

EUROPEAN COATINGS LITERATURE



Peter Wißling

Metallic Effect Pigments



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Fundamentals and Applications

Translated by John Haim and David Hyatt

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Foreword

Silver cars, shiny metallic mobile phones and televisions, gold labels on beer bottles, glittering lipsticks and sparkling fireworks – these are just a few examples of the everyday applications of metallic pigments which are becoming more widespread and more diverse every day.

Metallic pigments are distinguished by their optical effects. Objects coated with metallic effect pigments appear shiny and metallic. From different angles of observation, a pronounced light/dark or flip-flop effect accentuates the shape of the objects and draws attention to curved surfaces. More than that, metallic pigments based on their reflective properties also contribute to UV protection of coatings. A special group of metal pigments, is used for technical applications such as light-weight concrete, pyrotechnics and corrosion protection where, as a rule, the chemical and physical rather than the optical properties are of most importance.

This book gives a comprehensive overview of metallic effect pigments. Starting with the manufacturing process through technical properties to areas of application, the individual chapters offer condensed specialist knowledge based on many years of experience at the Eckart Company. The importance of metallic effect pigments, their wide range of applications and related specifications as well as their development potential are explained.

The contents are aimed at a broad audience. The fundamentals and applications of metallic effect pigments presented here will certainly help to provide basic knowledge to students and laymen with technical interest. In addition, they will also enable qualified personnel to deepen their knowledge on specific topics.

Dr Klaus Greiwe

Eckart GmbH & Co. KG
Velden/Germany, April 2006

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1 Coatings systems and their applications

1.1 Coatings systems

1.1.1 Solvent-based coatings

Current aspects in formulating metallic effect pigments in solvent-based coatings are discussed in Chapter 2 of Part II. Further important formulation criteria for are given here.

Slurry preparation with metallic pigments

Dispersion of pigments is particularly important and therefore discussed in detail here. Dispersion is the procedure where individual pigment particles are wetted with solvent so that they exist in mono-dispersed state (pigment slurry). The slurry is prepared using a suitable solvent in the ratio between 1:1 and 1:2 (pigment/solvent). Practical experience has shown that the 1:2 ratio is particularly of advantage when fine (average particle size less than 12 μm) or coated pigments with a large specific surface area are being used. Sometimes wetting additives must also be added during dispersion. It can also be helpful in some cases to allow a soaking time of the pigment/solvent blend of up to 10 hours – before active dispersion is started.

Polar solvents are favourable as they have a high wetting potential for metal flakes. They are only suitable for non-leafing pigments as wetting is not desired with leafing types. Leafing grades would lose their effect and thus should be made into a paste with non-polar solvents. The dissolver disc must not have any sharp corners or edges otherwise the ductile pigment can be easily damaged. A high speed mixer rather than dispersing equipment is preferable. The stirrer should be centrally positioned in the stirring container and the diameter of the disc should be at least half that of the container. Careful conversion to pastes is particularly important with gold bronze grades, which are often supplied as powders.

Pigment content

For coatings with leafing aluminium pigments, pigment content between 8% and 20% is used depending on the fineness. The pigment content for non-leafing aluminium pigments in full-shade metallics ranges from 4% for fine grades (d_{50} ca. 12 μm) to 15% for coarse grades (d_{50} ca. 40 μm). Exceptions to this are wood coatings and thermally stable coatings which can have up to 35% pigmentation. In polychromatic mixtures, significantly smaller amounts of metallic effect

pigments are used. Depending on the actual shade, the pigment content ranges from 0.5% for dark tones to 3% for bright colours. Compared with aluminium flakes, gold bronze pigments have a lower opacity and copper and brass pigments are generally used with twice the pigment loading of aluminium pigments of the same particle size.

Pigment orientation

For the application of metallic effect pigments in coatings it is important to achieve optimal orientation. Various factors have an influence on this. The most important factors include:

- dilution with solvent mixtures containing both rapid and slow evaporating solvents. (The mixing ratio depends on the ambient temperature and method of application – as an approximate figure a 1:1 mixture of xylene and butyl acetate can be recommended)
- avoidance of fillers
- use of orientation promoters such as waxes and/or cellulose acetate butyrate

Pigment orientation and solids

Good pigment orientation is always obtained in paints with low solids. This can lead to film shrinkage and thus optimal pigment orientation parallel to the substrate surface (Figure IV-1.1.1.1). From this point of view, traditional low-solid systems are preferred over high-solid systems. However, low solvent emissions

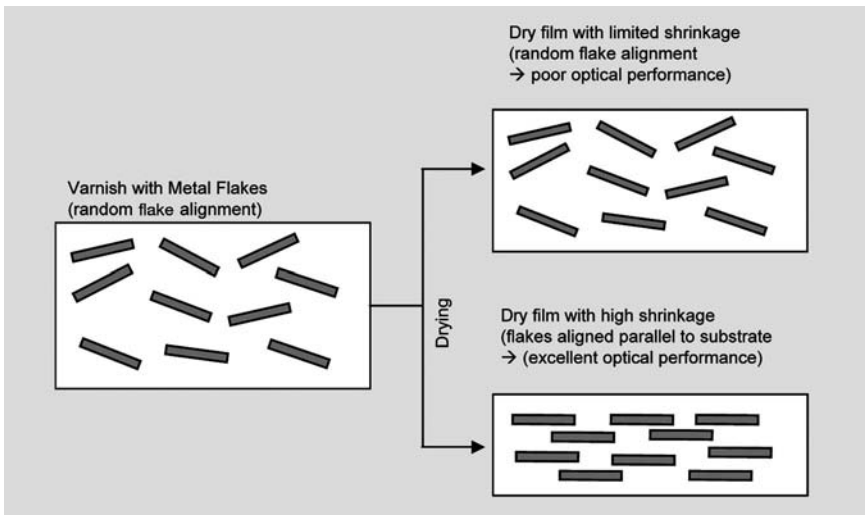


Figure IV-1.1.1.1: Orientation of metallic flakes in a coating during drying process

and the consequently lower environmental impact argue in favour of high-solid coatings.

Low-solid coatings typically have a pigment/binder ratio of about 1:5 (solid/solid) whereas for high-solid coatings the ratio is in the range 1:10 to 1:15.

Stability of metallic effect pigments

As already indicated, aluminium is an amphoteric metal which is attacked by both acids and alkalis. In many coatings, the thin oxide layer on the metal surface which is formed during grinding is sufficient to protect the aluminium pigment in the coating from the attack of aggressive agents in the environment. This is especially true for non-leaving pigments which are enclosed in a binder matrix. Basically, the purer an aluminium pigment, the better its chemical resistance and aluminium pigments are therefore normally offered with aluminium purity greater than 99.7% and in a highly pure, chemically resistant form. Acid resistant types are suitable for use in formulations with aggressive components, for example raw materials with a high acid number. Any contamination with water (for example from cleaning procedures or from impure solvents) leads to liberation of gas. In case of doubt, molecular sieves or other inhibitors should be used. The position of gold bronzes (that is copper and copper-zinc alloys) in the electrochemical series means that they are chemically even more susceptible. The mechanism of de-zincing has been described in Part II, Chapter 2.

It is therefore essential when using gold bronzes to use low-reactivity raw materials with low numbers of functional groups. It is also important to ensure water-free formulations. Green coloration and, in advanced stages, full gelling of the system are the results of inappropriate formulation.

If even greater pigment stability is required, coated types must be used. These are discussed in Part IV, Chapter 1.1.2.

Sedimentation

Metallic effect pigments settle when metallic coatings are stored. This is particularly true for specific heavy gold bronze pigments. Consequently, suitable thixotropic agents must be added to the coating especially if pigment concentrates are used which will be further processed in a mixer. Sedimentation cannot always be avoided but it should be possible to be re-stirred in a manner which avoids excessive shearing of the metallic effect pigment. Before further processing, the coating must be stirred and homogenised to avoid colour variations caused by uneven, inconsistent pigmentation.

Application of coatings containing metallic effect pigments

Coatings containing metallic effect pigments tend to flow down when applied to vertical surfaces. This sagging causes marked greying of the coating and often

occurs with airless spraying in cases where high film thicknesses are applied in a single pass (cf. p. 143 et seq.). It is therefore essential that rheology is adjusted accordingly.

Clouding

Orientation of the pigments especially on large surfaces must be homogeneous. Otherwise, differences in pigment orientation can lead to differences in brightness which are visible as cloudiness. This frequently occurs with water-based coatings and must be prevented by properly designed formulations. Cornflake aluminium pigments are little susceptible to clouding as the flakes become entangled with each other via their edges and corners and so are self-fixing. Because of their rounded particle morphology, silver dollars do not have this possibility and therefore have a greater tendency to clouding.


Higher pigmentation and coarser pigments further reduce the tendency to clouding. During application, the passes should overlap as far as possible; the coating thickness should be uniform and the spraying pressure low (guide value 4 bar), in order to produce as homogeneous an orientation of the metallic effect pigment as possible. Quicker film shrinkage – by using highly volatile solvent(s) – and a low solid content further contribute to a reduction of clouding.

Use of PVD pigments

The use of PVD pigments (cf. Part III, Chapter 1) requires use of special coatings. This is the only way of ensuring good orientation of the pigment particles and reproduction of the chrome effect. Coatings formulations used for normal aluminium or gold bronze flakes will result in an unsatisfying effect. When using PVD pigments it is important to have the lowest possible solids content, ideally between 5% and 8%. Pigmentation level of the PVD pigment lies between 3% and 6%. With higher amounts, the PVD flakes lie disordered over each other which make it difficult to produce a mirror-like effect. Orientation promoters such as cellulose acetate butyrate and/or waxes should be included in the formulation to optimise the plane parallel orientation of the PVD particles. Furthermore, with the low solid content, every imperfection in the substrate surface diminishes the chrome effect. The thin (2 to 4 μm) film layers cannot level out imperfections and the structure of the substrate is then noticeable. Therefore a high-gloss, good-flow primer should always be applied before the PVD coating. Dust particles on the substrate also reduce the effect.

Experience shows that coatings with low amounts of binder have only limited resistance to moisture, etc. Scratch resistance is limited even when two-component lacquers are used and therefore over-coating is advised if excellent scratch resistance is required. The solvent used in the clear coat can initiate dissolution

of the coating containing the PVD pigment, disorienting the PVD pigments and thus reducing the optical effect. For these reasons clear coats with non-polar solvents that are with low re-dissolving effect should be used. Overcoating with a water-based or powder coating, which inherently have only a low tendency to initiate dissolution, is ideal.

Guiding formulation Base coat for polyamide substrates air drying		ECKART 
		Rec. No. 50-09018 A
Aluminium paste ...	6.0	www.eckart.net
Butyl acetate 85	8.0	
predisperse		
Synthalat A 333, 40% supply form	41.3	www.synthopol.com
Aerosil 380	0.3	www.degussa.com
Resin: Haftharz LTW, 60% supply form	4.1	www.degussa.com
Xylene	6.7	
dissolve		
Cerafak 100, 10% supply form	7.9	www.byk-cera.nl
CAB 551-0.01, 20% in butyl acetate 98	17.1	www.eastman.com
Butyl acetate 85	8.6	
	100.0	
Viscosity: app. 21 sec, DIN cup 4 mm /20 °C		
Adjust to spraying viscosity of 16 sec with the following mixture:		
Butyl acetate 98	25.0	
Ethyl acetate	20.0	
Xylene	30.0	
Ethoxy propyl acetate	25.0	
	100.0	

1.1.2 **Water-based coatings**

Water-based coatings offer an environmentally-friendly alternative to solvent-based coatings. Because of their relatively low solid content there is a significant volume contraction of the pigmented binder layer when water evaporates on drying or stoving. This leads to plane-parallel orientation of the pigment particles resulting in a very good metallic effect with a quality comparable to that of conventional, solvent-based systems [1].

Aluminium pigments react with water liberating hydrogen according to the following equation:



When using aluminium pigments in water-based coatings it is therefore important to prevent this chemical reaction from occurring. Making the aluminium surface water repellent by use of lubricants such as oleic or stearic acids in the already described ball mill process is not sufficient. Because of the large specific surface area of aluminium pigments (1 to 10 m²/g, BET method [2, 3]) the reaction can be very vigorous. Even in case this reaction occurs slowly, there is loss of metallic gloss and storage stability is affected (agglomeration). To prevent the undesirable gas formation, aluminium pigments in water-based coatings need efficient corrosion protection not only in the liquid paint but also for the complete lifetime of a coating [4].

In practice there are three ways of achieving corrosion protection. One possibility is to use corrosion inhibitors with high affinity for the aluminium surface and thus, within limits, form the protective layer. Typically organo-phosphorous compounds are in use (see below). Secondly, chemical reactions can be used to produce so-called conversion layers. These result out of a reaction between the aluminium surface and the corrosion inhibitor. From a chemical point of view, formation of conversion layers marks the borderline between inhibition and encapsulation. Such layers are certainly much thinner than true encapsulation but have a comparable barrier effect. The third stabilising principle is encapsulation of the aluminium pigment in a chemically inert and essentially transparent layer. Such homogeneous protective layers are usually produced by sol/gel processes (see below).

Of importance in coatings practice are the applicational properties of the effect pigment and these will therefore be considered in detail. In a second section the properties decisive for satisfactory application in water-based coatings will be described using as an example special, newly-developed, SiO₂-coated aluminium pigments. The properties are:

- wetting in the binder matrix
- visual appearance
- gassing stability
- resistance to condensation
- resistance to shear
- weather resistance
- storage stability

The examples described in the Application properties Section can be transferred to all aluminium pigments for water-based coatings. Formulation advice makes up the final part of this chapter.

Additive process and organo-phosphorous stabilisation

It is well known that compounds of phosphor have a great affinity to aluminium. Esters of phosphoric acid and substituted phosphoric acid derivatives have proved particularly suitable for inhibiting corrosion of aluminium [5 to 7]. If necessary the pH of these chemicals can be adjusted by addition of suitable neutralising agents. In practice, these organo-phosphorous compounds are blended or “dried onto” the aluminium pigment by a mixing process or a combined mixing and drying process. By adsorption onto the pigment surface they form a relatively thick protective layer. Compared to untreated aluminium pigments this results in a significant and permanent reduction of hydrogen formation in mild water-based paints. As additives are applied onto the pigment surface, this type of stabilisation is known as the “Additive process”.

Organo-phosphorous protective layers make it possible to supply aluminium pigments as water-based pastes which can be formulated without any organic solvent in delivery form. This is particularly important when there is incompatibility of the solvent with the binder or for some reason organic solvents are not tolerable. Examples of completely solvent-free water-based pastes are aluminium pigments of the STAPA® Hydroxal W range (Eckart). Aluminium pigments of the STAPA® Hydrolac W, Hydrolac BG or PM ranges (Eckart) contain solvent/water mixtures and are manufactured without intermediate drying-step.

As the adsorption layers are a result of an adsorption/desorption equilibrium, adsorption layers on aluminium pigment surfaces can never completely prevent liberation of hydrogen. Moreover organo-phosphorous layers lose their inhibiting effect at high pH. This means that encapsulated aluminium pigments are necessary for particularly aggressive water-based industrial or automotive finishes. However, organo-phosphorous inhibition of aluminium pigments offers sufficient stabilisation for many water-based applications and is recommended for water-based coatings with pH between 7 and 8, such as industrial coatings or mild automotive finishes and water-based printing inks. The suitability of pigments stabi-

lised in this manner should always be confirmed by a gassing test (cf. Part II, Chapter. 3: Accelerated gassing stability test).

A further possibility for stabilising aluminium pigments is the addition of anti-corrosive pigments to coatings systems or pigment pastes. These are mainly mixtures of phosphate silicates which are soluble only with difficulty. The protective effect has two origins (i) formation of phosphate at the reactive centres of the aluminium particles and consequently the barrier effect of a thin protective layer, and (ii) the electrochemical effect. Aluminium pigments stabilised in this way are commercially available as pigment preparations in the form of pastes, dispersions and granules

Conversion layers by chromating

A well-known technique for passivating aluminium pigments is chromating. In this aluminium pigments are treated with a solution of chromic acid [8]. This rapidly oxidises the reactive aluminium surface and forms a thick, passivating conversion layer. This is mainly a mixed oxide consisting of aluminium oxide, chromium oxide and the corresponding hydroxides. A similar method of passivation is based on using molybdic acid [9].

Chromated aluminium pigments have excellent gassing stability in water-based coatings and are even stable in very aggressive water-based formulations. If necessary they can tolerate pH values up to about 9.5. Additionally this type of treated aluminium pigment has very good resistance in condensation tests (DIN EN ISO 6270-2). The processing properties of chromated aluminium pigment pastes with common co-solvents and coatings additives are very good. The low viscosity of such semi-finished products (pigment slurries) provides easy incorporation into water-based binders.

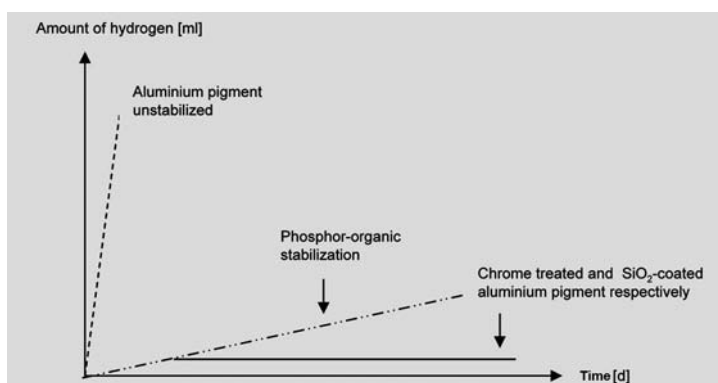


Figure IV-1.1.2.1: Gas evolution of various stabilized aluminium pigments