% w/w) and high concentrations (0.5% to 5% w/w). Among the tested clays, smectite demonstrated superior colloidal stability compared to the control. At low concentrations, smectite produced the most stable dispersions, while at higher pigment concentrations, a critical threshold was observed at approximately 1.0% w/w smectite.

Keywords: clay, dispersant, organic pigment, coatings
Kulcsszavak: agyag, diszpergálószer, szerves pigment, bevonatok

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1. Introduction

Organic pigments are a class of colourants renowned in the industry for their vibrant colours, high tinting strength, and excellent hiding power. However, due to their inherent insolubility, which arises from strong noncovalent interactions, they require an energy-intensive grinding process and the use of specialised additives to achieve proper dispersion in formulations.

Additives such as dispersants are added in a paint formulation to enhance the dispersibility of organic pigments. These can be in the form of small molecule surfactants or polymeric surfactants. The most popular dispersants are alkylphenol ethoxylates (APEs), particularly nonylphenol ethoxylates (NPEs), due to their cost-effectiveness and adaptable properties for many paint applications. However, APEs have been indicated in several studies to have found their way in municipal and industrial wastewaters undergoing complex degradation processes resulting in persistent estrogenic metabolites. These metabolites present significant health and environmental hazards, as they accumulate in soil and the tissues of fish. As a result, heavy restrictions have been imposed in many regions such as the EU, ASEAN, Canada, and the US on the use of these dispersants. While alternative APE-free wetting agents have been explored such as alkyl ethoxylates (AEs), their acute toxicity on freshwater fish notwithstanding its inferior dispersing and wetting capabilities.

Despite the widespread use of clays in the paint industry due to their versatile surface and rheological properties, their application remains largely confined to their role as viscosity modifiers (thixotropic agents). These clays help ensure that paint maintains its intended consistency and finish upon application. However, their potential as dispersing agents has yet to be thoroughly explored.

It has been demonstrated that clays serve as excellent dispersing agents for nanomaterials at low concentrations, including carbon nanomaterials [7–12], metallic nanoparticles [13], polymers [14], and pigments [15], with several mechanisms theorised to explain this phenomenon.

Lan and Lin (2011) [15] proposed the theory of "factor of geometric shape homogeneity" in the use of organic pigments stabilised by fluorinated mica clay (FMC). In their study, they successfully demonstrated the effect of increasing clay content on the stability of pigment dispersion through zeta potential, particle size, and UV-Vis spectroscopic measurements. The researchers proposed that the difference in geometric shape between the FMC and the organic pigment disrupts the natural agglomeration process of the latter, thereby reducing aggregation.

On the other hand, Cullari *et al.* (2021) [16] proposed the theory of "kinetically arrested particle". In their study, graphene sheets were dispersed within a fibrous sepiolite clay. The fibrous network structure of the clay effectively trapped the graphene, preventing particle agglomeration.

Etika *et al.* (2009) [17] proposed that the mechanism involved in the stabilisation of clay is the haloing effect. Etika *et al.* proposed that the interaction of high surface charge clay particles and the negligible charge of carbon black (CB) causes a synergistic stabilisation similar to previous studies observed by Tohver *et al.* (2001)[18] involving mixture of charged zirconia nanoparticle and uniform silica spheres.

In this study, we aim to prepare pigment dispersions based on Pigment Yellow 138 (PY138) using clay materials as dispersing agents, with the goal of developing a sustainable, surfactant-free, water-based paint. This research explores the potential of clays as an environmentally friendly and sustainable alternative to conventional dispersants.

2. Experimental

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 & Lin (2011) [15].

Distilled water, pigment, and a particular type of clay (as dispersants) were pre-weighed and placed in 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 Characterization

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:

$$\epsilon_{Apparent} = \frac{A}{\mu_{F_{dil}} c l} \quad (1)$$

where:

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

Films were prepared by drop casting dispersions on a microscope glass slide and then these were dried for at least a week. The films were then analyzed using a USB digital microscope with the scale of the taken images determined using its included micrometer calibrated ruler. Since clay films are colorless, methyl red was used to stain the clay dispersion before drop casting for better visual.

3. Results and discussion

3.1 Clay specimen screening

Fig. 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.

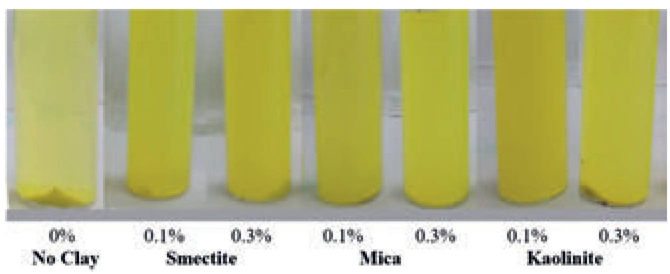

Fig. 1 Photographs of clay-assisted dispersions of 0.1%w/w PY138
1. ábra A 0,1% w/w PY138 agyag tartalmú diszperzióinak fényképei

Sedimentation refers to the settling of dispersed particles towards the bottom of a sample. The rate of sedimentation directly reflects the stability of the mixture, as the dispersed particles gradually settle and the concentration in the aqueous phase decreases. As sedimentation is a time-dependent process, a standardised centrifugation was performed to simulate long-term ambient storage conditions, enabling a precise evaluation of dispersion stability across samples.

The absorbance of the aqueous phases of the clay-assisted dispersions was measured after conducting standardised centrifugation and dilution to 1/5 of the starting concentration, as recorded in *Fig. 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.

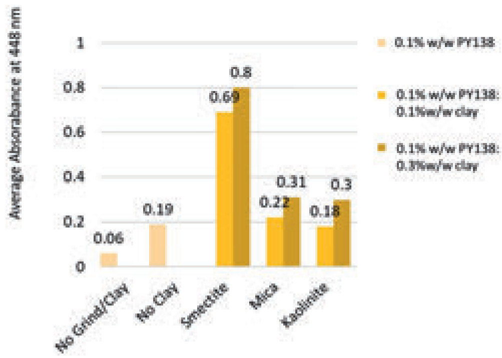

Fig. 2 *UV-Vis absorbance of clay-assisted dispersion at 0.1%w/w PY138 at 448 nm diluted to 1/5 of its starting concentration*
2. ábra *A 0,1% w/w PY138 agyag tartalmú diszperzió UV-Vis abszorbanciája 448 nm-en, kiindulási koncentrációjának 1/5 részére hígítva*

However, the absorbance of PY138 with mica and kaolinite did not show any significant improvement compared to the control. The lack of enhancement in kaolinite-dispersed PY138 can be attributed to its inferior surface charge properties relative to the other clays.

Due to the greater increase in measured absorbance, the pigment dispersion with smectite was selected for further investigation at higher PY138 concentrations.

3.2 Determination of critical concentration

Fig. 3 illustrates the apparent absorptivity, calculated using *Equation 1*. The apparent absorptivity represents the quantity of dispersed organic pigment remaining in the system following standardised 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 dispersion of PY138 is approximately 0.5% to 5.0% w/w PY138 in combination with 1.0% w/w clay. The presence of a critical concentration on clay-assisted dispersion is evident, similar to observations in studies on oil-in-water Pickering emulsions using clays and cationic layered double hydroxide (LDH). At the critical concentration, clays are capable of undergoing interparticle association, forming 3D network clay structures that surround the oil-in-water globules which are analogous to mechanisms being proposed on clay-assisted dispersions.

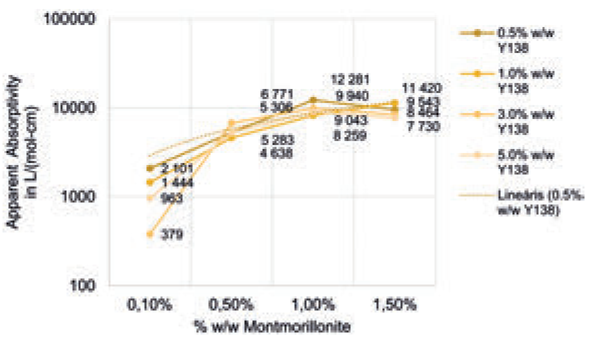

Fig. 3 *Average apparent absorptivity values of smectite-assisted pigment dispersions at 0.5% to 5% w/w PY138 concentration*
3. ábra *A szmektit tartalmú pigmentdiszperziók átlagos látszólagos abszorptivitási értékei 0,5%–5% w/w PY138 koncentráció mellett*

The proposed microstructure of the dispersed particles is depicted in *Fig. 4*. At low clay concentrations, the presence of clay disrupts the natural agglomeration process of pigments, leading to improved dispersion. This process continues as the clay concentration approaches 1.0%, resulting in a significant number of suspended clay particles in the medium, which leads to clay-particle association. The presence of associated clay particles increases the free volume in the system, effectively immobilizing the particles within gel-like cages and concurrently increasing the viscosity of the dispersion.

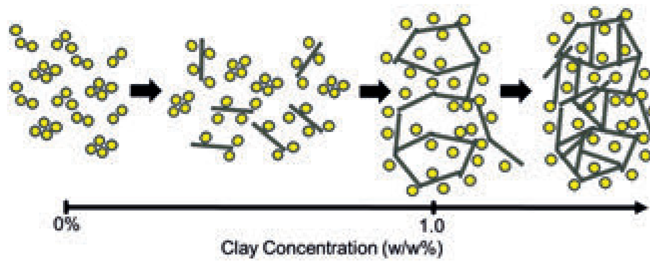

Fig. 4 *Proposed microstructure of clay-assisted pigment dispersion at increasing clay concentration*
4. ábra *A növekvő agyagkoncentráció mellett kialakuló agyag tartalmú pigmentdiszperzió javasolt mikroszerkezete*

However, beyond 1.0% w/w clay concentration, the free volume of the system decreases, resulting in the presence of fewer immobilized pigments and the expulsion of water through syneresis. This leads to a decrease in the stability of the dispersion.

3.3 Film morphology studies

Fig. 5a shows the film consisting of 10% w/w smectite stained with methyl red, demonstrating the ability of smectite clays to undergo uniform self-assembly on glass. The resulting dispersion exhibits a homogeneous appearance, indicating the delamination of smectite clay. As the smectite dries, the layers of clay form a continuous network of platelets without any observable voids, indicating a well-structured film formation.

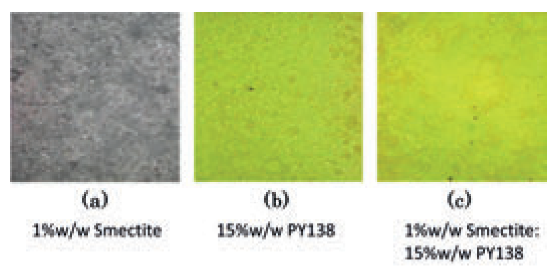

Fig. 5 *Morphology of drop-casted clay-assisted pigment dispersion under a light microscope*
5. ábra *A cseppöntött agyaggal agyag tartalmú pigmentdiszperzió morfológiája fénymikroszkóp alatt*

In contrast, *Fig. 5b* is that of 15% w/w PY138 film characterised by the presence of clusters of pigment aggregates with areas of low contrast, indicating a smaller number of aggregated pigments. However, when 1.0% smectite is added to the 15% w/w PY138 dispersion, a more uniform continuous structure with higher opacity and smaller aggregates is formed compared to the clay-free counterpart. This suggests that clays enhance the dispersibility of PY138 in water.

Overall, the results highlight the beneficial effects of smectite clays on the formation of well-structured films, resulting in an improved dispersibility of the PY138 pigment in water.

4. Conclusions

The present study highlights the significant potential of clays as dispersing agents for pigment dispersions. Findings from film morphology analysis and UV-Vis spectroscopy support this conclusion. Among the various clays investigated, smectite-assisted PY138 dispersion demonstrated remarkable improvements in stability. The critical concentration of smectite was determined to be 1.0% w/w for pigment dispersions containing 0.5% to 5% w/w PY138, as indicated by apparent absorptivity measurements.

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References

[1] Lin, L. (2003). Mechanisms of pigment dispersion. *Pigment & Resin Technology*, Vol. 32., No. 2, 78-88.

[2] Acir, I. H., Guenther, K. (2018). Endocrine-disrupting metabolites of alkylphenol ethoxylates–a critical review of analytical methods, environmental occurrences, toxicity, and regulation. *Science of the Total Environment*, Vol. 635, 1530-1546.

[3] Jérôme, F., Luque, R. (Eds.). (2017). Bio-based solvents. *John Wiley & Sons.*

[4] Ying, G. G., Williams, B., Kookana, R. (2002). Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. *Environment International*, Vol. 28, No. 3, 215-226.

[5] Talmage, S.S. (1994). Environmental and human safety of major surfactants: alcohol ethoxylates and alkylphenol ethoxylates. *Lewis Publisher.*

[6] Koleske, J. V. 1995. Paint and coating testing manual.

[7] Hwang, G. L., Tsai, S. J., Lin, J. J., Lan, Y. F. (2009). U.S. Patent No. 7,625,952. Washington, DC: U.S. Patent and Trademark Office.

[8] Ivanoska-Dacikj, A., Bogoeva-Gaceva, G., Buzarovska, A. (2017). Clay improved dispersion of carbon nanotubes in different solvents. *Contributions, Section of Natural, Mathematical and Biotechnical Sciences*, Vol. 36, No. 1.

[9] Lan, Y. F., Lin, J. J. (2009). Observation of carbon nanotube and clay micelle-like microstructures with dual dispersion property. *The Journal of Physical Chemistry* A, Vol. 113, No. 30, 8654-8659.

[10] Loginov, M., Lebovka, N., & Vorobiev, E. (2012). Laponite assisted dispersion of carbon nanotubes in water. *Journal of Colloid and Interface Science*, Vol. 365, No. 1, 127-136.

[11] Pai, Y. H., Ke, J. H., Chou, C. C., Lin, J. J., Zen, J. M., Shieu, F. S. (2006). Clay as a dispersion agent in anode catalyst layer for PEMFC. *Journal of Power Sources*, Vol. 163, No. 1, 398-402.

[12] Yaroshchuk, O., Tomylko, S., Kovalchuk, O., Lebovka, N. (2014). Liquid crystal suspensions of carbon nanotubes assisted by organically modified Laponite nanoplatelets. *Carbon*, Vol. 68, 389-398.

[13] Dong, R. X., Chou, C. C., Lin, J. J. (2009). Synthesis of immobilized silver nanoparticles on ionic silicate clay and observed low-temperature melting. *Journal of Materials Chemistry*, Vol. 19, No. 15, 2184-2188.

[14] Lan, Y. F., Lee, R. H., Lin, J. J. (2010). Aqueous dispersion of conjugated polymers by colloidal clays and their film photoluminescence. *The Journal of Physical Chemistry B*, Vol. 114, No. 5, 1897-1902.

[15] Lan, Y. F., Lin, J. J. (2011). Clay-assisted dispersion of organic pigments in water. *Dyes and Pigments*, Vol. 90, No. 1, 21-27.

[16] Cullari, L. L., Masiach, T., Peretz Damari, S., Ligati, S., Furo, I., & Regev, O. (2021). Trapped and alone: Clay-assisted aqueous graphene dispersions. *ACS Applied Materials & Interfaces*, Vol. 13, No.5, 6879-6888.

[17] Etika, K. C., Liu, L., Hess, L. A., Grunlan, J. C. (2009). The influence of synergistic stabilization of carbon black and clay on the electrical and mechanical properties of epoxy composites. *Carbon*, Vol. 47, No. 13, 3128-3136.

[18] Tohver, V., Smay, J. E., Braem, A., Braun, P. V., Lewis, J. A. (2001). Nanoparticle halos: A new colloid stabilization mechanism. *Proceedings of the National Academy of Sciences*, Vol. 98, No. 16, 8950-8954.

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