

The influence of production conditions and thermal treatment on the properties of cadmium yellow obtained from different cadmium precursors

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ABSTRACT

This study investigated the influence of raw materials, synthesis routes, and thermal treatment on the physico-chemical properties of cadmium yellow (CdS-based) pigments, with particular emphasis on the relationships between crystal structure and functional properties. Cadmium chloride, sulphate, nitrate, and carbonate were used as cadmium precursors, while sodium sulphide and elemental sulphur served as sulphur sources. Pigments were synthesised via two approaches: precipitation from aqueous solutions under controlled pH conditions, followed by drying (90 °C) and calcination (600 °C), and a direct solid-state reaction of cadmium carbonate with sulphur at 600 °C. Comprehensive characterisation was carried out using CIELab colour analysis, atomic absorption spectrometry (AAS), thermogravimetric methods (TG/DTG/DTA), X-ray diffraction (XRD), FTIR spectroscopy, and XPS analysis. The results demonstrated that both precursor selection and processing conditions significantly affect pigment composition, crystallographic structure, and optical properties. Thermal treatment promotes the transformation of CdS into a stable hexagonal phase and induces the formation of secondary phases (e.g., sulphates, carbonates), which influence colour parameters and thermal stability. From a materials engineering perspective, the precipitation method in an acidic environment yields pigments of higher purity and well-developed hexagonal CdS structure, resulting in improved optical performance. However, from a process engineering standpoint, the direct solid-state synthesis route offers a simplified and scalable alternative with reduced processing steps and competitive material properties. The findings provide valuable insight into the design and optimisation of CdS-based pigments for high-temperature applications.

Keywords: cadmium sulphide, cadmium yellow, precipitation synthesis, solid-state reaction, thermal stability, structure–property relationship, X-ray diffraction, pigment engineering.

INTRODUCTION

The basic component of cadmium yellow is cadmium sulphide. In nature, it occurs in the form of a mineral called grinokite, which is characterized by a dark yellow or orange colour. The colour of synthetic cadmium sulphide can vary from yellow to lemon, depending on the method and conditions of its production. [1,2]. Cadmium sulphide has a dimorphic structure and crystallises in a cubic or hexagonal system,

with hexagonal CdS being used as a component of pigments [1,5]. The most commonly used pigments are solid solutions of cadmium sulphide with zinc sulphide or cadmium selenide with a very wide range of colours and shades. Pigments in which the dominant component is cadmium sulphide and solid compositions of cadmium sulphide with cadmium selenide are light yellow, showing, depending on the selenium content, a colour from light orange through red to purple.

Cadmium pigments are characterised by high resistance to light and solar radiation, as well as to some atmospheric and chemical factors and elevated temperatures. At elevated temperatures, they undergo oxidation, which may lead to colour changes or partial decomposition. However, when heated under oxygen-free conditions, the pigments retained their original colour [3,4].

Due to these properties, cadmium-based pigments are used in ceramic inkjet printing technologies, where high chromatic intensity, thermal stability during firing, and resistance to aggressive processing conditions are essential for maintaining colour quality and reproducibility [6].

One of the unresolved issues concerns the origin of the different colours exhibited by cadmium sulphide pigments. Previous theories explained this phenomenon by the different degree of polymerisation of its molecules. Earlier studies suggested that the structure of lemon-coloured cadmium sulphide is monomeric and the molecules of the orange pigment were a cyclic polymer. Nevertheless, it has not yet been possible to find a relationship between the colour and the structure of the obtained compounds [7]. However, it is known that the factors influencing the colour of cadmium yellow are the size of the pigment particles, the nature of their surface or the degree of particle aggregation [8]. One possible explanation is that dark yellow and orange cadmium yellow consists of larger particles, while light yellow or lemon pigments correspond to smaller particles. The size of the pigment particles alone cannot explain all the differences occurring between the colours of the same pigment [2,4]. Previous studies have shown that cadmium yellows are subject to degradation under certain conditions. In order to solve this problem, all methods of their production were tested and evaluated. This allowed for the reconstruction of the oldest recipes, which allowed for a better understanding of the individual synthesis operations and for determining their influence on the properties of yellow cadmium pigments. The results showed that the pigments synthesised according to historical indications were characterised by a typical crystal structure, and their grains and crystal aggregates were much smaller than in the case of reference pigments. The presence of chlorine atoms on their surface in the form associated with cadmium was also detected. A high ability of the pigment crystallites to emit photoluminescence was observed [9]. Similar studies were conducted on the photoluminescent

emission from the excited states of cadmium yellow, which was enhanced by the surface reactivity of its particles and the subsequent degradation of the coating. Cadmium yellow exhibits semiconductor properties, and its surface crystal defects could trap free charge carriers. The results presented demonstrated how photoluminescence studies helped identify defects on the surface of cadmium yellow crystals and contributed to a better understanding of the complex mechanisms behind coating degradation [10]. Another type of research presented results concerning the preparation and physicochemical characterisation of cadmium yellow pigment obtained from used nickel-cadmium batteries [11]. It was found that most of the factors responsible for the degradation of cadmium yellow pigments are still unknown. A number of oil paint coatings containing cadmium pigments with different stoichiometries, and crystal structures were studied before and after aging under variable relative humidity and light exposure. Based on the conducted studies, the mechanisms of coating degradation and the photocatalytic activity of the pigments were proposed [12]. To explain the origin of optical emission from cadmium yellow, the role of structural defects has been extensively investigated. The presence of vacancies on the CdS surface modifies the electronic structure and is considered one of the factors responsible for pigment degradation. Surface defects may also promote the adsorption of oxygen and moisture, facilitating photooxidative degradation processes [13–16]. The study of optical properties was also carried out using UV–Vis–NIR absorption and emission, as well as Raman spectroscopy. The final goal was to determine the stoichiometry of cadmium pigment solid solutions [17]. Cadmium and sulphur atoms in the crystal structure of the pigment can be replaced by other atoms to produce ternary systems with a wide range of colours. The possibility of creating quaternary solid solutions based on partial substitution of cadmium with zinc or barium was also accepted [18]. Precise determination of the stoichiometry of CdS–ZnS solid solutions is crucial for understanding their chromatic properties. It has been found that the colour and ability to absorb and emit light depend on the electronic structure, which can be modified, among others, by the presence of other elements [19]. Recent studies have also demonstrated that the functional performance of advanced materials is strongly governed by the evolution of their microstructure

and surface properties during thermal processing. Correlating structural changes with physicochemical properties has become an important approach in the optimisation of functional materials and coating systems for demanding operating conditions [20,21]. Similar relationships are expected for CdS-based pigments, where phase evolution and surface oxidation play a key role in determining their optical performance and thermal stability.

The aim of this work was to comprehensively evaluate the relationship between synthesis conditions, crystal structure, and the functional properties of cadmium sulphide-based pigments. The novelty of the present study lies in the systematic comparison of different cadmium precursors, precipitation conditions, and a direct solid-state synthesis route, combined with a comprehensive evaluation of the effects of calcination on phase evolution, surface chemistry, thermal stability, and optical properties. By integrating complementary characterisation techniques (CIELab, TG/DTA, XRD, FTIR, AAS, and XPS), this work provides a comprehensive structure–property relationship for CdS pigments and offers practical guidelines for the design of thermally stable cadmium yellow materials.

EXPERIMENTAL PART

Materials

The following chemical reagents were used to synthesise the pigments:

- Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\geq 98\%$ purity, Merck Life Science Sp. z o.o.) with a decomposition temperature of 120°C ,
- Cadmium chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$ purity, Merck Life Science Sp. z o.o.) with a melting point of 565°C and a boiling point of 964°C ,
- Cadmium sulphate ($\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\geq 99\%$ purity, Merck Life Science Sp. z o.o.) with a melting point of 41°C and a decomposition temperature above 80°C ,
- Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$ purity, Merck Life Science Sp. z o.o.) with a melting point of 59°C and a boiling point of 350°C ,
- Cadmium carbonate (CdCO_3 , $\geq 99\%$ purity, Merck Life Science Sp. z o.o.) with a melting point of 343°C and a decomposition temperature of 412°C

- Sulphur (S , $\geq 99.5\%$ purity, Merck Life Science Sp. z o.o.) with a melting point of 115°C and a boiling point of 444.61°C .

The pH of the solutions was adjusted using concentrated sulphuric acid (H_2SO_4 , 95–98% purity, Merck Life Science Sp. z o.o.). The industrial cadmium pigment with the trade name cadmium yellow ST supplied by Zakłady Chemiczne Permedia SA in Lublin (Poland) was additionally purified by extraction with ethyl acetate.

Methods

Preparation of cadmium yellow

Cadmium yellow was obtained using two methods, i.e. precipitation from solution according to reaction (1–4) and melting according to reaction (5):



Table 1 presents the proposed compositions of samples prepared for the pigment syntheses. The calculations included 0.1 moles of starting substrates.

Pigment precipitation reactions were carried out at $90\text{--}98^\circ\text{C}$ for one hour. After the pigments were precipitated, the reaction of the solution was tested, which in each case was $\text{pH} = 12$. In order to remove residual reactive Na_2S and stabilise the precipitate, the reaction environment of sample P2 was changed by adding concentrated sulphuric acid to $\text{pH} = 1\text{--}2$. Then the pigment suspensions were cooled and filtered. The pigment precipitates were washed with distilled water until the filtrate had a neutral pH. The wet pigments were dried at a temperature of approx. 100°C for one day in a dryer with forced air circulation until the water was completely removed. The dried pigments were ground in a porcelain mortar to obtain homogeneous powdered products. Then, half of each pigment was calcined at 600°C for 1.5 h in a muffle furnace. The calcination temperature was selected based on literature data and authors' preliminary experimental studies, which indicated that 600°C promotes the

Table 1. Designations and initial compositions of test samples

Pigment designation	Qualitative and quantitative compositions of reaction mixtures			Preparation method	pH
	Cd	S	H ₂ O, cm ³		
P1	CdCl ₂ · 2H ₂ O, 5.7 g	Na ₂ S · 9H ₂ O, 6.0 g	400	Precipitation	12
P2	CdCl ₂ · 2H ₂ O, 5.7 g	Na ₂ S · 9H ₂ O, 6.0 g	400	Precipitation	1-2
P3	CdSO ₄ · 8H ₂ O, 8.8 g	Na ₂ S · 9 H ₂ O, 6.0 g	400	Precipitation	12
P4	Cd(NO ₃) ₂ · 4H ₂ O, 7.7 g	Na ₂ S · 9H ₂ O 6.0 g	400	Precipitation	12
P5	CdCO ₃ , 4.3 g	Na ₂ S · 9H ₂ O, 6.0 g	400	Precipitation	12
P6	CdCO ₃ , 4.3 g	S; 0.8 g	-	Melting	-
P7	Industrial pigment- cadmium yellow ST			-	-

transformation of CdS into the thermodynamically stable hexagonal phase while minimising excessive oxidation and preserving the desired physicochemical and optical properties of the pigments. The fusion method consisted of the direct reaction of cadmium carbonate with sulphur in a closed porcelain crucible. The synthesis was carried out at 600 °C for 1.5 h in a muffle furnace. After calcination, the crucible containing the pigment was allowed to cool, and the product was subsequently crushed and homogenised in a porcelain mortar.

Diffuse reflectance spectroscopy

Pigment colour tests were carried out using a CROMLAVIEW CR100 colour sensor (ASTECH, Germany) equipped with a fibre optic probe. Measurements were carried out in reflectance mode, in direct contact with the sample. The amount of light reflected from the pigment surface was converted into numerical values that correspond to specific colour parameters in the CIELab space. In this system, each colour can be described by L*, a*, b* coordinates. The L* parameter determines the lightness of the colour. L* = 0 means black, and L* = 100 means white. The a* parameter determines the colour position between red and green. Values a* > 0 indicate shades of red, and values a* < 0 indicate shades of green. The b* parameter determines the colour position between yellow and blue. Values b* > 0 indicate shades of yellow, and values b* < 0 indicate shades of blue. Before the test, the apparatus was calibrated on a titanium white standard. The temperature of the pigment samples was equal to the ambient temperature and amounted to 20 °C. Each pigment sample was measured in triplicate, and the reported CIELab parameters represent the

average values. The measurements showed good repeatability, with an estimated measurement uncertainty of approximately 2%. They were used to calculate the total colour difference:

$$\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5} \quad (6)$$

In the development of the results, the criterion was used, according to which absolute colour differences (ΔE^*) above 5.0 indicated a large deviation [22–23].

Atomic absorption spectrometry (AAS)

Concentrated nitric acid (HNO₃) was used to mineralise the pigments (CdS) to release cadmium ions (Cd²⁺), which were then determined by atomic absorption spectrometry (AAS). The cadmium content was determined using a CE 3000 Thermo-Scientific atomic absorption spectrometer [24,25].

Thermogravimetric analysis

Thermogravimetric studies of pigment samples were performed using a Q1500D derivatograph of the Paulik-Paulik-Erdey system of the Hungarian company MOM in an air atmosphere. Ceramic crucibles and 200 mg samples were used. The sample mass loss was continuously recorded as the temperature increased to 600 °C at a rate of 5.0 °C/min. The thermal effects associated with pigment decomposition reaction of pigments were calculated from the DTA curve in relation to the standard benzoic acid [26,27].

X-ray diffraction analysis (XRD)

X-ray examinations of pigment samples were performed to analyse the crystal structure. The analysis was performed using a Seifert URD 6 X-ray diffractometer equipped with a goniometer enabling precise scanning of samples in a

wide angular range. The diffraction spectrum was recorded using CuK α radiation with a wavelength of $\lambda = 1.5406 \text{ \AA}$. In order to reduce the influence of K β radiation on the obtained spectrum, a nickel filter was used [28,29].

FTIR spectroscopy

Infrared (IR) spectroscopic studies of pigment samples were performed using a Bruker Alpha-P instrument with a reflective diamond head. Opus 6.5 software was used to record the spectrum. The measurement was performed in the wavenumber range of 350–4000 cm^{-1} . The spectra were recorded with a resolution of 4.0 cm^{-1} [30,31].

XPS photoelectron spectroscopy

Photoelectron spectra (XPS) were recorded under ultrahigh vacuum conditions (base pressure in the analysis chamber $\leq 2 \cdot 10^{-10}$ mbar). An AlK α lamp with an energy of 1486.6 eV was used as a source of monochromatic excitation radiation. The angle of incidence of the X-ray beam with respect to the normal to a surface of the samples was 55°. The energy of photoelectrons emitted from the sample surface was recorded using a hemispherical VG-Scienta R3000 analyser. The main axis of the analyser was oriented perpendicular to the sample surface. High-resolution spectra of individual regions were recorded with a step of $\Delta E = 100 \text{ meV}$. The experimental data after modelling the Shirley background were fitted to Gaussian-Lorentz shapes using CasaXPS software. The results were interpreted based on the data presented in the work [32–35].

RESULTS

Determination of the colour of pigments

The CIELab method was used to assess the colour of the tested pigments, which enabled the determination of their colour parameters L^* , a^* , b^* . On this basis, the colour change parameter, ΔE^* , was calculated using Equation 6. Table 2 provides the values of the determined and calculated colour parameters of cadmium pigments.

The data presented in Table 2 show that the highest brightness (L^*) was characteristic of the cadmium yellow obtained using the method of fusing a mixture of cadmium carbonate with sulphur (P6), which was comparable to the brightness of the industrial pigment sample (P7). Among the samples obtained via the unroasted precipitation method, the highest brightness was shown by the yellow pigment synthesised from cadmium chloride and sodium sulphide in an acidic medium (P2) and the pigment precipitated from a cadmium carbonate solution in an alkaline medium (P5). The brightness of the pigments obtained from cadmium sulphate or nitrate (P3 and P4) was similar. The lowest brightness was shown by the pigment obtained from cadmium chloride and sodium sulphide in an alkaline medium (P1).

The second value describing the pigment colour was the a^* parameter. Analysis of this value showed that the largest share in the colour of pigments obtained from cadmium chloride, sulphate and nitrate in the reaction with sodium sulphide in an alkaline environment (P1, P3, P4) had a red shade. In turn, in the case of the pigment obtained

Table 2. Values of the L^* , a^* and b^* parameters of pigments before and after calcination and the color change of pigments, ΔE^*

Pigment before additional heat treatment†					Pigment after calcination					ΔE*
Pigment designation	Color	L*	a*	b*	Pigment designation	Color	L*	a*	b*	
Precipitation method										
P1		69.27	31.54	74.83	P1r		77.34	6.56	60.48	29.9
P2		87.18	-2.43	87.31	P2r		64.52	13.42	41.47	53.5
P3		72.69	29.13	77.51	P3r		93.28	-14.18	90.10	49.5
P4		74.72	24.55	77.44	P4r		86.95	-1.76	85.35	30.1
P5		80.32	12.05	81.13	P5r		94.41	-5.76	39.07	47.7
Melting method										
P6		97.3	-20.26	83.52	-	-	-	-	-	-
Industrial sample										
P7		96.62	-20.61	94.10	-	-	-	-	-	-

as a result of the reaction of cadmium chloride with sodium sulphide in an acidic environment (P2), a negative a^* value indicated a small share of the green component. The green shade is also characteristic of the pigment obtained as a result of the fusion of components (P6) and the industrial pigment (P7).

The analysis of the b^* parameter values shows that the yellow shade dominates in the colour of all pigments. The largest share of this component was found in the sample obtained by the fusion method (P6) and in the industrial pigment (P7). The yellow shade occurs with significantly lower intensity in pigments obtained from cadmium chloride solution precipitated in an acidic environment and from cadmium carbonate solution (P2 and P5, respectively). The smallest share of the yellow shade was observed in the pigments obtained from cadmium chloride, sulphate and nitrate solutions in an alkaline environment (P1, P3 and P4). No blue component was found in the colour of any of the pigments.

Comparing the colour of pigments before and after calcination, it was found that in many cases the effect of high temperature on pigments was a change in their colour. The greatest increase in brightness after calcination was observed in the case of the pigment obtained from cadmium sulphate (P3r). The brightness of the pigment obtained from cadmium nitrate and cadmium carbonate (P4r, P5r) also increased, and only slightly in the case of the pigment precipitated from cadmium chloride in an alkaline medium

(P1r). The brightness of the pigment obtained from cadmium chloride in an acidic medium (P2r) decreased significantly.

The a^* values generally decrease significantly after calcination, which suggests a decrease in the red and an increase in the green component of the colour. The colour of compounds obtained from cadmium chloride, regardless of the environment in which they were precipitated (P1r, P2r), is dominated by the red component, although with a lower intensity than in the case of non-thermally treated samples. In the colour of the P3r, P4r and P5r pigments, a green shade appeared, with the highest intensity in the sample obtained from cadmium sulphate (P3r).

On the other hand, the analysis of the b^* parameter shows that the colour of all pigments after calcination is dominated by a yellow shade, the most intense in the case of the sample obtained from cadmium sulphate (P3r), while the intensity of the yellow shade increased in comparison to the unannealed sample, similarly to the pigment obtained from cadmium nitrate (P4r). The yellow shade of the pigments obtained from cadmium chloride in an acidic environment (P2r) and from cadmium nitrate (P4r) was almost twice as intense in comparison to the unannealed pigments.

Calculations of the colour change (ΔE^*) performed on the basis of eq. 1, taking as a basis the colour parameters of the pigments before and after their calcination, led to the conclusion that the colour of pigments obtained from cadmium chloride or nitrate in an alkaline environment (P1 and P4) changed the least.

Table 3. Cadmium content in the tested pigments depending on the raw material composition and the method of their production

Pigment designation	Raw material composition	Cadmium content in pigments, wt%
P1	$\text{CdCl}_2, \text{Na}_2\text{S}$	42.00
P1r		66.21
P2	$\text{CdCl}_2, \text{Na}_2\text{S}$	61.72
P2r		65.45
P3	$\text{CdSO}_4, \text{Na}_2\text{S}$	66.80
P3r		67.45
P4	$\text{Cd}(\text{NO}_3)_2, \text{Na}_2\text{S}$	62.34
P4r		61.14
P5	$\text{CdCO}_3, \text{Na}_2\text{S}$	85.96
P5r		58.60
P6	CdCO_3, S	62.62
P7	Industrial pigment	68.22

Chemical composition of pigments

In order to relate the colour of the synthesised pigments to their chemical composition, the Cd content in individual samples was determined. The results are summarised in Table 3.

According to the stoichiometry of the compound, the percentage of Cd in CdS is 77.81% by weight. However, the data presented in Table 3 show that the percentage of cadmium in pigments is different from that calculated theoretically and depends both on the type of raw materials used for synthesis and its method, as well as on additional thermal treatment.

The highest cadmium content after precipitation and drying of pigments, higher than theoretically calculated, was found in the precipitate obtained from cadmium carbonate and sodium

sulphide. As a result of incomplete precipitation reaction, some cadmium ions may remain in solution, which affects the actual content of the element. High cadmium content after precipitation may also be caused by contamination of substrates, which may co-precipitate with CdS. In other cases, especially in the samples obtained from cadmium chloride and sodium sulphide in an alkaline environment, the cadmium content is lower than theoretically calculated. This may indicate that cadmium pigments, in addition to the basic component in the form of CdS, contain other compounds with a polysulphide structure, which was shown in the further part of this paper. The presence of cadmium polysulphides in the pigment causes that there is more than one sulphur atom per cadmium atom, hence the lower cadmium content in such a pigment compared to pure cadmium sulphide. The increase in the Cd content in the calcined pigments (P1r, P2r and P3r) probably results from the loss of bound water, which occurs during thermal treatment. During calcination, partial oxidation of CdS to CdO and SO₂ is also possible. This process is accompanied by a decrease in the sample mass, and consequently an increase in the cadmium content in the sample. The decrease in the Cd content after calcination (P5r) can be explained by the sublimation of CdS from the surface of the material, which leads to a decrease in its mass and thus in the cadmium content.

Figure 1 shows the dependence of one of the colour parameters of pigments, i.e. brightness, on the amount of cadmium they contain.

The data presented in Figure 1 show that the pigment brightness parameter was not a simple dependence of the cadmium content. Generally,

it can be stated that a higher cadmium content in the pigment does not always accompany a higher brightness. In particular, the pigments after calcination (Figure 1B) showed similar brightness regardless of whether they contained a smaller or larger amount of cadmium.

Thermal stability

Thermogravimetric studies allowed determining the type of changes that pigments underwent under the influence of increasing temperature. An interesting research task was to determine the effect of calcination pigments on their thermal stability. As a reference point for the DTG analysis of the synthesised pigments, a thermogravimetric analysis was performed of those substrates that decompose under the conditions of synthesis (p. 1.1). The data from thermograms are presented in Table 4.

The data presented in Table 4 show that sodium sulphide hydrate undergoes three different thermal transformations. The first decomposition peak meant the loss of crystal water by the compound. The second and third peaks meant the decomposition of sulphide and sodium polysulphides, which could be sodium disulphides and trisulphides or other compounds. Due to the proximity of the maximum decomposition rate temperatures, they corresponded to one common endothermic thermal effect. The thermal decomposition of cadmium sulphate octahydrate also consisted in the loss of crystal water and then its decomposition. On the other hand, cadmium carbonate underwent thermal decomposition in several stages. In the first stage, the so-called surface moisture was removed from the compound.

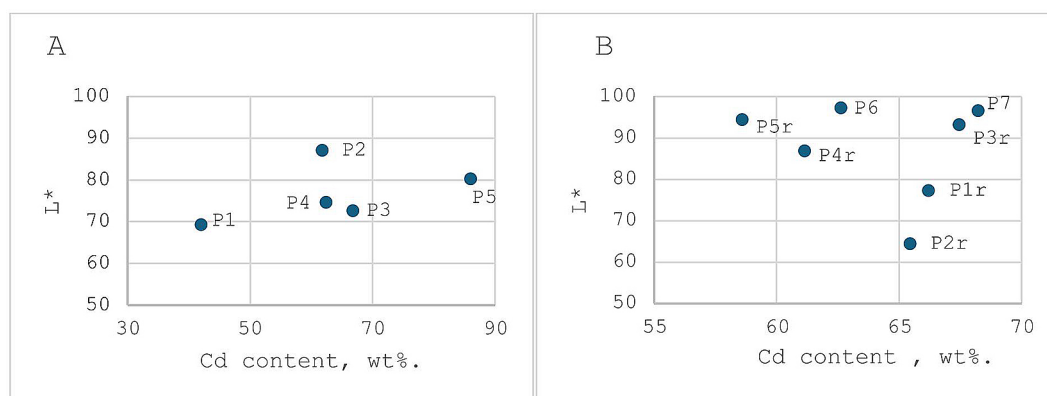


Figure 1. Dependence of the brightness of pigments on their cadmium content. Explanations: A – pigments before calcination, B – pigments after calcination

Table 4. Values of transformation temperatures, mass changes and thermal effects of raw materials used for the synthesis of pigments

Type of chemical compound	Decomposition stage	Initial decomposition temperature, °C	Temperature of maximum decomposition rate, °C	Final decomposition temperature, °C	Weight loss of sample, %wt	Endothermic heat effect, kJ/g
Na ₂ S·9H ₂ O	1	74.3	144.0	160.7	-7.7	0.310
	2	188.7	203.6	209.6	-13.6	0.587
	3	209.8	215.5	256.3	-18.9	
CdSO ₄ ·8H ₂ O	1	57.6	85.5	154.6	-6.40	0.160
	2	154.6	179.1	253.1	-9.12	0.269
CdCO ₃	1	60.0	68.8	115.6	-1.42	-
	2	131.0	177.3	208.0	-2.80	0.019
	3	256.3	324.8	368.3	-21.0	0.379
	4	374.3	405.3	440.0	-5.50	0.046

This was evidenced by the change in the mass of the substance without the occurrence of a thermal effect. In the second stage of thermal decomposition, crystal water was removed from the compound. The third stage began the basic decomposition of cadmium carbonate to cadmium oxide. In the fourth stage, other substances, probably contained in it, could have decomposed.

Figure 2 shows the curves defining the mass change of the pigment samples (TG) and the thermal effects (DTA) of the process.

Table 5 characterises the individual stages of pigment decomposition.

Thermogravimetric studies of sample P1 showed that it decomposed in two stages. In the first stage, there was a loss of crystal water expressed by a decrease in mass and a small endothermic thermal effect. In the second stage, a clear change in the crystalline form of the pigment was observed. This was evidenced by a significant exothermic effect and a loss of a small amount of pigment mass. The loss of mass during annealing is explained by the increase in the percentage of Cd as a result of calcination this pigment (Table 3).

Pigment P2 underwent small phase changes, which could indicate the ordering of the crystal structure and a small oxidation of CdS in the presence of air to CdO and SO₂, which could have affected the decrease in the sample mass and the increase in the cadmium content (Table 3). However, the results of the TGA analysis indicate an increase in the sample mass occurring during its heating. The reason may be different thermal and time conditions during calcination of sample P2 and heating during the measurement.

The decomposition of sample P3 also occurred in two stages. In the first stage, water was removed from the crystal structure of the pigment. Its removal confirms the sample mass loss and the thermal endothermic effect. In the second stage, structural changes occurred in the pigment, expressed by the thermal exothermic effect and a small increase in mass, most likely caused by oxidation. The negative resultant mass change explains the increase in Cd content in this sample after calcination (Table 3).

In the case of sample P4, in the first stage of decomposition, crystal water was removed, expressed by a decrease in the sample mass and the endothermic thermal effect. In the second stage, the pigment structure changed and its small oxidation occurred, expressed by an increase in the sample mass and the exothermic thermal effect. The sample mass loss compared to the result of determining the Cd content in this pigment (Table 3) indicates the oxidation of sulphur to sulphur dioxide, similarly to pigment P2.

The DTA and TG curves of the P5 pigment showed that the first stage involved the decomposition of unreacted carbonate to cadmium oxide, which reacted with sodium sulphide to form cadmium yellow. The evidence for their simultaneous course was the decreasing mass of the pigment sample and the exothermic thermal effect. In the second stage, the produced pigment changed its structure and underwent slight oxidation.

Sample P6 was a homogeneous mixture of solid substrates, i.e. cadmium carbonate and elemental sulphur. The changes occurring during heating consisted of the decomposition reaction of the carbonate to cadmium oxide and then its

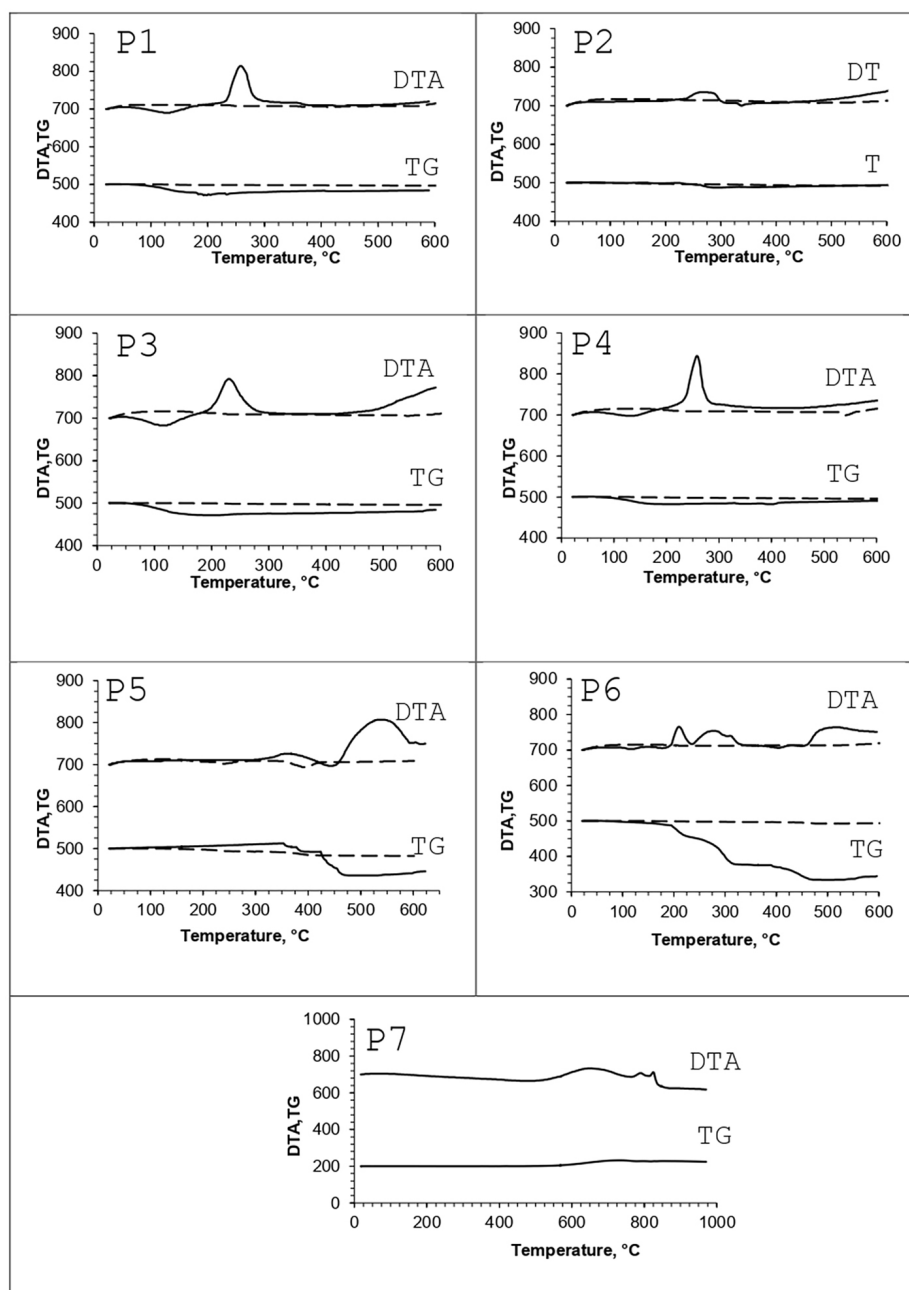


Figure 2. Thermogravimetric curves of cadmium pigments. Continuous lines refer to pigments obtained by precipitation before calcination (P1–P5) and the mixture of components for the synthesis of pigment P6. Dashed lines refer to roasted pigments

reaction with sulphur, which resulted in the resulting pigment. Such a multi-stage mechanism for the formation of cadmium yellow is confirmed by the stepwise decrease in the sample mass. The course of subsequent reactions is indicated by several exothermic thermal effects.

The CdS samples reached a thermally stable state after calcination. There are no longer any processes, such as oxidation, sublimation or decomposition, which could cause mass changes and be visible on DTG curves. The exception is

sample P5r, where a small peak related to oxidation processes was observed.

The thermal effects observed during TG/DTA analysis can be explained by oxidation processes occurring during calcination in an air atmosphere. According to the literature, the oxidation of CdS may proceed through the oxidation of sulphide ions, leading to the formation of sulphur oxides via the intermediate oxidation of CdS. Under oxidising conditions, SO_2 may be further converted to SO_3 , which subsequently reacts with

Table 5. Phase change temperature values read from cadmium pigment thermograms

Pigment	Decomposition stage	Initial decomposition temperature, T_i , °C	Temperature of maximum decomposition rate, T_{max} , °C	Final temperature, T_f , °C	Change in sample weight in %wt, (-) weight loss, (+) weight increase	Thermal effect in kJ/g, (-)endothermic, (+)exothermic
P1	1	81.1	129.1	168.4	-4.25	-0.063
	2	228.9	255.0	280.9	-1.62	0.387
P2	1	224.1	276.1	303.2	2.49	0.166
P3	1	51.1	112.3	170.2	-5.53	-0.118
	2	189.1	230.5	300.0	0.66	0.448
P4	1	75.6	130.8	176.3	-3.44	-0.054
	2	227.3	256.9	270.5	0.28	0.303
P5	1	291.2	362.8	466.5	-12.42	0.240
	2	468.8	539.7	594.4	1.69	0.887
P6	1	160.0	215.7	235.1	-9.36	0.107
	2	238.5	279.3	326.1	-16.82	0.252
	3	386.1	429.8	471.2	-10.42	0.01
	4	473.6	505.4	579.9	2.43	0.317

cadmium-containing species to form cadmium sulphite and, upon further oxidation, cadmium sulphate. These oxidation products are consistent with the secondary crystalline phases identified by XRD and with the sulphur-containing species detected by FTIR and XPS analyses. Therefore, the TG/DTA results are in good agreement with the structural and surface analyses, confirming that oxidation is one of the main processes occurring during calcination.

Structure of pigments

The X-ray diffraction method allows the determination of the chemical structure of the pigments studied. Figure 3 shows X-ray diffraction patterns recorded for the pigments before and after calcination, which allowed the identification of crystalline phases in the post-reaction mixtures, as well as the determination of the average crystallite size (D) using Equation 7:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (7)$$

where: K is the crystallite shape constant, λ denotes the X-ray wavelength, β stands for the peak half width (taking into account apparatus correction) and θ is the Bragg angle corresponding to the peak position. In order to compare the crystallite sizes in the tested samples, calculations were

performed for the peak at the angle 2 theta of approximately 26.5 degrees, except for sample P5, for which the peak with the maximum height was used. For the constant K , values of 0.9 and 0.94 were assumed for regular and other structures, respectively [36]. Calculations were performed using an online calculator [37].

Table 6 presents the results of the diffraction pattern analysis.

Table 6 shows that pigment P1 before calcination exhibited a poorly developed, metastable regular CdS structure, which after calcination changes into a stable hexagonal structure. The average crystallite size increases almost 64 times (Table 6). This process is associated with an increase in the pigment brightness [36], which is confirmed by the results of the L^* parameter measurement for this pigment (Table 3). Moreover, it was found that small amounts of sodium chloride and cadmium sulphate crystallised from the sample during the calcination process. Their white colour could also have influenced the pigment brightening. The transformation of CdS from the metastable cubic structure to the thermodynamically stable hexagonal phase is accompanied by improved crystallinity and significant crystal growth, as confirmed by the increase in crystallite size. Better crystal ordering reduces the density of structural defects, which may affect light absorption and scattering within the pigment

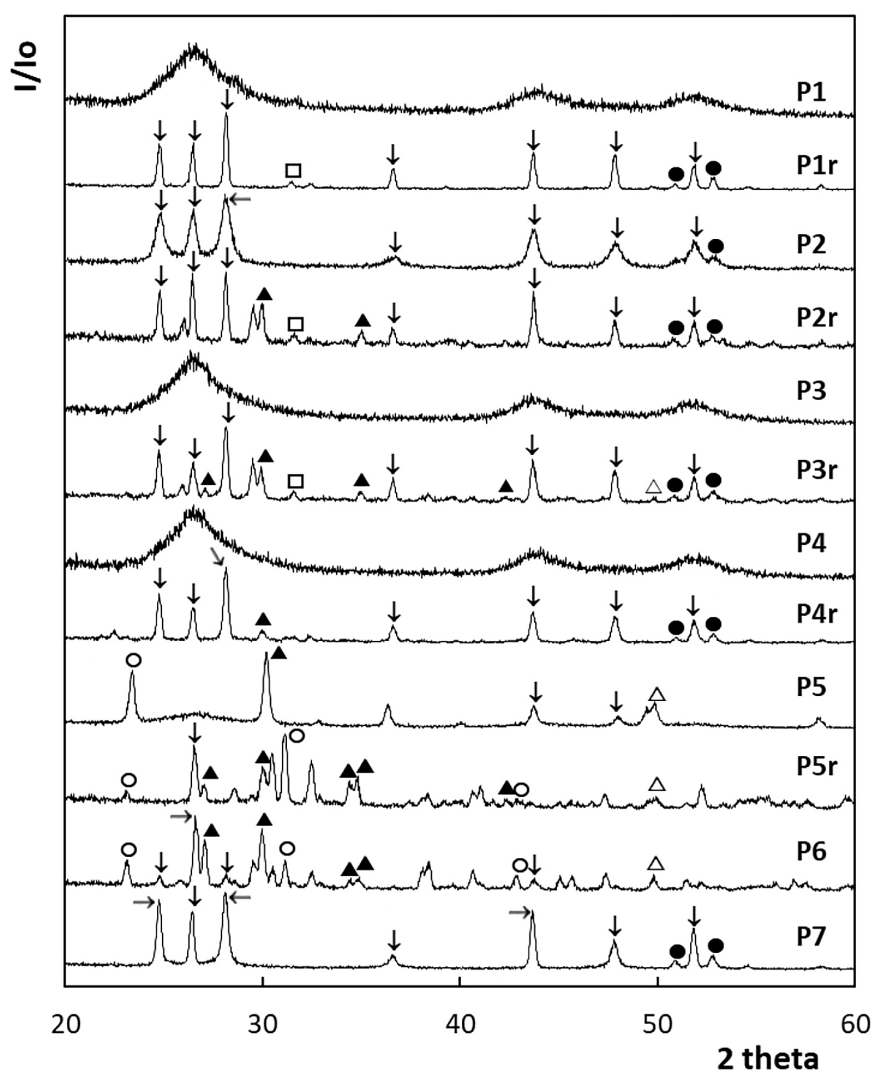


Figure 3. X-ray diffraction patterns of the tested pigments.
 Symbols: ↓ – CdS, □ – NaCl, ● – CdSO₃, ○ – CdSO₄, ▲ – Na₂CO₃, △ – CdCO₃

Table 6. Results of X-ray examinations of synthesised cadmium pigments

Pigment	Basic substrates	pH	Structure of the CdS crystallographic cell	Other by-products formed *)	Average crystallite size (D), nm
P1	CdCl ₂ , Na ₂ S	12	Regular		3.20
P1r		-	Hexagonal	NaCl, CdSO ₃	204.02
P2	CdCl ₂ , Na ₂ S	1-2	Hexagonal	CdSO ₃	45.34
P2r		-	Hexagonal	NaCl, CdSO ₃ , Na ₂ CO ₃	163.21
P3	CdSO ₄ , Na ₂ S	12	Regular		4.90
P3r		-	Hexagonal	CdSO ₃ , Na ₂ CO ₃ , NaCl	102.01
P4	Cd(NO ₃) ₂ , Na ₂ S	12	Regular		3.44
P4r		-	Hexagonal	CdSO ₃ , Na ₂ CO ₃	81.61
P5	CdCO ₃ , Na ₂ S	12	Mixture of different crystallographic cells	CdCO ₃ , CdSO ₄ , Na ₂ CO ₃	2.65
P5r		-	Mixture of different crystallographic cells	CdCO ₃ , CdSO ₄ , Na ₂ CO ₃	81.61
P6	CdCO ₃ , S	-	Hexagonal	CdCO ₃ , CdSO ₄ , Na ₂ CO ₃	116.61
P7	Industrial pigment	-	Hexagonal	CdSO ₃	90.67

Note: *JCPDS database standard card numbers: 6–314 for hexagonal CdS, 5–628 for NaCl, 31–238 for CdSO₃, 36–897 for CdSO₄, 8–456 for CdCO₃, 18–1208 and 25–815 for Na₂CO₃.

particles. Consequently, the structural transformation contributes to the observed increase in pigment brightness, together with the formation of secondary white phases during calcination.

Pigment P2 before calcination had a fairly well-developed hexagonal CdS structure. Cadmium sulphide was accompanied by trace amounts of CdSO_3 crystals, which could have caused it to have a lighter colour than pigment P1. Calcination of sample P2 led to the crystallisation of the next pigment components: sodium chloride and sodium carbonate. The carbonate was most likely formed in reaction with CO_2 contained in the air, and its significant amount may be responsible for the increase in the brightness of this pigment (Table 3). In this case, thermal treatment also resulted in an increase in the average crystallite size, which was 3.6 times (Table 6).

In the composition of pigment P3 before calcination, similarly to sample P1, CdS with a cubic structure was identified, which after calcination transformed into the thermodynamically stable hexagonal phase. This transformation was accompanied by a significant increase in the average crystallite size, i.e. more than 20 times (Table 6). Thermal treatment also promoted the crystallisation of cadmium sulphite (IV) and sodium carbonate. Therefore, the increase in pigment brightness after calcination can be attributed to two simultaneous effects: the transformation of CdS into the hexagonal phase with improved crystallinity and the formation of secondary white phases, which further contributed to the increase in pigment lightness.

A similar behaviour was observed for sample P4. After precipitation, the pigment contained CdS with a cubic structure, which transformed into the hexagonal phase after calcination, while the average crystallite size increased more than 23-fold (Table 6). Heat treatment also resulted in the formation of cadmium sulphite (IV) and sodium carbonate. Consequently, the improved optical properties of the pigment can be explained by both the structural transformation of CdS and the formation of secondary white phases.

As a result of the synthesis of pigment P5, a solid mixture was obtained containing more crystals of accompanying substances than hexagonal CdS. The pigment consisted of: unreacted substrate – sparingly soluble cadmium carbonate and additional reaction products, i.e. cadmium sulphate and sodium carbonate. For this reason, pigment P5 is one of the lighter ones among the

samples not subjected to calcination (Table 3). Heat treatment of the pigment did not affect its qualitative composition, but changed the proportions of the crystalline components of this mixture (almost 31-fold increase in the average crystallite size, as shown in Table 6), translating into an increase in brightness (Table 3).

The method of synthesis of yellow cadmium pigment directly by reaction of cadmium carbonate with sulphur (sample P6) was innovative. As a product of substrate fusion, a pigment containing CdS with a hexagonal structure was obtained, heavily contaminated with cadmium carbonate and sulphate(VI) and sodium carbonate. Large amounts of by-products determined the high brightness of this pigment (Table 3). The average crystallite size in this sample is slightly above 116 nm, which is similar to that in the calcined P3r sample (Table 6). The comparative sample (P7) was an industrial pigment. Analysis of the X-ray diffraction pattern of this sample showed that in addition to CdS with a stable hexagonal structure, it contained a small amount of crystalline cadmium sulphate(IV). The average crystallite size of this sample reached a value of approximately 90 nm, which is similar or even lower than those calculated for the synthesised and calcination pigments (Table 6).

Infrared spectrometry

The study of the qualitative composition of the pigments was supplemented by the analysis of the IR spectra presented in Figure 4.

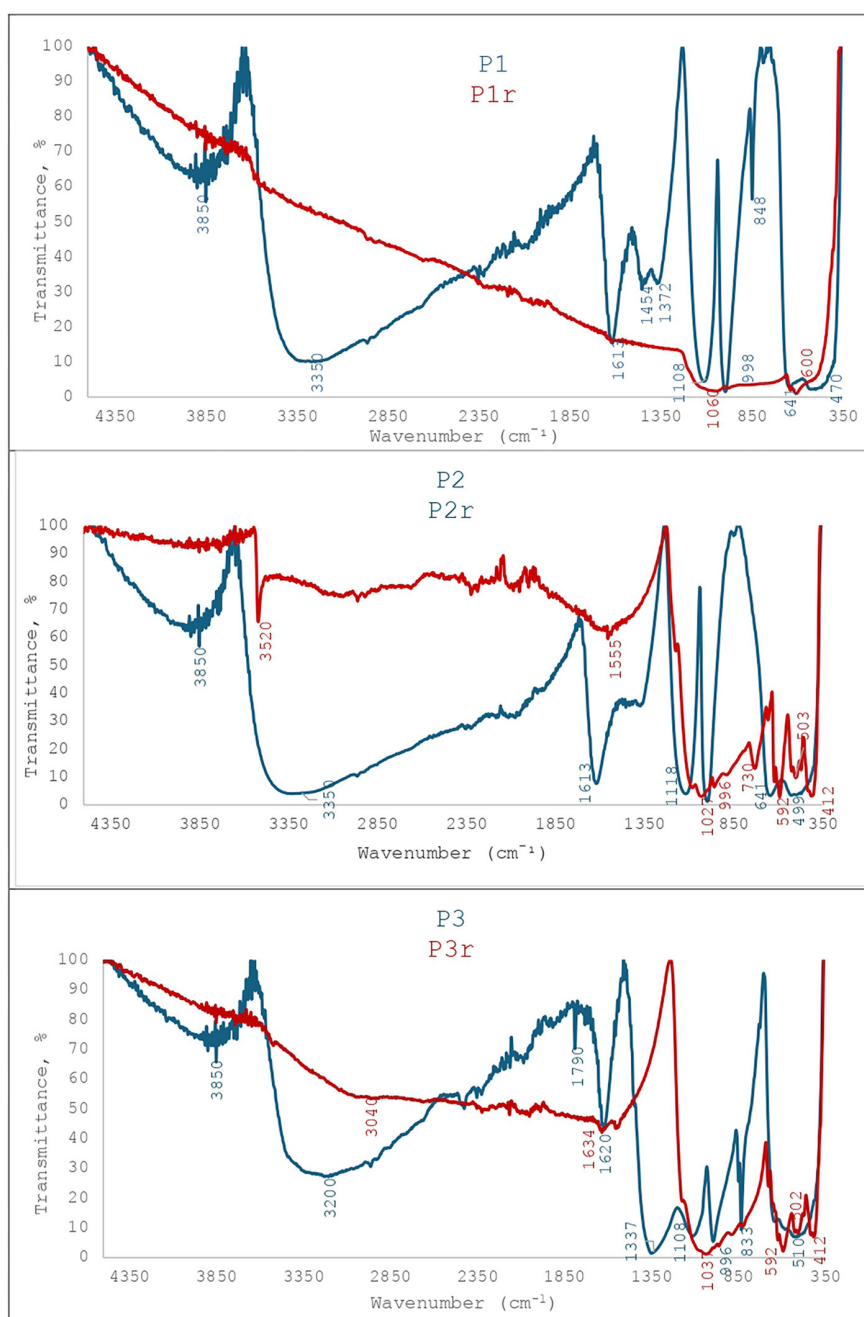
Characteristic bands in the spectra of pigments, originating from vibrations of specific groups, were taken from literature data and are presented in Table 7 [30,31].

The data presented in Table 7 and Figure 5 show that in the case of pigment P1, before calcination, the presence of hydroxyl groups (3850 , 3350 and 1613 cm^{-1}), sulphide and polysulphide groups (1454 and 1372 cm^{-1} and $641\text{--}470\text{ cm}^{-1}$), as well as sulphite (848 cm^{-1}) and sulphate (1108 and 998 cm^{-1}) can be observed. In turn, after calcination, the hydroxyl groups disappeared, and the spectrum contained bands associated with sulphide and polysulphide groups ($641\text{--}470\text{ cm}^{-1}$) and carbonate (1060 cm^{-1}).

In the spectrum of pigment P2, strong bands of hydroxyl groups (3850 , 3350 and 1613 cm^{-1}), sulphide (499 cm^{-1}) and sulphite (641 cm^{-1}) groups were observed. After its calcination, strong sulphide (592 and 503 cm^{-1}), sulphite (730 cm^{-1}) and

Table 7. Wavenumber values related to elements or their groups occurring in the synthesised pigments

Wave number (cm ⁻¹)	Before calcination	After calcination	Assignment	Literature
3200–3600	Present	Absent	O–H stretching vibrations (bound water, humidity)	3200–3600
2550–2600	Present	Weak/absent	S–H stretching vibrations (thiol, H ₂ S)	2550–2600
1613–1624	Present	Weak	H–O–H deformation vibrations (water)	1600–1650
1553–1543	Weak	Strong	Asymmetric vibrations of sulphates (SO ₄ ²⁻)	1500–1560
1386–1058	Weak	Strong	Carbonate vibrations CO ₃ ²⁻ (pollutants, carbonates)	1390–1050
1108–998	Weak	Strong	Asymmetric S–O vibrations (sulphate residues)	1100–1000
901, 858, 821	Present	Present	S–S vibrations	850–550
641–470	Present	Present	Cd–S vibrations (characteristic of CdS)	640–470


Figure 4. Infrared spectra of the tested pigments

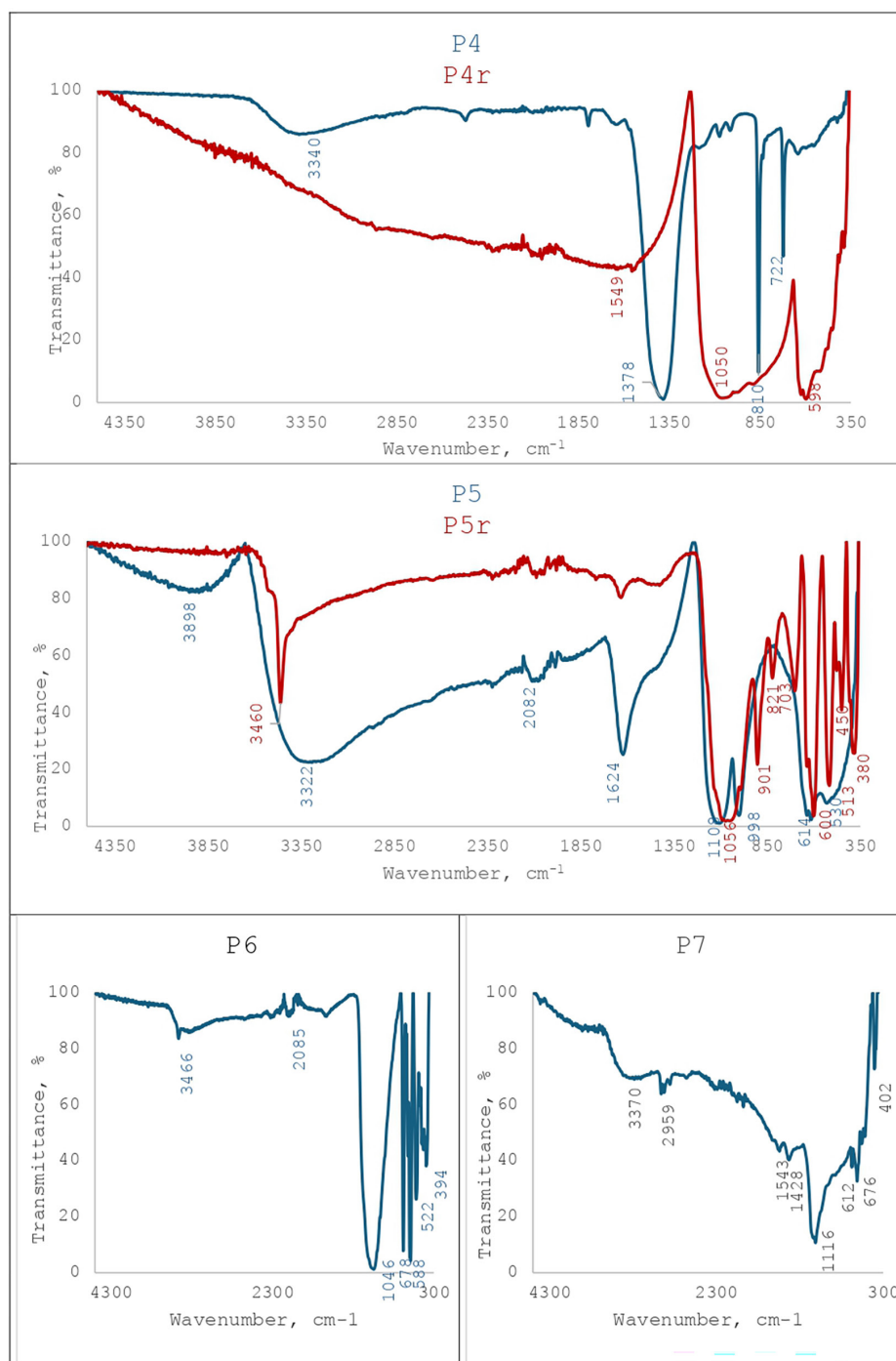


Figure 4. Cont. Infrared spectra of the tested pigments

sulphate (1555 cm^{-1}) bands and a weak carbonate band (1027 cm^{-1}). Carbonates in sample P2 could have appeared as a result of calcining the pigment in an air atmosphere. The course of the spectra of pigments P2 and P3 is basically similar.

Pigment P4 was characterised by a fairly high purity. Only a small amount of hydroxyl groups was found in it (3360 cm^{-1}). The band at 1350 cm^{-1} may come from carbonate ions or other foreign substances. After calcination, the pigment

showed a change in the intensity of the bands in the range of $400\text{--}600\text{ cm}^{-1}$, which may indicate a change in the CdS structure.

Pigment P5 showed the presence of hydroxyl (3898 and 3322 cm^{-1}), sulphate (1624 cm^{-1}), carbonate (1108 and 998 cm^{-1}) and sulphide (530 cm^{-1}) groups. The calcination process caused a decrease in the intensity of the band originating from hydroxyl and carbonate groups, the disappearance of the sulphate group band and the

appearance of an additional band originating from sulphide groups (600 cm^{-1}).

In the spectrum of pigment P6, the bands of sulphide groups (676 and 612 cm^{-1}), as well as carbonate (1428 and 1116 cm^{-1}) and sulphite (678 cm^{-1}) groups are clearly visible.

The spectrum of the commercial P7 pigment is dominated by the bands of carbonate groups (1428 and 1116 cm^{-1}), there are also bands of lower intensity originating from hydroxyl groups (3370 and 2959 cm^{-1}) and sulphide groups (676 and 612 cm^{-1}).

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was used to determine the detailed chemical composition of the pigments studied. XPS spectra were recorded for all pigment samples. In this way, ranges were determined in the obtained spectra, which included the main lines characteristic of individual atoms occurring in the pigments. They corresponded to their high resolution. An example spectrum of the pigment sample is shown in Figure 5.

In the presented spectrum, peaks from the cadmium atom clearly dominate. Spectral lines created by photoelectrons come from the L shell of sulphur and show much lower intensity. This results from a significant difference between the active cross sections of the above elements to excitation by X-ray radiation. This in turn was the main reason for the significant difference in the relative sensitivity coefficients of cadmium and sulphur in the XPS technique. After calcining all pigment samples, a clear broadening of the Cd3d peak was observed. Similar broadening of the Cd3d signal has been reported for

oxidised CdS materials and is commonly attributed to changes in the local chemical environment of cadmium associated with the coexistence of Cd–S and oxidised sulphur species on the surface [38]. While for the precipitated material this level can be deconvoluted relatively well with a single doublet, after modification the spectrum clearly broadens towards higher binding energies and requires fitting with at least two components. The broadening of the Cd3d level for the exemplary sample (3) is shown in Figure 6 a) and b).

An even more evident change caused by calcination is observed in the case of the S2p level. This is shown in parts c) and d) of Figure 5. In the samples before calcination, a single doublet is recorded at an energy of approximately 161.6 eV ($\text{S}2\text{p}_{3/2}$). This energy is consistent with literature data for sulphides, including cadmium sulphide. The calcination process causes the appearance of a second peak, strongly shifted to higher binding energies. It is recorded at approximately 169.3 eV and most likely comes from the sulphur constituting cadmium sulphate. The appearance of this high-binding-energy component is consistent with previous XPS studies of oxidised CdS materials, where it has been attributed to oxidised sulphur species, including sulphite and sulphate, formed during surface oxidation of CdS [39]. Tables 8 and 9 present detailed values of the surface concentration of individual atoms constituting the pigments expressed in atomic percent. The tables take into account the pigments after their precipitation and drying and after their calcination.

The Cl2p spectra for samples (P1) and (P2) showed no significant chemical shifts due to sample modification, but after calcination, there was

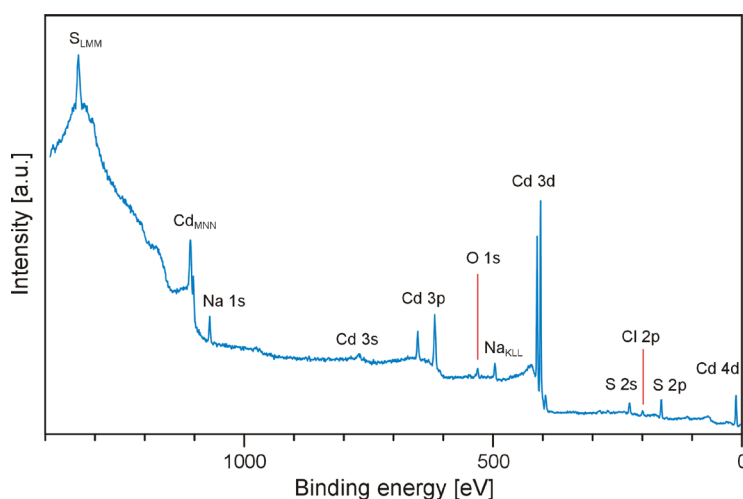


Figure 5. Survey spectrum of the selected sample (P1) with the designations of individual peaks

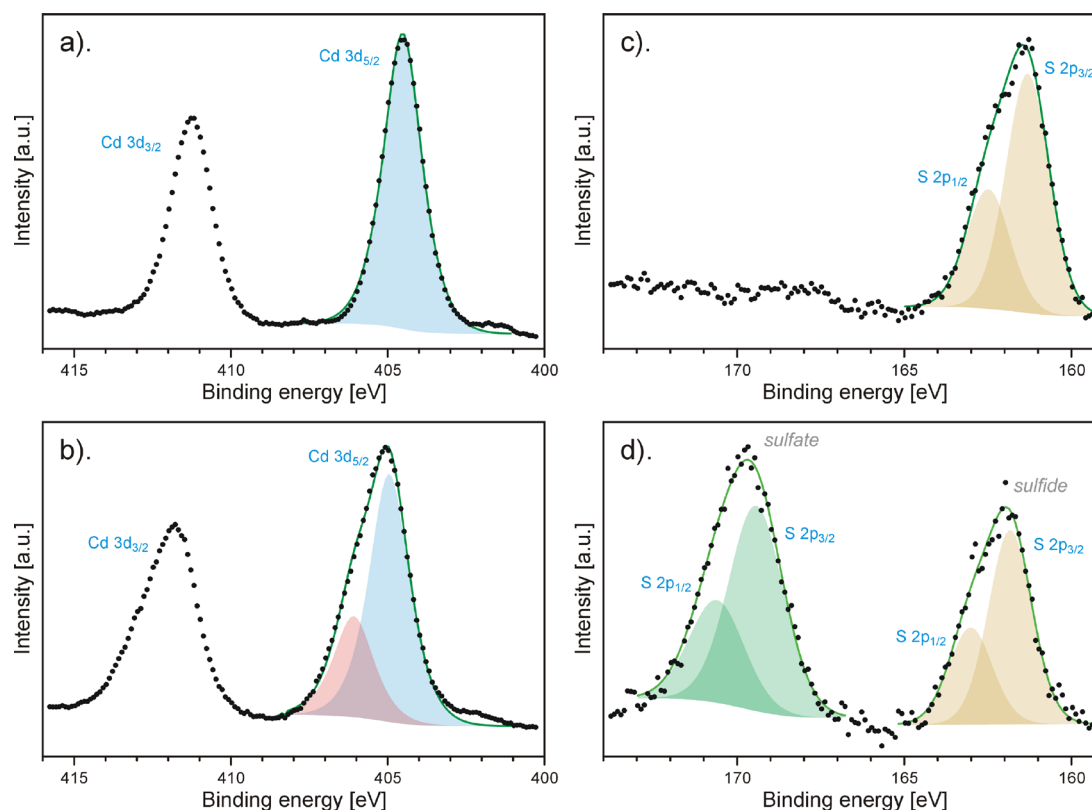


Figure 6. High resolution XPS spectra of Cd3d and S2p levels of sample no. (P3) – a). and – c) compared to these levels after calcination – b). and d)

Table 8. Atomic concentration values (at.%) of individual elements on the surface of pigments after their precipitation and drying

Pigment	Na	O1	O2	O3	Cd1	C1	C2	C3	Cl	S1	S2
P1	7.66	8.07	2.04	2.61	35.73	3.67	1.50	1.90	6.34	30.48	-
P2	2.64	4.85	1.52	0.73	42.84	4.52	2.91	1.26	3.80	34.93	-
P3	16.77	17.56	15.04	4.23	20.22	3.70	0.47	5.06	-	16.95	-
P4	5.22	7.97	1.65	0.88	43.61	4.92	0.09	0.84	-	34.82	-
P5	8.42	14.88	0.93	2.88	35.26	2.31	0.90	0.70	-	30.16	3.56

Table 9. Atomic concentration values (% atm.) of individual elements on the surface of pigments after calcination

Pigment	Na	O1	O2	O3	Cd1	Cd2	C1	C2	C3	Cl	S1	S2
P1r	7.38	21.30	1.02	3.43	12.81	3.33	23.27	2.29	1.84	7.63	9.52	6.19
P2r	1.19	20.37	6.69	0.40	14.13	13.37	14.41	1.97	1.01	9.81	11.46	5.19
P3r	4.73	33.51	10.13	1.18	16.59	6.74	4.17	0.85	1.16	-	8.95	11.99
P4r	5.50	30.27	7.78	2.18	16.66	5.39	7.07	2.32	1.34	-	10.89	10.60
P5r	2.62	48.75	6.08	0.55	10.10	11.39	4.35	1.52	0.60	-	0.58	13.46
P6	-	49.30	5.76	0.20	9.34	12.54	5.60	0.88	0.48	-	0.57	15.33
P7	-	10.00	5.46	0.55	26.36	15.01	5.82	2.40	1.45	-	31.31	1.64

an increase in chlorine signal intensity, especially in sample (P2r). The Na1s spectra showed no notable chemical shifts, though a slight decrease in intensity was observed after calcination,

except for sample (P4r), where the Na1s intensity increased slightly. Sample (P3) had a significantly higher sodium content before modification, but after calcination, this decreased considerably.

Oxygen (O1s) and carbon (C1s) levels were also recorded for all samples. The interpretation of their contribution to the surface composition was uncertain due to surface contamination. Oxygen levels showed three components: O1 and O2 at 531.0 eV and 532.8 eV, likely from adsorbed oxygen and -OH groups, and a third peak at 535.5 eV, attributed to adsorbed water. After precipitation and drying, some water remained in the pigment structure, confirmed by infrared spectroscopy. The C1s spectrum was fitted with three components (C1, C2, and C3) corresponding to C-C, C-H, C-O, and C=O bonds. Calcination increased carbon content in most samples, except for sample (P3), where the C1s peak intensity decreased significantly after calcination.

Colour measurements showed that pigment brightness and hue were influenced by both the chemical composition of the starting materials and the reaction environment. The highest lightness was observed for the pigment prepared from cadmium chloride and sodium sulphide under acidic conditions. The pigments prepared from cadmium sulphate or cadmium nitrate and sodium sulphide under alkaline conditions exhibited similar lightness, whereas the pigment prepared from cadmium chloride and sodium sulphide under alkaline conditions showed the lowest lightness. The strongest red component was observed for the pigments synthesised from cadmium chloride, cadmium sulphate and cadmium nitrate with sodium sulphide under alkaline conditions. In contrast, the most pronounced green component was found for the pigment synthesised from cadmium chloride and sodium sulphide under acidic conditions and for the pigment obtained by the direct reaction of cadmium carbonate with sulphur. Among the calcined pigments, the highest lightness was observed for the samples prepared from cadmium carbonate and sulphur and from cadmium sulphate and sodium sulphide under alkaline conditions. In the remaining samples, calcination increased both the lightness and the intensity of the yellow colour.

The cadmium content determined in the synthesised pigments showed that the highest concentration was found in the product obtained from the reaction of cadmium carbonate with sodium sulphide. In this sample, the cadmium content exceeded the theoretical value. The pigments containing less cadmium than theoretically expected consisted of compounds in which

sulphur was present not only in the form of CdS but also as cadmium polysulphides and other sulphur-containing species. The results also indicate that pigment brightness is not directly correlated with cadmium content. Instead, calcination had a much greater influence on the optical properties of the pigments by modifying their crystallographic structure and promoting reactions leading to the formation of new sulphur-containing compounds.

The optical behaviour of CdS pigments depends not only on their chemical composition but also on their crystal structure. Calcination transforms metastable cubic CdS into the thermodynamically stable hexagonal phase, which is characterised by improved crystallinity and larger crystallite size. Improved crystal ordering reduces structural defects that may act as light-scattering or light-absorbing centres. Consequently, the optical response of the pigments changes, which is reflected in the CIELab parameters, particularly in the lightness (L^*). The increase in brightness is further promoted by the formation of secondary white phases, including cadmium sulphates and sodium carbonates, identified by XRD, FTIR and XPS analyses.

The correlation between the XRD, FTIR and XPS results confirms that the optical properties of the pigments are governed by both structural and chemical changes occurring during calcination. While the phase transformation of CdS improves crystal ordering and modifies the interaction of the pigment with visible light, the simultaneous formation of sulphite, sulphate and carbonate phases further influences the measured colour parameters. Therefore, the final optical behaviour of the pigments results from the combined effect of crystal structure evolution and changes in chemical composition.

The formation of cadmium sulphite and cadmium sulphate during calcination can be explained by the progressive oxidation of sulphide species in an air atmosphere. Initially, partial oxidation favours the formation of sulphite species, whereas prolonged heating and continuous oxygen supply promote their further oxidation to the more stable sulphate phase. The extent of these reactions depends on the synthesis conditions and oxygen availability, explaining the differences in the secondary phases identified by XRD, FTIR and XPS analyses.

Thermogravimetric studies confirmed that some of the raw materials used for pigment

synthesis consisted of mixtures of different compounds; for example, sodium sulphide also contained polysulphides. The results also showed that pigments obtained by precipitation and drying lost crystal water during heating, and their structure and composition changed accordingly. In contrast, the calcined pigments behaved as homogeneous materials, and the observed changes were mainly associated with the transformation of the crystal structure.

The crystallographic structure and qualitative composition of the synthesised pigments were determined by X-ray diffraction analysis. The precipitated and dried pigments exhibited either cubic or hexagonal CdS structures, while one sample contained a mixture of different crystal structures. After calcination, however, all CdS-containing pigments exhibited the thermodynamically stable hexagonal structure. The pigments also contained by-products originating from both the raw materials and the synthesis process, including sodium chloride, sodium carbonate, cadmium sulphite, cadmium sulphate and cadmium carbonate.

The structural analysis was complemented by FTIR spectroscopy. The FTIR results confirmed the presence of hydroxyl, sulphide, polysulphide, sulphite and sulphate groups in the pigments after precipitation and drying. Chloride and carbonate species, originating from the starting materials and secondary reactions occurring both in solution and during heat treatment, were also detected. Calcination resulted in the removal of hydroxyl groups in the form of water and promoted oxidation, leading to increased amounts of sulphite, sulphate and carbonate species.

The presence of the same impurities and oxidation products was confirmed by XPS analysis, which provides higher surface sensitivity and enables the identification of specific chemical species, including different sulphur oxidation states. XPS confirmed that cadmium and sulphur were the dominant elements in all synthesised pigments, while the presence of sulphites, sulphates, carbonates and chlorides was consistent with the FTIR results. Identification of cadmium and sulphur species was relatively straightforward for the precipitated and dried pigments, whereas the analysis of calcined pigments required higher binding energies because of the presence of oxidised sulphur species. The occurrence of sulphite, sulphate, carbonate and sodium chloride phases confirms that oxidation

and exchange reactions take place during pigment synthesis and calcination. The detection of carbon-containing species additionally indicates the occurrence of surface reactions during calcination in an air atmosphere.

CONCLUSIONS

This study demonstrates that both precursor selection and synthesis conditions have a decisive impact on the colour, chemical composition, and crystallographic structure of cadmium yellow pigments. Calcination was accompanied by a significant increase in the average crystallite size, confirming improved crystallinity and the transformation of CdS into the thermodynamically stable hexagonal phase. Thermal treatment plays a key role in modifying pigment properties, promoting the transformation of CdS into a stable hexagonal phase, altering sulphur bonding, and inducing the formation of secondary phases such as sulphites, sulphates, and carbonates, which contribute to increased pigment brightness.

Among the investigated methods, the direct solid-state synthesis via melting of cadmium carbonate with sulphur was identified as the most promising route. This approach enables the formation of pigments with stable structure and favourable composition, ensuring desirable optical properties and thermal durability. In addition, the process offers technological simplicity, reduced number of synthesis steps, and potential economic advantages due to the elimination of additional precursors and lower by-product formation.

The results provide useful guidelines for the design and optimisation of CdS-based pigments with tailored properties, particularly for applications requiring high thermal stability and controlled optical performance.

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