

Article

# Photopolymerised Coatings with Nanopigments Based on Dye Mixtures

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**Abstract:** The properties of new coatings with nanopigments (NPs) prepared by the dye mixture treatment of montmorillonite modified with cationic surfactants were investigated. The colorimetric parameters of polymer films with nanopigments were determined. The mutual interference of the dyes in their adsorption on nanoparticles and their colourfastness (photostability) to light was analysed. The properties of oligomer/monomer compositions with synthesised nanopigments designed for the printing of non-metallic surfaces were discussed. The structure of nanopigments and polymerised oligomer/monomer compositions was revealed by small-angle X-ray diffraction, UV–Vis spectra, and atomic force microscopy. NPs with a wide colour range were prepared using dye mixtures. One other advantage of these NPs over NPs based on individual dyes is the possibility to increase the total concentration of the colouring components in the NPs and to increase the colourfastness.

**Keywords:** coating; nanopigments; dye; montmorillonite; surfactant; surfaces printing



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## 1. Introduction

Photopolymerised compositions are widely used in various fields of technology, but their use as materials for 3D printing [1], in holography [2,3], and in flexographic printing [4] seems to be particularly promising. The use of nanomaterials for coatings is also encouraging [5]. It seems obvious that the combination of these technologies can lead to the production of new materials and products with new, unique properties.

Nanopigments (NPs) produced by different methods represent a rather interesting class of nanomaterials. Therefore, their preparation and the analysis of their properties can be quite interesting to investigators in various branches of chemistry and chemical technology [6–14]. The main efforts are currently concentrated on the synthesis and study of inorganic NPs [6–14]. Such nanoparticles, in particular, can be used in order to obtain magnetically sensitive holographic images [3].

However, the development of a method for the preparation of organic pigments with a nano-sized structure is also of interest [12–14]. Intermediate to these research topics is the synthesis of hybrid organic–inorganic NPs [15–21], which can be achieved in particular by applying organic dyes on inorganic nanoparticles, such as natural montmorillonite [16] or montmorillonite modified by cationic surfactants (MMCS) [19–21]. The advantage of MMCS is the good compatibility of NPs with monomers, oligomers, and polymers, which significantly contributes to high colour quality. The essential limitations of such NPs are the relatively low concentrations of the colouring component (a dye)—which usually does not exceed 30 wt%—and restricted colour range. The latter circumstance is associated less with the “discreteness” of colours of individual dyes and more with the incapability of many of them to withstand the severe conditions of use in NPs, particularly during

photopolymerisation in oligomer/monomer compositions. As shown previously, the colour range can be significantly improved using NPs based on dye mixtures [19,20].

The goals of this investigation were to extend the class of NPs based on MMCS and dye mixtures, to analyse their composition and properties, and to analyse the possibility of using NPs in oligomer/monomer compositions.

The scientific novelty of this work was in analysing the possibility of obtaining nanopigments based on dye mixtures, evaluating the adsorption of each of the dyes from their mixture, and identifying the specific effects of increasing the total amount of adsorbed dyes compared to individual dyes. The dyes' nanopigment colourfastness to light in a polymer matrix, along with the effects of the mutual influence of dyes on colourfastness, was studied. The effects of the nanopigments on the photopolymerisation of oligomer/monomer compositions in comparison with that of the conventional pigments were evaluated. The structure and the resistance of the coatings to physical and chemical influences were analysed.

Our approach to solving these problems is based on three hypotheses: (1) dyes can be adsorbed independently on the surface of montmorillonite, and this can lead to an increase in the total content of the colouring component in the NPs; (2) dyes can mutually affect their resistance to light due to shielding action or intermolecular energy transfer; (3) NPs based on mixtures of dyes, as well as NPs based on individual dyes, can be used in photopolymerising compositions intended, in particular, for printing on textile materials.

Experimental verification of these hypotheses constitutes the novelty of this work and its potential practical significance.

The choice of Cloisite 20A and Cloisite 10A products as nanoparticles for the production of NPs was due to the fact that they contain the same modifying surfactants, but at significantly different contents. This allows modification of the NPs' properties. An important additional argument was the availability of data obtained earlier for similar NPs based on individual dyes [21], as well as the high quality and commercial availability of the products.

The choice of dyes for the production of NPs was determined by the expediency of testing the possibility of using dyes of various colours and different classes (i.e., cationic, anionic, and dispersed) used in the textile industry. In particular, this guarantees the availability of acceptable hygienic characteristics. An additional factor, as before, was the availability of data on the properties of NPs based on the individual use of some of these dyes.

## 2. Experimental

### 2.1. Materials

The samples of montmorillonite modified by the cationic surfactants  $(\text{HT})_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$  (MMCS-1) and  $\text{HTN}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5\text{Cl}^-$  (MMCS-2)—manufactured by Southern Clay Products, Inc. (Austin, TX, USA) under the brand names Cloisite 20A and Cloisite 10A, respectively—were used as nanoparticles for NP preparation, where HT is alkyl  $\text{C}_{18}$  (~65%),  $\text{C}_{16}$  (~30%), and  $\text{C}_{14}$  (~5%).

The dyes Basic Red 13 (CI 48015), Basic Red 18 (CI 11085), Acid Red 18 (CI 16255), Acid Red 73 (CI 27290), Acid Red 441, Mordant Red 7 (CI 18760), Direct Red 239 (CI 29160), Acid Yellow 76 (CI 18850), Basic Yellow 13 (CI 48056), Direct Yellow 1 (CI 22250), Disperse Yellow 13 (CI 58900), Acid Violet 49 (CI 42640), Direct Violet 9 (CI 27885), Acid Green 25 (CI 61570), Direct Blue 151 (CI 24175), Direct Blue 199 (CI 74190), Disperse Blue 7 (CI 62500), Disperse Blue 56 (CI 63285), Direct Brown 95 (CI 30145), Disperse Orange 11 (CI 60700), Disperse Orange 30 (CI 11119), Disperse Red 50 (CI 11226), Reactive Red 247 (produced by "Novocheboksarsky Chemical Plant" OJSC (Novocheboksarsk, Russia)), and Reactive Blue 38 (SCPL, India) were used as colouring components of the NPs.

For NP preparation and film-casting, analytical-grade ethanol, acetone, benzene, and methylene chloride were used.

The main binder components for the oligomer/monomer compositions were a laboratory sample of oligourethane methacrylates with an average molecular weight of 1400, based on oligotetrahydrofuran with tolylene isocyanate end groups (OUMA), which were synthesised by the Polymer Department of Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow Russia. The industrial products of the interaction of 2,4-toluylene diisocyanate with Laprol 2000 and hydroxypropyl methacrylate (OUMA-2002T) or hydroxypropyl methacrylate (OUMA MTM, “Khimtranzit” LLC, (Dzerzhinsk, Russia)) were used as well.

In order to increase the colour composition fixing rate, trimethylolpropane triacrylate (“Yarsintez” JSC RI, Yaroslavl, Russia) was used as a crosslinking agent.

The photoinitiator was 2,6-di-tert-butyl anthraquinone (NIOPiK, Moscow, Russia), and the non-ionogenic surfactants were polypropylene glycol (Schuchardt, Munchen, Germany), polyoxyethylene sorbitol monostearate (Tween 20, Merk KGaA, Darmstadt, Germany), and polyethylene glycol (Ferak Berlin GmbH, Berlin, Germany).

Poly(methyl methacrylate) (PMMA) of the Plexiglas 8N brand with  $M \approx 160,000$  and polystyrene (PS) of the PSM-115 brand were the model media for the study of the NPs' colorimetric parameters and the phototransformations of the dyes in terms of composition.

The choice of dyes was determined by the need to study dyes of different classes (i.e., cationic, anionic, dispersed, and active), by their colour characteristics, and by the ability to compare the obtained results with similar data for nanopigments based on individual dyes.

The purity of the nanopigments was determined by the purity of the modified montmorillonite and dyes used. These products were directly obtained from manufacturers who guarantee their quality in accordance with specifications. Chemically pure solvents and distilled water used during the application of dyes cannot lead to contamination of the resulting nanopigments.

## 2.2. Methods

Dyed films with NPs were formed by the slow evaporation of the solvent from PMMA or PS solution in a benzene–methylene chloride mixture. To improve the distribution of NPs in the polymer solution, samples were preliminarily processed using an ultrasonic disperser for 30–60 s.

The oligomer/monomer compositions were produced by mixing oligourethane methacrylate (67.5 wt%), trimethylolpropane triacrylate (22.5 wt%), 2,6-di-tert-butyl anthraquinone (2.6 wt%), NPs (3.7–7.4 wt%) and, in individual cases, non-ionogenic surfactants (0–7 wt%). The mixtures were then processed by an ultrasonic disperser for 30–60 s.

Photochemical aging was applied using a Q-SUN (Q-Lab corporation, Cleveland, OH, USA) device utilising filter systems matching the spectral composition of sunlight under natural conditions (i.e., radiation wavelength greater than 290 nm), with a light intensity of  $1000 \text{ W/m}^2$ .

The colorimetric parameters of dyed films in the CIELAB-76 system were determined using a ColorFlex spectrophotometer (HunterLab, Reston, VA, USA). The values of  $L^*$ ,  $a^*$ , and  $b^*$  were determined directly from the measurements of the reflection spectra and their processing by the ColorFlex instrument software (version 1.32B).

Colourfastness was tested in accordance with the following standards: ISO 105-B04 (to light), ISO 105-C06 (to washing), ISO 105-E01 (to distilled water), ISO 105-E04 (to perspiration), and ISO 105-X12 (to dry rubbing).

The NP sizes and the surface parameters of the dyed compositions were determined using an atomic force microscope (NT-MDT, Ltd, Moscow, Russia). Small-angle X-ray measurements were performed using a Bruker NANOSTAR device (Bruker Inc., Billerica, MA, USA).

The UV–Vis absorption spectra of dyes in solutions and films were recorded using a MultiSpec-1501 spectrophotometer (Shimadzu, Kyoto, Japan).

### 3. Results and Discussion

#### 3.1. NP Synthesis Based on Dye Mixtures

NPs based on dye mixtures were prepared in accordance with the synthesis techniques for NPs based on individual dyes [21].

NP synthesis was carried out by simply adding a mixture of dyes in water or a mixture of water and acetone (for cationic and anionic dyes), or in acetone (for dispersed dyes), to modified montmorillonite while stirring the solution, after which they were isolated by filtration. The dye content in the NPs was determined based on the differences in their contents in the solution before and after treatment of the montmorillonite, estimated based on the changes in the absorption spectra of the solutions.

It was shown that, after the addition of the dye, the filtrate can be reused for the synthesis of NPs; therefore, this method of obtaining NPs is largely waste-free.

Numerous experimental data indicated that the total dye concentration in NPs depends on a number of factors, including the following:

- The structure, ratio, and total concentration of the applied dyes in the solution;
- The structure of the surfactants used for MMCS production and their contents of montmorillonite;
- The ratio of the quantity of MMCS to the volume of the dye solution.

The data obtained provide qualitative proof that, during the preparation of NPs based on dye mixtures, the dye features and surfactant structural effects are the same as those for the individual dyes [21].

#### 3.2. Some Features and Advantages of NPs

Colorimetric analysis of PMMA with NPs based on dye mixtures (Table 1) proves that their use can yield paints of various colours and hues.

**Table 1.** Conditions of nanopigments preparation, dyes' loading in nanopigments, and colour coordinates of the coloured PMMA films.

MMCS	Dyes (wt%)	Solvent	Dye Loading in NP <sup>a</sup> (wt%)	NP Content in PMMA (wt%)	Colour Coordinates		
					L*	a*	b*
MMCS-2	Disperse Blue 56 (10)/Disperse Yellow 13 (10)	EtOH	17.0	8	18.50	−41.11	0.10
MMCS-2	Disperse Blue 56 (5)/Disperse Yellow 13 (15)	EtOH	16.1	10	23.28	−46.16	19.57
MMCS-1	Direct Blue 199 (5)/Direct Yellow 1(15)	EtOH/H <sub>2</sub> O	13.4	10	27.97	−52.43	36.56
MMCS-1	Direct Blue 199 (10)/Direct Yellow 1 (10)	EtOH/H <sub>2</sub> O	13.3	10	17.52	−43.47	18.55
MMCS-2	Disperse Orange 30 (15)/Disperse Blue 7 (15)	Me <sub>2</sub> CO/H <sub>2</sub> O	15.0/15.0	30	31.87	−32.91	25.44
MMCS-2	Direct Red 239 (30)/Direct Violet 9 (10)	EtOH/H <sub>2</sub> O	16.9/7.8	4	8.50	34.55	11.92
MMCS-2	Direct Red 239 (20)/Direct Violet 9 (20)	EtOH/H <sub>2</sub> O	10.5/16.4	4	4.97	23.32	4.56
MMCS-1	Basic Yellow 24 (20.4)/Direct Yellow 1 (10)	EtOH/H <sub>2</sub> O	20.3/9.8	8	58.67	32.10	93.80
MMCS-2	Acid Violet 49 (18)/Disperse Blue 56 (18)	Me <sub>2</sub> CO/H <sub>2</sub> O	2.4/18.0	8	1.96	3.63	−6.62
MMCS-2	Basic Red 18 (30)/Acid Violet 49 (3.3)	EtOH/H <sub>2</sub> O	19.6/3.3	8	4.71	15.78	4.70
MMCS-2	Acid Violet 49 (20)/Acid Yellow 76 (30)	EtOH/H <sub>2</sub> O	6.7/28.8	4	0.73	0.38	0.13
MMCS-2	Direct Yellow 1 (20)/Direct Red 239 (20)	EtOH/H <sub>2</sub> O	16.0/8.2	4	35.24	60.67	56.96
MMCS-2	Acid Yellow 76 (20)/Reactive Blue 38 (20)	EtOH/H <sub>2</sub> O	16.9/15.3	4	10.86	−24.02	14.92

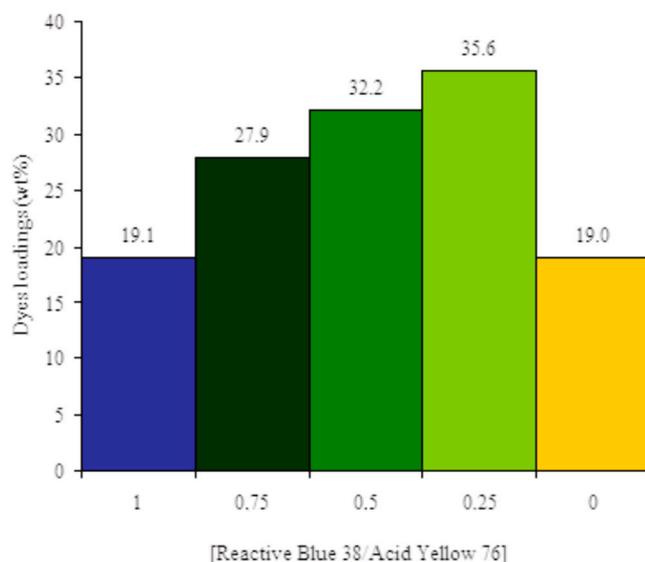
<sup>a</sup> Weight percent per mass of MMCS.

For instance, NPs based on yellow and blue dyes, red and violet dyes, and red and yellow dyes produce green, vinous, and orange tints, respectively. This expected result can be considered to be the first advantage of NPs based on dye mixtures over NPs based on individual dyes.

NPs based on dye mixtures were also found to possess an additional, unexpected feature: In a number of cases, when the dye mixtures were applied on MMCS, their total content in the NPs significantly exceeded the contents of individually applied dyes under the same NP production conditions (Table 1). This important feature has a potentially valuable practical application: the possibility of achieving strong hues without increasing the NP concentration in the dye composition. This phenomenon is general, being observed for both mixtures of dyes of the same class and for mixtures of various classes, including

dyes of the same colour (Table 1). This feature can be considered as a second important advantage of NPs based on dye mixtures.

A more sophisticated analysis of the effect of total dye content in NPs on their ratio in the mixture of Acid Yellow 76 and Reactive Blue 38 dyes (Figure 1) reveals a parabolic shape with downward-directed branches, where the top is usually located in the area of comparable quantities of each dye. Such plots are typical for well-known synergistic effects of the oxidation processes of organic compounds and polymers [22]. It is interesting that the relationships for dye loadings are in close agreement with the relationships for dye concentrations in solutions used for the NP preparation process (1, 0.70, 0.48, and 0.24 versus 1.0, 0.75, 0.50, and 0.25, respectively). Among these effects, a special group is composed of those explained by trivial mechanisms, in accordance with which the synergistic effect is associated with the limited solubility of one or both of the additives [23]. This synergistic effect is due to the interactions of dyes when the adsorption of one dye does not interfere with, but rather promotes the adsorption of another. Formally, a similar effect is observed for polymer light stabilisers when one stabiliser improves the distribution (solubility) of the other in the polymer [23]. In the first case, each of the additives dissolves independently, and their total concentrations increase relative to their individual concentrations. In the second case, one of the additives increases the solubility of another additive, increasing its concentration in the mixture. In the case of dye adsorption, possible synergistic mechanisms may also be trivial. If each of the dyes is mostly adsorbed on centres of different types, the total content will be higher than that in the case of the adsorption of individual substances. Correspondingly, in the case of multilayer adsorption, one of the dyes may form new centres for the adsorption of another dye. Particular ratios of dye concentrations at which the synergistic effect is strongest can only be determined empirically at present, because of the lack of experimental data allowing the determination of the mechanism.



**Figure 1.** The effect of limited dye loading in MMCS-2-based NPs on the relationship of concentrations of Reactive Blue 38 and Acid Yellow 76 in the ethanol/water solutions used for NP preparation. (Blue is Reactive Blue 38 only, dark green, medium green and light green is Reactive Blue 38/ (Reactive Blue 38 + Acid Yellow 76) relation 0.75, 0.5 or 0.25, and yellow is Acid Yellow 76 only).

The use of NPs based on dye mixtures was also found to produce increasing colourfastness to light (photostability) (Table 2), evaluated in points (i.e., ISO 105-B04: 1997); colour resistance to artificial weathering; xenon arc lamp attenuation test).

In some cases, the effect was rather significant: the colourfastness of the mixed pigment not only reached the colourfastness of the most stable component, but even noticeably exceeded it (Table 2). For such systems, the phenomenon can be considered as truly synergistic one, because the effect observed exceeds not only the sum of the effects of the

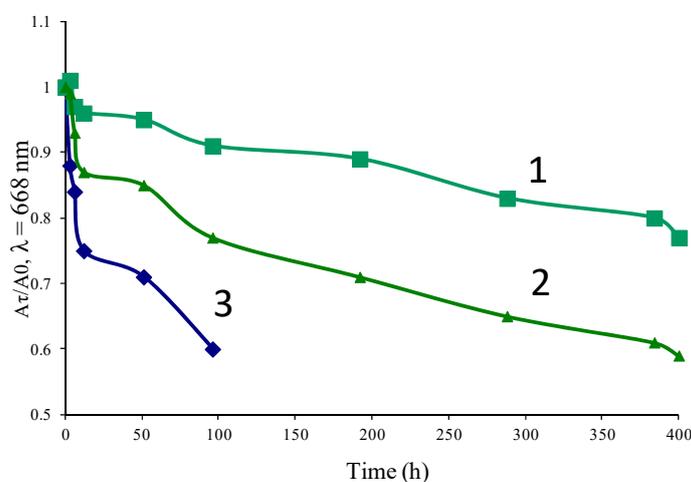
components with regard to their ratio in the mixture, but even the value that might be provided by the most efficient component. This can be considered as one other advantage of NPs based on dye mixtures compared with NPs based on individual dyes.

**Table 2.** Colourfastness of PMMA films <sup>a</sup> with nanopigments.

Nanopigment	MMCS	Dye Loading in NP (wt%)	NP Content in PMMA (wt%)	Colourfastness
Direct Violet 9	MMCS-2	19.8	4	4–5
Direct Red 239/Direct Violet 9	MMCS-2	10.5/16.4	4	5–6
Direct Red 239/Direct Violet 9	MMCS-2	16.9/7.8	4	3–4
Direct Red 239	MMCS-2	18	4	2–3
Direct Blue 199	MMCS-1	10.5	4	4
Direct Blue 199/Direct Yellow 1	MMCS-1	13.3	10	7
Direct Blue 199/Direct Yellow 1	MMCS-1	13.4	10	6–7
Direct Yellow 1	MMCS-1	9.8	8	6–7
Basic Yellow 24	MMCS-1	20.4	4	5
Basic Yellow 24/Direct Yellow 1	MMCS-1	20.3/9.8	8	5

<sup>a</sup> The thickness of the PMMA films was ~400  $\mu\text{m}$ .

The mechanism of this synergistic stabilising action is rather complicated. It is necessary to take into account the colourfastness (photostability) of the dyes themselves, estimated based on the relative rate of their consumption, as measured by the decrease in absorption in the visible region. The simplest explanation is based on experimental facts indicating a (frequently significant) reduction in the consumption rate of the less-stable dye, caused by light in the presence of the more stable dye (Figure 2, curves 1 and 3).



**Figure 2.** Kinetic curves of the photodegradation of Reactive Blue 38 in PS films coloured by MMCS-2-based NPs with a mixture of Reactive Blue 38 (8.6 wt%) and Acid Yellow 76 (27.0 wt%) (1) and in mixtures of NPs with Reactive Blue 38 (19.1 wt%) and NPs with Acid Yellow 76 (19.0 wt%) only (2). Curve 3 shows the kinetics of Reactive Blue 38 consumption in the film coloured by NPs with Reactive Blue 38 (19.1 wt%) only. The NP contents in the films are 1.5 (1), 0.7 (2), and 0.8 wt% (3). The film thickness is 400  $\mu\text{m}$ . The measured parameter is the optical density at time (h) after photolysis ( $A\tau$ ) and initial one ( $A_0$ ) at a wavelength of 668 nm, corresponding to the absorption maximum of Reactive Blue 38, as determined experimentally based on the UV–Vis absorption spectrum of PS film containing NPs with Reactive Blue 38 only.

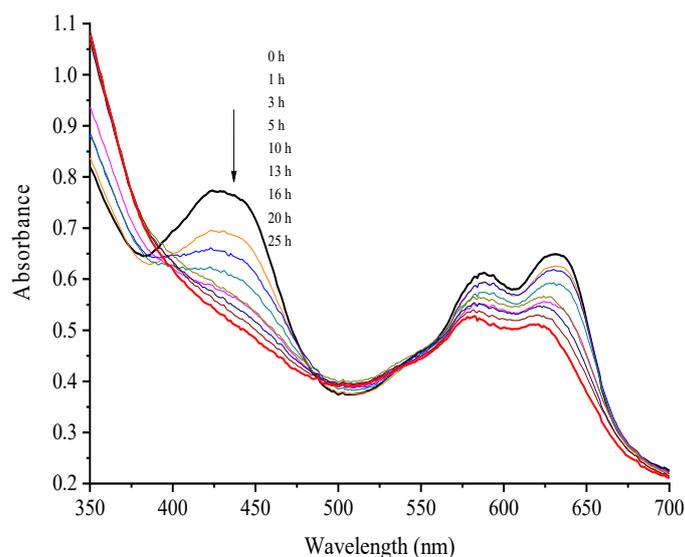
Figure 2 describes the changes in optical density at a wavelength of 668 nm, corresponding to the maximum of the absorption spectrum of Reactive Blue 38. As can be seen in Figure 2, the kinetic curves have a complex shape—a fast initial section is followed by a slower stage. The criterion of stability in this case is a decrease in optical density by 40%,

corresponding to a pronounced change in the colour of the composition; therefore, further continuation of irradiation is of no practical importance.

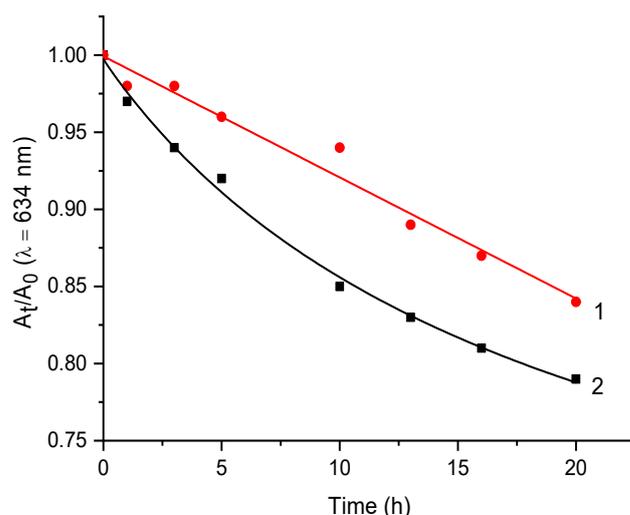
In the example under consideration for NPs based on Acid Yellow 76 and Reactive Blue 38, the screening effect contributes significantly. This screening action is due to the fact that the light-resistant yellow dye strongly absorbs light in the short-wavelength visible region and, thus, reduces the amount of light absorbed by the blue dye in this—the most dangerous area for it. In this case, Acid Yellow 76, which is a more light-stable dye, protects (screens) Reactive Blue 38—the less stable dye—against the most dangerous UV light. The contribution of the screening effect can be assessed by analysing the consumption kinetics of Reactive Blue 38 in the mixture of NPs based on dyes individually applied on MMCS (Figure 2, curve 2). Importantly, in this experiment, for the samples that include a pigment based on a mixture of dyes and a mixture of pigments containing individual dyes, equal optical density in the absorption range of every dye was required. Comparing curves 1–3 in Figure 2, the screening effect contributes significantly to the retardation of the consumption of Reactive Blue 38—the less light-stable dye—in both the initial fast stage and the later slower stages.

It is worth mentioning that the presence of clearly defined bands in the absorption spectra and the absence of noticeable light scattering are important proof of the adsorption of the dyes at the molecular level. It is essential that absorption spectra are also recorded for ionic dyes that are not soluble in organic solvents and cannot be directly embedded in organic polymers and photopolymerising systems.

When NPs with extremely low colourfastness dyes were used (Figure 3), a significant increase in the consumption rate for the more stable dye was observed (Figure 4), leading to low colourfastness. For instance, in the presence of NPs based on a mixture of Disperse Blue 56 and Disperse Yellow 13, the colourfastness of the PMMA films was only 2, whereas that for NPs based on individual Disperse Blue 56 dye was 3. However, even in this specially selected example, where a photochemically active dye predominates over a stable dye, the antagonism for dye mixtures in NPs was not observed. This is because the more stable Disperse Blue 56 dye retards the consumption of the Disperse Yellow 13 dye. Consequently, the colourfastness for NPs based on dye mixtures is much higher than for NPs based on Disperse Yellow 13, the colourfastness of which is only 1.



**Figure 3.** Variation in the near-UV and visible absorption spectra of PMMA films coloured by MMCS-2-based NPs with Disperse Blue 56 and Disperse Yellow 13 with the duration of photolysis, as determined by Suntest. The NP content in the film was 1.04 wt%, and the loadings of Disperse Blue 56 and Disperse Yellow 13 in the mixture were 16.1 wt%. The film thickness was 400  $\mu\text{m}$ . The numbers in the figure next to the arrow indicate the irradiation time, hours.



**Figure 4.** Kinetic curves of the photodegradation of Disperse Blue 56 in PMMA films coloured by MMCS-2-based NPs with Disperse Blue 56 (17.5 wt%) only (1) or a mixture of Disperse Blue 56 and Disperse Yellow 13 (16.1 wt%) during irradiation in Suntest. The NP contents in the film were 2.45 wt% (1) and 3.1 wt% (2), and the film thickness was 300  $\mu\text{m}$ . The measured parameter was the optical density at a wavelength of 634 nm, corresponding to the maximum absorption of Disperse Blue 56, as determined experimentally by the UV–Vis absorption spectrum of a PS film containing NPs with Reactive Blue 56 only.

### 3.3. UV Inks Based on NPs with Dye Mixtures

NPs based on mixtures, similar to those based on individual dyes [21], may be used as the colouring components of photopolymerisable oligomer/monomer compositions (UV inks). These inks preserve all of the advantages in comparison with UV inks based on common pigments, among which higher colourfastness to rubbing and reduced UV radiation time required for the fast fixing of colouring compositions are of the highest importance (Table 3). In this respect, compared with NPs based on individual dyes, NPs based on dye mixtures used in UV inks naturally preserve all of the advantages associated with the possibility of varying colour and hue over a broad range due to the increasing concentration of the colouring agent, and they also exhibit increased colourfastness.

**Table 3.** Colourfastness of textile materials coloured by UV inks<sup>a</sup> with nanopigments or pigments to physicochemical impacts.

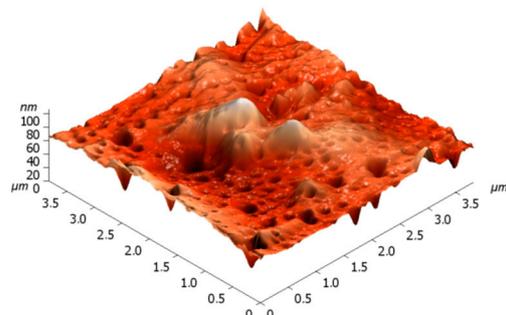
Nanopigment (wt%)	MMCS	Dye Loading in NP <sup>a</sup> (wt%)	Content of Colouring Component (wt%)	Physicochemical Impacts				Irradiation Time (min)
				Dry Rubbing	Distilled Water	Perspiration	Washing	
Acid Yellow 76/Reactive Blue 38	MMCS-2	16.9/15.3	4	5/4	5/5/5	5/5/5	5/5/5	2
Acid Yellow 76/Reactive Blue 38	MMCS-2	8.5/19.4	4	5/4	5/5/5	5/5/5	5/5/5	2
Direct Yellow 1/Direct Red 239	MMCS-2	16.0/8.2	4	5/3	5/5/5	5/5/5	5/5/5	2
Disperse Blue 56/Disperse Yellow 13	MMCS-2	17.0	7	5/5	5/5/5	5/5/5	5/5/5	2
Direct Blue 199/Direct Yellow 1	MMCS-1	13.3	7	5/5	5/5/5	5/5/5	5/5/5	2
Direct Blue 199/Direct Yellow 1	MMCS-1	13.4	7	5/5	5/5/5	5/5/5	5/5/5	2
Acid Violet 49/Disperse Blue 56	MMCS-2	2.4/18	7	5/4–5	5/5/5	5/5/5	5/5/5	3
Direct Red 239/Direct Violet 9	MMCS-2	10.5/16.4	4	5/4	5/5/5	5/5/5	5/5/4	2
Direct Red 239/Direct Violet 9	MMCS-2	16.9/7.8	4	5/4–5	5/5/5	5/5/5	5/5/4	2
Pigment Irgalite Blue NGA	-	-	2	4/2–3	5/5/5	5/5/5	5/5/5	12

<sup>a</sup> OUMA (67–70 wt%), TMPTA (23 wt%), 2,6-di-tert-butylanthraquinone (3 wt%).

### 3.4. Nano-Sized Structure of Printing Composition with NPs Based on Dye Mixtures

Similar to the case with NPs based on individual dyes [21], the advantages of UV inks with NPs based on dye mixtures are likely the result of their nano-sized structure. One important source of support for this hypothesis is provided by the AFM data (Figure 5), which indicate the absence of structures higher than 100 nm and wider than 500 nm at the

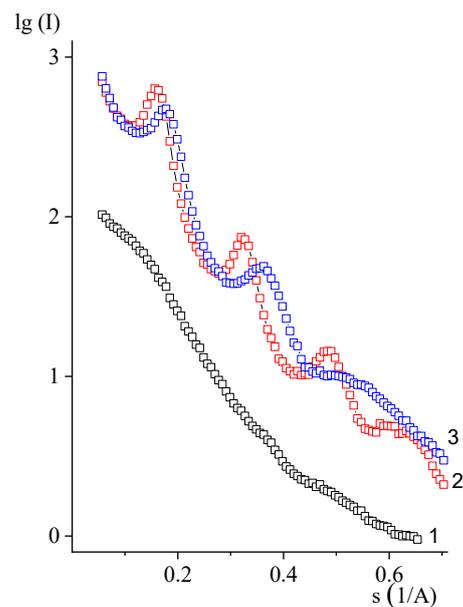
base from the film surface produced by curing UV inks with NPs based on a mixture of Acid Violet 49 and Disperse Blue 56 dyes. As mentioned above [21], inks with NPs are fundamentally different from UV inks based on common pigments. In the latter case, the surface has heterogeneities with typical sizes of 0.8–1.2  $\mu\text{m}$  in height and 1–2  $\mu\text{m}$  in width at the base.



**Figure 5.** AFM image of a UV-cured film containing OUMA (67 wt%), TMPTA (23 wt%), 2,6-di-tert-butylanthraquinone (3 wt%), and MMCS-2-based NPs with a mixture of Acid Violet 49 and Disperse Blue 56. The NP content is 7 wt%, and the loadings of Acid Violet 49 and Disperse Blue 56 on the MMCS-2 are 2.4 and 18.0 wt%, respectively.

Figure 3 shows that, compared with films coloured by common pigments, films containing NPs based on dye mixtures have an additional feature: they are transparent in the visible range beyond the absorption bands of the dyes. Thus, the NP sizes do not fundamentally exceed the light wavelength (400–700 nm). Therefore, the spectrophotometric analysis corroborates the conclusion about the nano-sized structure of NPs and materials based on these NPs, supporting the AFM results.

A more in-depth study of the films by small-angle X-ray diffraction analysis, however, indicates that some of the NP nanoparticles are present in the form of aggregates (packs), each comprising several tens of MMCS plates with applied dyes (Figure 6). The presence of clearly expressed basal reflexes, which are absent in similar films without NPs and in films with a common pigment, proves the presence of regulation zones provided by the formation of MMCS plate aggregates (30 nm thick) with a characteristic distance between layers (plates) of 3.5 nm. These assessments correlate well with the data obtained for analogous samples containing MMCS in the absence of a dye (i.e., an aggregate thickness of ~35 and an interlayer distance of 3.9 nm). Because the interlayer distance in these aggregates exceeds the MMCS interlayer distance (1.9 nm), the data obtained indicate intercalation of the oligomer/monomer binder to almost the same extent in both NPs and MMCS without the dye. These results are fully consistent with what is known about the structure of polymer mixtures with montmorillonite nanoparticles, in accordance with which both polymers intercalate into the interlayer space when mixed, and nanoparticles exfoliate [23]. The local microsurroundings of the dye molecules in such aggregates (i.e., oligomer/monomer binder and a surfactant fragment) do not significantly differ from their surroundings when they are located in individual MMCS particles. Consequently, the difference in spectral characteristics should not be significant.



**Figure 6.** The small-angle X-ray scattering of UV-cured films containing OUMA (67 wt%), TMPTA (23 wt%), and 2,6-di-tert-butylanthraquinone (3 wt%) without NPs (1), with MMCS-2 (7.0 wt%) only (2), and with MMCS-2-based NPs (7.0 wt%) containing a mixture of Reactive Blue 38 (21.7 wt%) and Acid Yellow 76 (20.0 wt%) (3).

#### 4. Conclusions

A new approach to the production of coloured coatings, with nanopigments (NPs) prepared by the dye mixture treatment of montmorillonite modified with cationic surfactants, was developed.

The application of dye mixtures on MMCS allows the preparation of NPs with a wide colour range. Additional advantages of these NPs over NPs based on individual dyes include the possibility of increasing the total concentration of the colouring component in the NPs, as well as increased colourfastness.

The use of NPs based on dye mixtures in the composition of UV inks preserves all of the advantages of NPs relative to common organic pigments, among which a decrease in the radiation time required for the fast fixing of colour composition and an increase in colourfastness to rubbing are the most important.

The nano-sized structure of NPs and compositions based on these NPs was proven through a number of physicochemical methods, including UV–Vis spectrophotometry, X-ray diffraction analysis, and atomic force microscopy.

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