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Sub-micrometer $CoAl_2O_4$ pigment particles — synthesis and preparation of coatings

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Sub-micrometer $CoAl_2O_4$ particles are prepared by applying the polyol method. Colloidal particles 50 to 200 nm in size with spherical shape are formed. Their average size can be controlled by adjusting the concentration of the components (metal precursor, water). The resulting suspensions in diethylene glycol can contain up to 10 wt.% $CoAl_2O_4$. The colloidal particles are well stabilized against agglomeration even when mixed with water. Based on such colloidal $CoAl_2O_4$ suspensions planar substrates (*e.g.* glass plates) as well as non-planar substrates (*e.g.* phosphor powder) can be covered homogeneously with thin pigment films. In order to establish the characteristic deep blue body colour of $CoAl_2O_4$, additional brief heating (15 min, 600 °C) is necessary. Further characterisation of $CoAl_2O_4$ powders as well as suspensions was carried out by diffuse reflection measurements, X-ray powder diffraction, scanning electron microscopy, laser diffraction and atomic force microscopy.

Introduction

Regarding technical significance, $CoAl_2O_4$ is one of the most important blue pigments.[1,2] Industrially the material is prepared by applying standard precipitation from water-based solutions. However, such a process normally yields hydroxides instead of water-free oxides at first. A treatment at elevated temperatures (up to 1000 °C) is required to obtain the pure, deep blue coloured oxide.[1,3,4] While heating condensation reactions occur resulting in a further growth of particles. Moreover, aggregation of neighboured particles to sometimes quite hard agglomerates can be caused.

Aiming at sub-micrometer sized $CoAl_2O_4$ particles, more advanced types of synthesis are required. Especially, for application as optical devices like colour filters or pigment layers on a luminescent material, the presence of sub-micrometer sized as well as non-agglomerated $CoAl_2O_4$ particles is indispensable.[5–7] Several approaches have been reported to prepare high surface area $CoAl_2O_4$, most of them based on the sol–gel process.[8–13] However, in all cases the synthesis suffers from the fact that either powders containing particle agglomerates or suspensions with quite low solids contents can be realized.

In this study the preparation of $CoAl_2O_4$ *via* the polyol method is described. Here, a suitable metal precursor is heated in a high boiling polyalcohol. Originally, the method was applied because of the reductive properties of polyalcohols to prepare sub-micrometer sized elemental metal particles, for instance, Sn, Fe, Re, Ru, Au.[14,15] With respect to oxides, until now only the preparations of sub-micrometer ZnO and α-Fe_2O_3 particles have been described.[16,17] We have synthesised polyol suspensions containing spherical $CoAl_2O_4$ particles of controllable size and describe their usage to produce homogeneous, thin pigment coatings on planar as well as non-planar substrates.

Experimental

Synthesis

A typical recipe for the preparation of sub-micrometer $CoAl_2O_4$ particles with the polyol method is as follows. 8.05 g $AlOH(CH_3COO)_2$ (Aldrich, aluminium content corresponds to 30% Al_2O_3) and 5.63 g $Co(CH_3COO)_2{\cdot}4H_2O$ (Aldrich, 99.999%) were placed in a round-bottomed flask fitted with a reflux condenser. 50 ml diethylene glycol (Merck, 99%) were added and the suspension stirred vigorously for 15 min. Afterwards, 1.0 ml demineralised water were added and the suspension stirred continuously. The mixture was heated with a silicon oil bath to 140 °C and the temperature was maitained at this level for 1 h. Then, the temperature was increased to 180 °C. After 2 h at this temperature, the suspension was cooled to room temperature and diluted with 50 ml ethanol. The preparation results in a reddish blue, stable suspension containing 4.0 g $CoAl_2O_4$. Solids content of the suspension can be increased up to 10 wt.% $CoAl_2O_4$. The suspensions are stable for weeks.

Characterisation

Diffuse reflection was measured with a home-built spectrometer equipped with an integrating sphere and monochromators for incoming as well as reflected light. Spectra were recorded between 350–800 nm applying semi-infinite layers of samples.

X-Ray powder diffraction (XRD) was performed with a Philips vertical goniometer PW1050 with Bragg–Brentano geometry. The diffractometer was equipped with a fixed divergence slit and a proportional counter. Cu-Kα radiation was used and monochromatised by a secondary graphite monochromator.

For scanning electron microscopy (SEM) a Philips SEM 525R equipped with a LaB_6 cathode was used. The samples were sputtered with gold. The investigations were carried out at a voltage of 15 to 25 kV, a spot size of 20 nm and a free working distance (FWD) of 9 to 12 mm.

Measurements of particle size were performed based on laser diffraction combined with polarisation intensity differential scattering. For this purpose a Coulter LS230 equipped with a laser (750 nm, 5 mW) and a PIDS lamp (tungsten–halogen, 150 lumens at 2900 K) as well as 126 photodiode detectors were used.

Investigations with atomic force microscopy (AFM) were performed with a Topometrix Explorer equipped with a

pyramidal Si_3N_4 tip. The vertical scanner span was <2 μm, the lateral scanner span <150 μm and the aspect ratio 1 : 1.

Results

Optical characterisation and phase analysis

The preparation of $CoAl_2O_4$ with the polyol method results in reddish blue suspensions (Fig. 1). Hereof, the solid material can be isolated by centrifugation. Its colour is also reddish blue. To obtain the characteristic deep blue body colour of $CoAl_2O_4$, additional brief heating is required. 15 min at 600 °C turned out to be sufficient (Fig. 1). Measurements of diffuse reflection (Fig. 2) indicate that the body colour thereafter is very comparable to a standard $CoAl_2O_4$ pigment (BASF Sicotrans). Likewise, right after preparation of $CoAl_2O_4$, the solid residue is amorphous. After 15 min at 600 °C crystallinity is increased strongly. X-Ray powder diffraction patterns indicate that pure $CoAl_2O_4$ is formed (Fig. 3). In fact, a close relation between crystallinity and materials colour is to be expected considering $^4A_2$–$^2T_1$(P) absorption as the origin of the deep blue colour of $CoAl_2O_4$.[18] In accordance with this relation the body colour itself is a very sensitive indicator for both the crystallinity as well as the composition (Co : Al ratio, OH and H_2O impurities) of the powder material.

Determination of particle size

After separation of $CoAl_2O_4$ from the polyol suspension, the particle size of the powder material can be estimated based on SEM micrographs. Here, spherical particles 70 to 90 nm in size are visible. While heating the material (15 min at 600 °C) the particle size remains unaffected. A typical powder sample after heating is depicted in Fig. 4. Although the particles are definitely sub-micrometer sized, SEM micrographs also indicate that particle aggregates are present. However, the strength of the polyol method is not the preparation of powder material but the realization of quite concentrated suspensions containing non-agglomerated oxide particles. This is mainly due to two effects. On one hand, the surface of the particles is covered with diethylene glycol right after formation. This complexation stabilizes the particles in such a way that agglomeration is prevented. On the other hand, at reaction temperatures of 150 to 200 °C most of the metal hydroxyl groups of the growing particles being separated by the polyol medium condense within one oxide particle and are not available for condensation between particles.

In order to determine the size of pigment particles suspended in the polyol medium, laser diffraction was applied. The investigations confirm that the primary particle size determined in powder samples indeed matches the particle size in suspension. Apparently, to a large extent non-agglomerated individual particles are present in diethylene glycol. A typical distribution curve is given in Fig. 5. Experimental studies have also shown that the size of $CoAl_2O_4$ particles can be controlled within limits of about 50 to 200 nm (Table 1). The concentrations of metal precursors as well as the amount of water added are the important parameters to consider here. In general, the particles grow larger at higher concentrations of the components. Another item is important with respect to industrial application of these $CoAl_2O_4$ suspensions. Aiming at pigment coatings on a given substrate, normally water is the preferred medium to use. Therefore, the behaviour of $CoAl_2O_4$ containing polyol suspensions was studied while mixing them with water. With a ratio H_2O : DEG equal to 10 : 1, the particle size remains stable within 15 min (Fig. 5). For this period, the surface of the particles seems to be further stabilized by diethylene glycol. After about 30 min diethylene glycol is more and more removed from the surfaces. The no longer stabilized

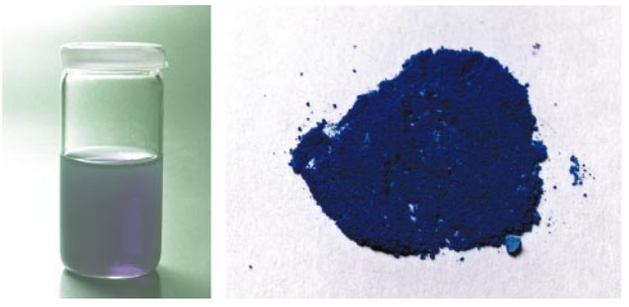

Fig. 1 Photographs of a polyol suspension containing $CoAl_2O_4$ particles (4.0 wt.%) and a $CoAl_2O_4$ powder (after 15 min at 600 °C).

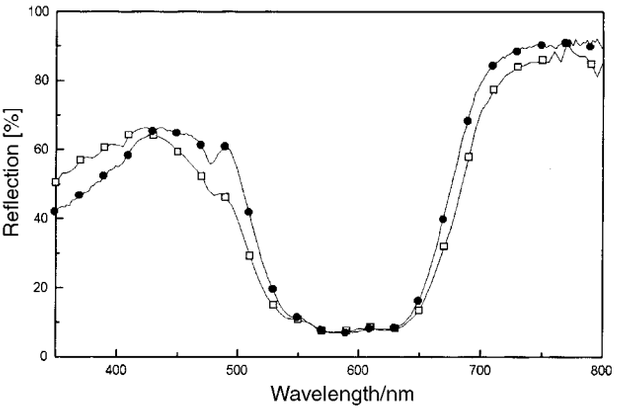

Fig. 2 Diffuse reflection of $CoAl_2O_4$ powder (after 15 min at 600 °C, squares); standard $CoAl_2O_4$ pigment added (BASF Sicotrans, circles).

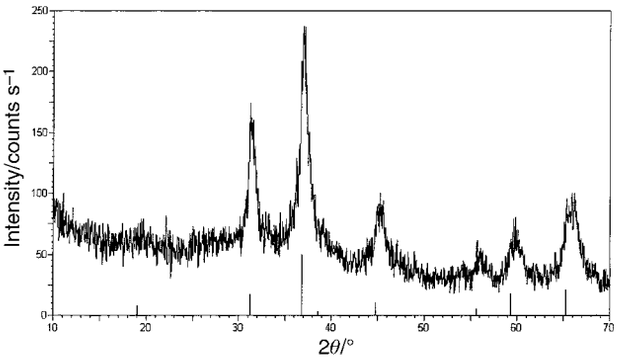

Fig. 3 Powder diffraction pattern of $CoAl_2O_4$ (after 15 min at 600 °C); ICDD reference diffractogram, $CoAl_2O_4$ 38-814, added.

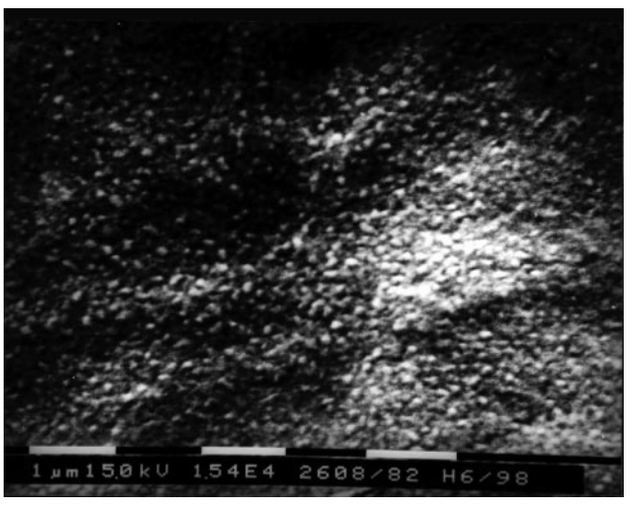

Fig. 4 SEM micrograph of $CoAl_2O_4$ powder (after 15 min at 600 °C).

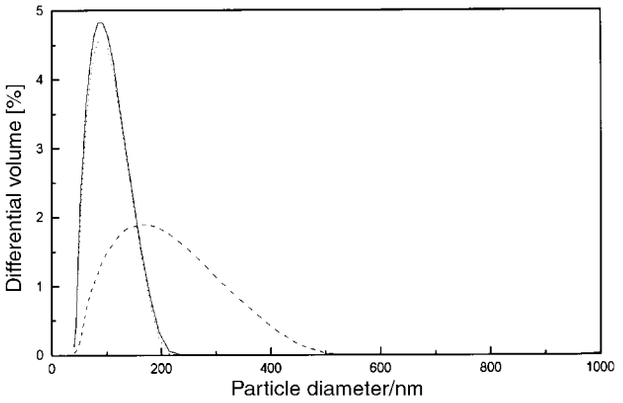

Fig. 5 Measurement of particle size of $CoAl_2O_4$ in diethylene glycol suspension (4.0 wt.%, solid) as well as 10 min (dotted) and 60 min (dashed) after mixing with water (DEG : H_2O = 1 : 10).

particles start to agglomerate. In agreement with this, the particle size increases and the size distribution becomes broader (Fig. 5).

Coating of substrates

A flow chart showing various possibilities to coat substrates with $CoAl_2O_4$ pigment particles is displayed in Fig. 6. Planar substrates can be covered with a homogeneous thin particle film applying common techniques like spin coating, dip coating or spraying. In all cases a dense thin layer can be realized. In order to arrive at the typical deep blue body colour of $CoAl_2O_4$ again 15 min heating to 600 °C is required. Although this heating leads to a slight agglomeration of particles, the size and spherical shape of particles remain unaffected. An AFM image of a typical layer is shown in Fig. 7. The layer was prepared by spin coating on a flat glass substrate (50 × 50 mm).

The special benefit of $CoAl_2O_4$ containing polyol suspensions is not the coverage of planar substrates as described in the case above, but the coating of non-planar surfaces. Such non-planar surfaces can be other particles which are significantly larger than the pigment particles, for instance a phosphor or ceramic powder material. Here, the blue emitting phosphor ZnS : Ag,Al is coated as a reference material. Such pigmented phosphors are widely applied for television tubes in order to improve the screen contrast.[5,19,20] Starting with a standard $CoAl_2O_4$ powder, the coating process is hindered by the fact that the powder consists of agglomerates. Such agglomerates do not adhere sufficiently on the surface of ZnS : Ag,Al and have to be cracked. Because standard $CoAl_2O_4$ is prepared at elevated temperatures (up to 1000 °C),[1,3,4] the agglomerates are quite hard so that very intense milling is required. Hard milling on the other hand often causes abrasion of the grinding medium which contaminates the samples. Furthermore, precautions against reagglomeration have to be taken. This can be achieved by addition of components leading to either electrostatic and/or steric stabilization.[21,22] On the other hand, again, this measure can cause impurities. Moreover, stabilizers can also hinder the adhesion of pigment particles to a substrate surface. Applying $CoAl_2O_4$ suspended in polyol medium, the difficulties described above can be circumvented easily. Deagglomeration is unnecessary and diethylene glycol as stabilizer can be removed simply by mixing the pigment suspension with a water suspension containing the phosphor material (Fig. 6). Because of its high miscibility, diethylene glycol covering the pigment surface is rapidly replaced by water.[23] Now, from the colloidal point of view the pigment particles are unstable and adhere to the surface of the phosphor particles. As a result very homogeneous particle layers are

Table 1 Influence of the reaction conditions on particle size of $CoAl_2O_4$

$Co(CH_3COO)_2 \cdot 4H_2O$/g	$Al(CH_3COO)_2OH$/g	H_2O/ml	DEG/ml	d_{50}/nm
0.50	0.72	1	50	56
2.00	2.86	1	50	96
2.00	2.86	3	50	143

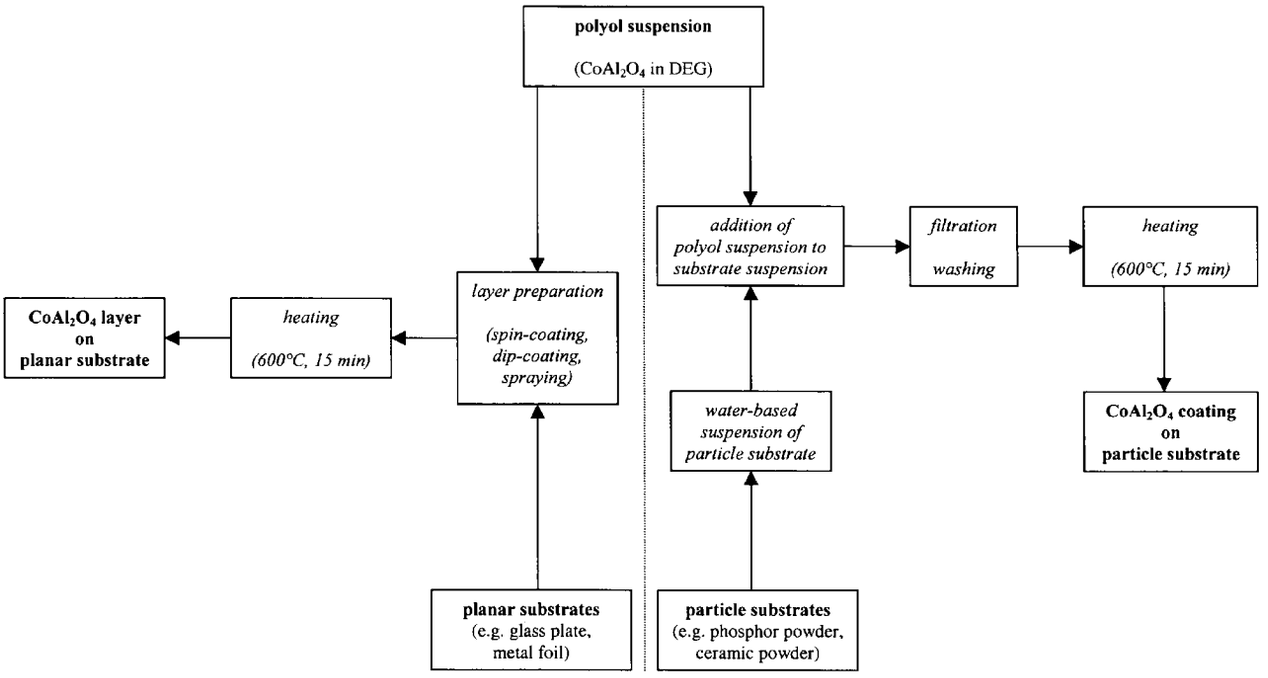

Fig. 6 $CoAl_2O_4$ coatings on different types of substrates.

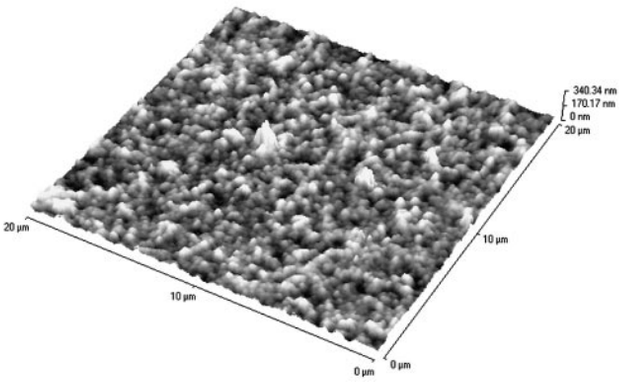

Fig. 7 AFM micrograph of a $CoAl_2O_4$ particle layer on a glass substrate.

prepared. Again, heating to 600 °C is required to obtain the characteristic body colour of the pigment. A SEM micrograph (Fig. 8) shows a ZnS : Ag,Al phosphor pigmented with $CoAl_2O_4$.

Conclusions

The present studies show that the polyol method is well suited for the preparation of sub-micrometer sized $CoAl_2O_4$ pigment particles. The particle size was determined for particles in diethylene glycol suspension as well as in the case of powder samples. Particles in suspension turned out to be well dispersed. By adjusting the concentration of components (metal precursors, water), it was possible to control the particle size between 50 and 200 nm. A special feature of the polyol method is the surface of the oxide particles being complexed by diethylene glycol and therefore stabilized against agglomeration, an effect that is even present for a limited period while mixing the polyol suspension with water. As a result, it is possible to cover planar (*e.g.* glass plates) as well as non-planar substrates (*e.g.* phosphor powder) homogeneously with thin pigment layers. Both can be quite interesting from the point of view of optical devices. To adjust the characteristic deep blue body colour of $CoAl_2O_4$ additional brief heating (15 min at 600 °C) is necessary. However, such a treatment does not lead to further growth of the particles.

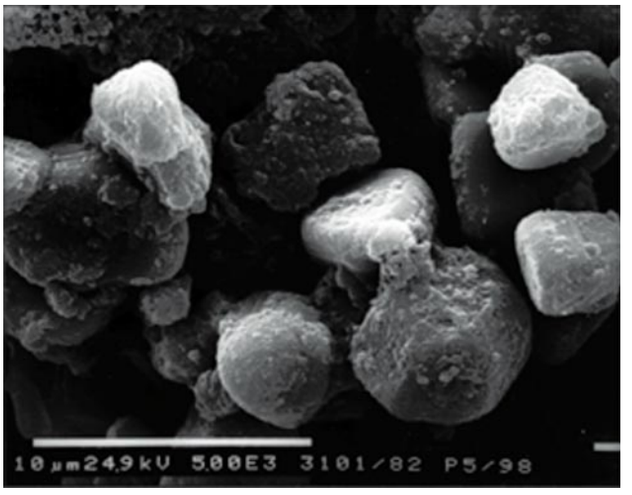

Fig. 8 SEM micrograph of a $CoAl_2O_4$ coating on a particle substrate (ZnS : Ag,Al).

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