Corrosion Inhibited Metal Pigments

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Summary: Flake-shaped particles of aluminium are well known in the coatings and printing ink industry as "silver bronze pigments". For their use in waterborne coatings or outdoor applications, an effective corrosion protection of the highly reactive aluminium surfaces is required.
The traditional stabilization techniques for aluminium pigments are based on the addition of corrosion inhibitors or on chromate passivation. This publication presents new developments in the encapsulation of metallic pigments that are based on modern sol-gel techniques. All products are heavy metal-free and provide excellent applicational properties.

Keywords: effect pigments, inhibition, encapsulation, sol-gel, surface modification

Introduction

Flake-shaped particles of aluminium and copper-zinc alloys are an important group of lustre pigments. They are well-known in the coatings and printing ink industry as "silver bronze pigments" and "gold bronze pigments". In their applications these pigments act as small reflectors of light with a spectral response very similar to that of metallic silver or metallic gold. This paper deals with aluminium pigments that imitate the optical appearance of metallic silver. The major problem in the practical use of these lamellar aluminium pigments is their exothermic reaction with water. Whenever this reaction takes place, the metallic gloss decreases significantly and hydrogen gas is evolved:

$$2\,Al + 6H_20 \rightarrow 2\,Al(OH)_3 + 3H_2\uparrow$$

Therefore the highly reactive aluminium surfaces need an efficient corrosion protection whenever aluminium pigments are used in water based coatings or in outdoor applications. In waterborne automotive OEM coatings, the need of corrosion protection of the aluminium pigments is obvious.

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Other compliant coatings like powder or coil coatings have no water in their formulations. For economical reasons, outdoor applications made with these coatings are usually realised as one-coat paints. This means that the pigments in the single coating layer are exposed to all changes of the weather conditions. Since the colour of a coating shall not change for the whole lifetime (as a rule several years), the need of highly stable aluminium pigments becomes evident.

Methods of corrosion inhibition

There have been developed two basic concepts for the stabilization of aluminium pigments.[1, 2] One is the inhibition of the gassing reaction by the addition of suitable corrosion inhibitors (1). These inhibitors or their reaction products are able to adsorb on the active sides of the aluminium surface. Chromate treating leads to the formation of a conversion layer around the aluminium flakes.[3-5]

The second method for stabilization (2) is the full encapsulation of the aluminium pigments with a chemically inert, transparent layer. This protective layer is usually formed by sol/gel processes and can be either of organic or inorganic nature.[1, 6]

1. Inhibition

1.1. Phosphor-organic chemicals

Typical examples of suitable corrosion inhibitors for aluminium flakes are the organic derivatives of phosphoric and phosphoric acid. If necessary, the pH of these chemicals can be adjusted by the addition of suitable amines.

When the inhibitive treatment is completed, the gassing reaction of the aluminium pigments decreases significantly. Nevertheless the passivating layer cannot provide a perfect corrosion protection of the aluminium, but is permeable to some extent. This means that inhibited aluminium pigments show a delayed gassing reaction. More information about inhibited aluminium pigments is described in the literature and references therein.[1, 2, 6]

The phosphor-organic passivation of aluminium pigments provides an acceptable stability of the aluminium flakes in a lot of mild water based coatings. It is recommended for waterborne paint systems in which the pH does not exceed 8.0-8.5. The exact pH limit is depending on the binder/resin type and the choice of neutraliser. At higher pH-values (pH>8.0) and for most outdoor applications, more efficient corrosion protection is required.

1.2. Chromate treatment

A well-known technical process for the passivation of aluminium flakes is the chromate treatment. In this procedure the aluminium pigments are treated with a solution of chromic acid. The aluminium surface is oxidised rapidly and a dense, passivating conversion layer is formed all around the aluminium flakes. This layer is a complex combination of aluminium oxide, chromium oxides and water.[3-5]

Chromate-passivated aluminium pigments have an excellent gassing stability even in aggressive water based coating systems. If necessary, they are able to tolerate pH values up to 9.5. Chromate-treated aluminium pigments have a high performance in the humidity test. Furthermore they show low viscosities in aluminium pigment slurries, which are always the first step in the industrial production of waterborne metallic paints.

The following picture illustrates the gassing characteristics of untreated, phosphated and chromated aluminium pigments. It is evident that the chromated metallic pigments provide the best gassing performance and do not show continuous hydrogen development, even after months of storage in water based paint systems.

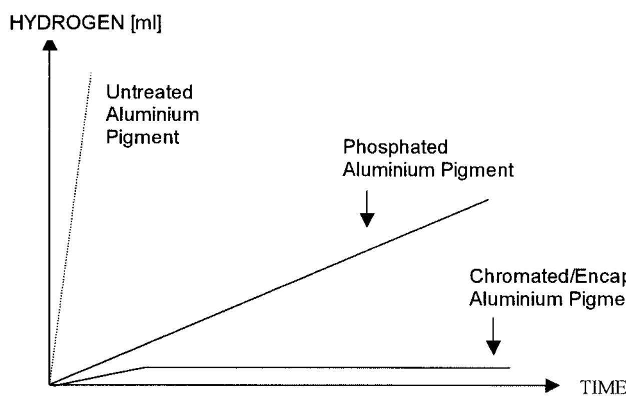

Figure 1.Gassing stability of stabilized aluminium pigments

Sol-gel encapsulated aluminium pigments provide a performance comparable to the chromated flakes. In the next chapter, this latest development will be discussed in detail.

2. Encapsulation

Inorganic coatings of the aluminium flakes with iron oxide, titanium dioxide or aluminium oxide provide unique coloured effect pigments.[1, 6-8] The oxide layers of these pigments are rather porous, for this reason often an additional stabilization is required.

The benchmark for stable aluminium pigments suitable for broad range of compliant coatings are the chromate passivated pigments.[5] Until now alternative, heavy metal-free stabilization methods like silica or polymer encapsulation have been applied successfully in some fields of application (e.g. powder coatings). But all these environmentally friendly stabilizations had considerable limitations in water based and outdoor applications.

This paper presents a new kind of sol-gel process that provides metallic pigments with a chemically stable, fully transparent silica encapsulation. The excellent application properties of these silica-encapsulated aluminium pigments in waterborne coatings will be described in detail.

Furthermore this paper will present a new type of aluminium pigment treated with a corrosion-resistant polymer encapsulation. This innovative technology has remarkable advantages in powder coatings for outdoor applications.

2.1. Silica Encapsulation

Synthesis

The process of silica encapsulation of aluminium pigments starts with the dispersion of the aluminium pigments of choice in an alcoholic solvent.[6] Any grade of untreated aluminium pigments can be selected as a starting material, preferably in paste form.

In the next step, tetraethoxy silane, water and a basic catalyst are added to the stirred suspension of aluminium pigments. The hydrolysis of the tetraalkoxy silane leads to the formation of silanole structures like $Si(OR)_3OH$, $Si(OR)_2(OH)_2$, $SiOR(OH)_3$ and finally $Si(OH)_4$. Under basic reaction conditions, all these silanole intermediates are able to undergo polycondensation reactions that finally lead to the formation of an insoluble SiO_2 network:

$$Si(OR)_4 + 4\ H_2O \xrightarrow{\text{Base}} Si(OH)_4 + 4\ ROH \quad \text{(Hydrolysis)}$$

$$Si(OH)_4 \xrightarrow{\text{Base}} SiO_2 + 2\ H_2O \quad \text{(Condensation)}$$

Many technical properties of effect pigments are related to their surface chemistry. It is a major advantage of the presented sol/gel chemistry to allow a controlled modification of the precipitated silica surfaces. The surface of the deposited layer can be modified by the addition of suitable bifunctional reagents like organosilanes.[9]

Controlled wetting properties

When the first reactive group of the bi-functional surface modifier has reacted with the silica surface of the pigment, the second functionality is still able to interact with the coating. The chemical nature of the second functional group directly affects the wetting properties and the orientation of the aluminium pigments in waterborne coatings. Under the curing conditions, the second functional group is able to react with the resin or other components contained in the coating. Since real chemical bonds can be created between the pigments and the coating, this process significantly improves the humidity resistance and the adhesion of the whole coating.[6,9] Last but not least the volume shrinkage of the coating during the curing process improves the planar orientation of the aluminium flakes.

If the surface treatment of the pigments is achieved with unpolar compounds like alkyl groups, a relatively poor wetting of the pigments in water based formulations results (Fig. 2). The visible effect is a "semi-leafing" with a parallel orientation of the aluminium flakes rather close to coating surface. This means an excellent brilliance of the application, but on the other hand the adhesion might be quite poor.

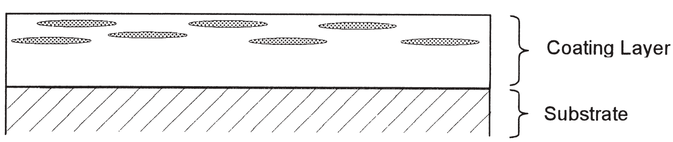

Figure 2. Poor wetting: "Semi-leafing"

If the surface modification is more polar (e.g. acrylic, amino, epoxy, ureido groups), the pigment wetting in waterborne coatings is improved. The orientation of the flakes in coating is still parallel but much more homogeneous in the whole layer (Fig. 3). Usually these conditions are the best compromise between a good pigment orientation and good adhesion properties.

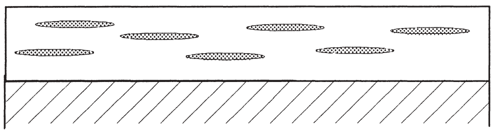

Figure 3. Wetting is OK: Flakes in parallel orientation all over the coating

When the polarity of the pigment surface is even higher, like with pure silica, the parallel orientation of the flakes in the coating starts becoming distorted (Fig. 4). There is a certain tendency of the flakes for precipitation and agglomeration. Consequently a very good pigment wetting in water often leads to a reduced brilliance and less hiding.

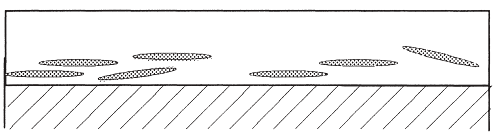

Figure 4. Very good wetting: Flakes tend to precipitate, orientation not strictly parallel

The wetting properties strongly affect the rheology of the pigment, too. A freshly precipitated silica surface contains many OH-groups leading to unacceptable high viscosity levels in most waterborne systems. The controlled end-capping of these OH-groups allows to adjust the rheological properties of the encapsulated aluminium pigments to the needs of a paint manufacturer.

Brilliant optics

When a coating with aluminium pigments is viewed face-on, it appears bright. If the application is turned sideways, the colour appears darker or in a different colour shade. This angledependant reflection of light is named "flop" or "two-tone effect". It is a characteristic criteria for all coatings with metallic effect pigments.

The metallic effect depends on the particle size of the flakes, the flake shape and on the wetting of the aluminium pigments in the coating system of choice. By means of the described sol-gel chemistry, pigments with tailor-made wetting properties can be manufactured.

Any passivation or coating of aluminium pigments has an effect on the optical appearance of the pigments, since the reflected light needs to pass the encapsulating layer. This means that the same basic aluminium pigment will show different optical appearances with different encapsulations. Table 1 shows the lightness differential ΔL of some sol-gel encapsulated aluminium pigments that are offered under the name Hydrolan. The ΔL values are calculated from the difference [L (silica passivation) – L (chromate passivation)] for each grade.

Table 1. ΔL values of silica-encapsulated aluminium pigments

Pigment	Particle Size (Cilas)			Lightness Differential ΔL		
	D10	D50	D90	25°	45°	75°
Hydrolan 2192	8	15	26	2,39	0,16	-0,95
Hydrolan 2156	10	17	28	2,38	-1,21	-1,56
Hydrolan 501	8	21	41	4,49	1,48	-1,58
Hydrolan 167	11	25	45	3,62	-1,29	-3,6
Hydrolan 214	17	34	57	3,54	-1	-2,23

All silica-encapsulated grades appear brighter viewed on face (25°) and darker viewed from the edges (75°). This means that the silica encapsulation yields aluminium pigments that do not only meet the optics of chromate passivated pigments, but appear slightly brighter and more "metallic".

Gassing stability

The test conditions for the gassing stability of aluminium pigments in water based coatings are described in detail in the literature.[6] Silica encapsulated aluminium pigments have an excellent gassing stability under these test conditions. Even in very aggressive paint formulations and at high pH values (pH>9) these pigments show no or a very small evolution of hydrogen gas. Their gassing stability is similar to the benchmark, the well-known heavy-metal passivated grades (chromate-passivation).

Controlled humidity resistance

All adhesion tests were performed with a commercial OEM coating system consisting of five layers: Phosphate primer (1), Cataphorethic Dip-Coat (2), Filler (3), Metallic Basecoat (4) and Clear Coat (5). The interaction of all these layers is responsible for the performance of the coating.

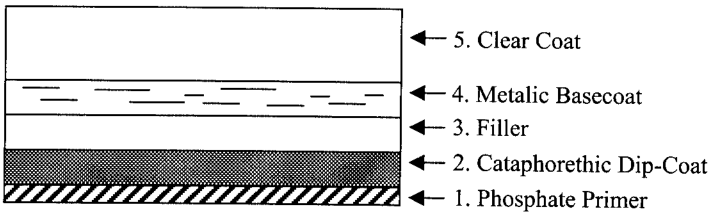

Figure 5. OEM coating

The standard test method for the humidity resistance of aluminium pigments is the condensation water test according to DIN 50017-KK (German standard). An OEM panel is exposed to high humidity conditions (100% with condensation) at 40°C for 240h.

After 10 days of humidity exposure, the adhesion of the coating is checked by the crosshatch test according to DIN ISO 2409. Table 2 clearly points out that the wetting properties of the silica encapsulated aluminium pigments can be controlled by the use of suitable surface modifications.

If silica encapsulated aluminium pigments without any surface modification are used, the humidity resistance of the coating is rather poor (GTC = 4-5). Water is able to penetrate layers with silica encapsulated pigments rather easily. Therefore blisters occur in the crosscut test.

When the silica surface is modified with groups of poor wetting properties (alkyl groups), the humidity resistance is improved, but still insufficient. The best results are obtained with an intermediate wet ability that can be obtained by the modification with amino or acrylic groups.

For automotive applications, the adhesion of a coating is also tested with an impact test with stone-chips or steel balls. An intermediate pigment wetting realised with amino or acrylic surface modifications showed the best performance in this test, too.

Table 2. Humidity resistance of modified pigments with sol-gel Encapsulation

Functionality	Cross Cut		
	1 min	1 h	24 h
Pure SiO_2	Gtc 5	Gtc 4	Gtc 4
Alkyl	Gtc 2	Gtc 2	Gtcl
Amino	Gtc 0	Gtc 0	Gtc 0
Acrylic	Gtc 0	Gtc 0	Gtc 0

Circulation stability

The circulation lines and pumps of the automotive industry can expose aluminium pigments to very high shear stress. This mechanical stress may result in deformations of the aluminium flakes leading to a significant colour shift of the coating. A suitable simulation of this effect can be done in a high-speed dissolver (20.000 rpm for 15 min) or a special kind of mixer called “Warring-Blendor”. The silica encapsulation of Hydrolan provides an excellent mechanical stabilisation of the ductile aluminium core. This criteria is called “degrading resistance” and is superior to untreated aluminium pigments and many other passivated grades.[6]

Resistance to weathering

The weathering resistance of the silica-encapsulated pigments was tested under Florida conditions. In this harsh test OEM panels are exposed for two years to the weather conditions of south Florida (panel orientation 5° south). The new silica encapsulated pigments showed an excellent weather fastness under these conditions ($\Delta E<1$ after two years).

2.2. Polymer Encapsulation

The encapsulation of aluminium pigments with an organic layer is described in the literature and references therein.[1, 2, 10] Recently a new process for polymer encapsulation has been developed. This technology is based on a modified polymerization process of acrylic monomers in the presence of aluminium flakes. In this paper, the encapsulated aluminium flakes manufactured by this process are called "New PCA". This improved polymerisation process yields aluminium pigments with an excellent performance in powder coatings for outdoor applications. All subsequent tests were carried out in a commercial polyester system with a pigmentation level of 4%.

Condensation test

The test conditions for the humidity test were in correspondence with DIN 50017-KK.

Table 3. Humidity resistance of powder coatings

Pigment	Encapsulation	First visible changes after
PCR 8154	Silica old	24h
Sillux 8154	Silica new (Sol gel)	168h
PCA 8154	Polyacrylic old	168h
New PCA 8154	Polyacrylic new	>1000h

The new type of polyacrylic encapsulation showed a superior humidity resistance. A humidity resistance of more than 1000h is considered to be sufficient for outdoor applications.

Kesternich test

The weathering conditions in an aggressive industrial atmosphere are often simulated by the Kesternich test (DIN EN ISO 6988). In this test, the powder-coated panel is exposed to humidity and SO_2 in several cycles.

Table 4. Kesternich test of powder coatings

Pigment	Particle Size D50	Encapsulation	First visible changes after
PCR 501	20μm	Silica old	7 cycles
PCA 501	21μm	Polyacrylic old	7 cycles
New PCA 501 ; V398	21μm	Polyacrylic new	11 cycles
New PCA 501, V535	21μm	Polyacrylic new	10 cycles
PCR 212	47μm	Silica old	12 cycles
PCA 212	53μm	Polyacrylic old	11 cycles
New PCA 212	54μm	Polyacrylic new	12 cycles

The improved polymer encapsulation has clear advantages for aluminium flakes of finer particle sizes. For coarse aluminium flakes, the chemical nature of the encapsulation seems to be of minor or no significance. Obviously the surface area of the aluminium pigments is more important for the results of the Kesternich test. Fine pigment particles have a much higher surface area, for instance the BET value of the new PCA 501 is around $6m^2/g$, whereas the values of the new PCA 212 are around 1 m^2/g.

Chemical resistance

For testing the chemical resistance of the pigments the powder coated panels are treated with drops of 1 M HCl, 10% HCl and 1 M NaOH. After 3 hours the effect of the corrosive agents on the pigment is visually examined.

The best samples of the New PCA showed no difference between the treated and untreated areas. Due to the short time of the treatment with chemicals, there occurs no significant deterioration of the base coat. Therefore this test is suitable for screening the chemical stability of corrosion inhibited aluminium pigments in powder coatings.

Table 5. Treatment of powder coatings with chemicals

Chemical Test with	**10 % HCl**	**1 M HCl**	**1 M NaOH**
Pigment	First changes after:		
PCA	30 min	1 h	5 min
PCR	30 min	1,5 h	5 min
New PCA	3 h	no change	no change

The chemical nature of the encapsulation proved to be the decisive criteria in this test, whereas the particle size distribution of the aluminium flakes was of minor importance.

It is obvious that the chemical resistance of the new PCA is far ahead of the resistance of standard silica (PCR)- or acryl ate (PCA)-encapsulated aluminium pigments. This opens up a wide scope of new applications.

Conclusions

The presented procedure of silica encapsulation provides a new class of aluminium pigments for waterborne coatings. These pigments have an excellent gassing stability, a very good mechanical stability and a high brilliance compared to the chromate-passivated types (flop). A patented surface-treatment allows to manufacture encapsulated aluminium pigments that are suitable for a broad scope of coating systems.

Furthermore there has been made remarkable progress in the polymer encapsulation of aluminium flakes. This new kind of aluminium pigments was especially developed for powder coatings that are used in corrosive media or in outdoor applications.

The examples in the article demonstrate that there are practically no limits for the use of aluminium pigments in coatings. Modern inhibition methods can provide a suitable stabilization of the aluminium flakes in almost any application.

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