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Characterization of orange pigments in decorative outdoor coatings and their weather fastness

Hana Erznožnik[a,*], Tina Razboršek[a], Marta Klanjšek Gunde[b]

[a] Helios TBLUS d.o.o, Količevo 65, 1230 Domžale, Slovenia
[b] National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia

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ABSTRACT

The shades of decorative coatings for façades are currently changing from white and pale to more chromatic ones. This also imposes a phase-out of heavy-metal pigments based on cadmium and lead, which cover the full range of yellow, orange, and red shades, and show excellent performance. The substitute pigments have many limitations regarding heat stability, colour strength, opacity, light fastness, or dispersibility. While all components of the final coating contribute to these properties, we have studied here the stability of four orange pigments suitable to replace the pigments with heavy metals in water-based coatings for outdoor applications in a different binder system (acrylate styrene with different amount of silicone resin, vinyl acetate versatate and acrylate based polymer). The accelerated weathering tests show that the stability of all samples strongly depends on the applied coating base and is systematically higher in white coating bases, especially when combined with pigment pastes prepared without a binder. The pigment chemistry, being inorganic, hybrid, or organic plays a role, but the stability of the coating gradually depends on the other components.

1. Introduction

Global trends for the shade of façade coatings are changing from pastel to more intensive shades. Heavy metal-based inorganic pigments had to be substituted due to strict regulations, occupational health concerns, and costly waste disposal and recycling, which require the complete phase-out of heavy-metal pigments [1]. Many coating producers are not satisfied with the exclusion of cadmium and lead pigments, which cover the full range of yellow, orange, and red shades. The basic reason is that these pigments can be used in the majority of polymers, showing good performance. Unfortunately, this is not true for substitute pigments, which includes organic and non-heavy-metal inorganic pigments, e.g. nickel and chrome titanates. These alternatives have limitations in heat stability, colour strength, opacity, light fastness, or dispersibility [2,3]. Yellow and red paints are commonly made with combinations of inorganic and organic pigments. Bismuth vanadate pigments are recommended for highly chromatic yellow shades, as hiding power and brilliancy are desired. Likewise, in many cases, orange to red shades are produced with iron oxide pigments or chromium titanates. These pigments are the best choice for pastel shades and medium chromatic colours when hiding and durability are important [1,2].

Façade coatings are commonly made using waterborne coatings, which comprise resin in an emulsion or dispersion phase, water as a solvent, and pigments, fillers, and additives. Formulating such paint is a complex task [4]. To make the process easier, the coating material is prepared by mixing a coating base and pigment pastes. The coating base contains all components of the final coating formulation except pigments; the addition of pigment pastes yield differently coloured paint. The most important ingredient of a coating base is a binder/resin that strongly defines the properties of the final coating material. The coating base could be transparent or white. A transparent coating base has no fillers or white particles, but a white coating base includes non-transparent white particles acting as fillers or additives. The transparent base gives intensive colour shades, whereas the white one is used for pastel shades. A pigment paste contains fully wetted pigment particles prepared with the smallest possible amount of wetting and dispersing additives and (not necessarily) some binder [5].

All components of the final coating (i.e. of a dry layer of paint) contribute to light, weather, thermal, and chemical stability [6], but the fastness of coatings also include the applied substrate, the incident radiation, and the surrounding atmosphere. The factors referring to the coating are the concentration of the pigment, the chemical and physical properties of the pigment and of the poly-

* Corresponding author.
E-mail address: hana.erznoznik@helios.si (H. Erznožnik).

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mer [7], the chemical and physical structure of the substrate, the diffusion of volatile substances from the polymer matrix, pigment solubility in the medium, potential energy transfer from the substrate to pigment coating and air, the presence of antioxidants or light stabilizers and of other additives. The other factors are the spectral distribution of the incident radiation and the composition of the atmosphere, especially humidity, and the presence of reactive contaminants (SO_2, NO/NO_2, O_3, etc.) [8,9]. Information on the stability of a pigment is unreliable if other data about the coating are not provided.

Since the mid-19th century, chemists have attempted to improve the light-fastness of colourants (dyes, pigments, pigment blends, pigment pastes) mostly on a purely empirical basis. Although many aspects are somewhat clearer today, every introduction of new colourants or improvement of the existing ones remains based almost exclusively on experience [8]. Understanding the mechanism of photochemical reactions in solutions is, in the majority of cases, not a reliable basis for application in such complex systems as coatings, since too many other parameters have to be taken into account. Very little is known about radiation-caused decomposition processes causing progressive degradation of pigment particles and of the surrounding coating medium. The fading mechanism on pigments is either based on a surface layer reaction or an associated optical filter effect or both [8]. The cumulative properties not only depend on the chemistry and the solid state properties of the pigment itself but to a large extent also on the interaction with a specific application medium. To achieve the desired properties for a given coating application, the pigment surface must be “optimized”. Several publications address this subject [10–13]. The pigment particle surface often needs to be treated to ensure its better dispersion and higher flocculation stability in the matrix, which guarantee improved mechanical properties, as well as impart better heat, light, chemical, and migration fastness of the coating on an object [8]. The fading of colourants can be assessed by the methods introduced by the International Standards Organization (ISO) or by a slightly different method, introduced by the American Association of Textile Chemists and Colorists (AATCC) [14,15]. Both standards refer to textiles but are also commonly used in the coating industry. Each pigment manufacturer has its own preparation procedure for testing the stability of pigments. They are tested in different binder systems' bases, in different reduction ratios and exposed to different weather tests. The reduction ratio is evaluated with the FIAF program [16], which indicates how many parts of titanium dioxide have to be mixed with one part of colour pigment to obtain 1/3 and 1/25 standard depth of a shade. The higher the colour strength of a pigment, the less pigment is required to achieve a standard depth of a shade; thus, the reduction ratio is higher. To evaluate lightfastness, the painted panel can be exposed to sunlight under a glass cover or to accelerated ageing in a chamber. Pigment producers apply different procedures for this purpose. BASF (Germany) uses light chambers with Xenon arc lamp for over 2000 h, and the resulting colour change is assessed using eight-step blue scale [17,18]. Fastness to weathering is carried out in a weather-accelerated tester or outdoors. Cappelle Pigments NV (Belgium) tests all inorganic and high-quality organic pigments using outdoor exposure in Menen, Belgium for 12 months [19]. After an ageing period, the change in colour properties between exposed and non-exposed surfaces is assessed according to the ISO 105-A02 grey scale [14].

The objective of this work was to study the light-fastness and weather-fastness of orange pigments with no heavy metals in decorative façade coatings. Because no other independent, reproducible scientific evaluation of the fastness of the used pigments in the studied coating systems has been presented, the results are of potential interest for anyone involved in using pigmented systems.

2. Materials and methods

Four different orange pigments were selected and used for the preparation of pigment pastes. Five different coating bases were prepared. Coating materials (paints) were obtained by combining a coating base with one pigment paste, applied on panels and dried. Accelerated weather resistance and lightfastness were measured and analysed.

2.1. Pigments

Four commercially available orange pigments, declared to be useful for waterborne coatings in an outdoor application, were selected: one organic, one hybrid, and two inorganic. The pigment particles were analysed using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). The field emission microscope, a Karl Zeiss Supra 35 V, equipped with Oxford INCA 400 EDS was applied for this purpose. The basic data of the applied pigments are collected in Table 1.

The organic pigment (BASF Germany) has good durability and very high saturation and is recommended for automotive and high-grade industrial paints with lead-free shades [17]. SEM indicates broad particle size distribution and an elongated shape of particles. No presence of metals has been detected by EDS.

The hybrid pigment (HEUBACH Germany) has a brilliant orange shade, high opacity, and good heat resistance. Due to its excellent fastness, it is claimed to be suitable for highly durable applications [20,21]. Quite regular but clumpy shapes were seen in SEM micrographs, and the presence of titanium was detected by EDS.

A tin-zinc-titanium inorganic pigment (BASF Coating & Plastic Chemicals, Germany) offers high chroma combined with excellent durability, high hiding power, and high colour strength. It is presented as having the highest grades for weather and light fastness in full shade and also in reduction ratios. This pigment is recommended for application in alkaline silicate/silicone paints and plaster finishes [18,22]. It is the so-called RTZ pigment (rutile tint zinc), characteristically modified with cerium in an undisclosed valence state [23]. The appearance of titanium, zinc and tin were obtained by EDS in a ratio of 1:1:5.

Another inorganic pigment (Cappelle Pigments NV, Belgium) is based on modified bismuth technology. The EDS analysis shows silicon and bismuth present at a ratio of 1:8.5. High pigment loading enables producing pigment paste or final paint without adverse effect on flow properties. The producer claims that the pigment's weather- and light fastness in the alkyd/melamine system is ranked among the highest scores in all reductions with TiO_2 and to slightly lower in full shades [19].

2.2. Pigment paste

Two types of pigment pastes were prepared by grinding each of the pigments, with and without binder, in both cases with the same amount of pigment. Pigments were dissolved in a mixture of water and additives and ground for one hour. The grinding process was carried out in a Dispermat Bead Mill APS (VMA-GETZMANN Germany). Only one pigment paste was used for each final coating.

Binder-free pigment pastes are the current state-of-the-art in waterborne formulations, particularly due to their universal compatibility. They include larger amounts of fatty acid derivatives as wetting and dispersing additives, having functional groups with affinity for pigments, which improves the interaction on the pigment surface. In contrast, pigment paste with resin contains a binder and a small amount of fatty acid ethoxylates as additives [5]. With such pastes, it is relatively easy to obtain outstanding mechanical properties, such as hardness-flexibility balance, excellent chemical or water resistance, as well as reduced drying times.