State-of-the-art technology in aluminium pigments for aqueous paints

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Introduction

Nowadays, it is not only a competitive advantage for coatings companies to offer a range of aqueous coatings. legislative pressures frequently make it essential to be able to offer aqueous products.

This situation is no longer the case only for the automotive industry, where such pressure resulted in large investments of money, man power and technological skills, to change from solvent-borne to water-borne technology. As Company figures show, the result is that the coatings industry has changed such that in Germany 50%, in Europe 30% and in America approximately 20% of paint production is now environmental friendly OEM and refinish lacquers. The consequent impetus created in the automotive fields, is now being transferred to the coatings industry in general. The different performance requirements for industrial applications, however, often demand different or modified materials to those developed for the automotive industry.

For the raw material suppliers, this means that a variety of products have to be offered, to meet the different technical requirements of each of these markets.

A most important demand for an aluminum flake is, (and historically has always been), for a product with a high resistance to 'gassing' in water-based paints.

This following equation shows the reaction that takes place during 'gassing'.

$$2\ Al + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2$$

Unprotected aluminum pigments can generate a large volume of hydrogen. For aluminum pigments to succeed as well in water-borne systems as they did in solvent-based coatings, the gassing problem had to be overcome first of all. According to Company figures, automotive colour fashion now dictates that in Europe 62% and in North America 87%, of automotive paints are metallic. (These figures include metallic/pearl pigment combinations).

Product types and performance

Additive technologies

The most generally used, and also historically the oldest method of preventing aluminum flakes from gassing, has been a treatment with phosphor-organic chemicals. These are called additive technologies and two types are available, blended additivea and precipitated additive.b

Blended additivea has chemical additives blended with aluminum flakes, which still contain some mineral spirit from earlier processing.

Precipitated additive[b] has the same chemical additives, precipitated onto the aluminum flakes. The precipitation occurs during the process when the mineral spirit in the blended additive[a] is removed.

These products are well established and have been available for many years. Both are offered as 65% aluminium flake pastes in a choice of 'solvents'. The normal choices available are water, butyl glycol or methoxypropanol and for simplicity the letters W, BG or PM appear in their grade names. The blended additive,a as already stated, also contains some mineral spirit.

The 'solvents' used and some benefits will be referred to later on.

The earlier mentioned phosphor-organic, stabilising additives used for blended additivea and precipitated additive,b protect the metal flakes against water attack. As a side effect some paint characteristics can be affected adversely, (eg drying time, intercoat adhesion, humidity resistance). To offset these effects, the additives can be applied at reduced levels from that used normally for the best protection.

Blended additive[a] or precipitated additive,[b] W, BG or PM, (normal level of additives)

Blended additive[a] or precipitated additive,[b] WH, BGH or PMH, (50% normal level of additives)

Blended additive[a] or precipitated additive,[b] WHH, BGHH or PMHH, (25% normal level of additives)

The precipitated additive[b] W products that contain only water, can be transformed into a most convenient product form, liquid Pre-dispersed Concentrates.[c]

The pre-dispersed concentrates,[c] contain 32-50% aluminum or bronze pigment. They are pourable, VOC-free and can be stirred directly into the finished paint.

Encapsulated technologies

The next step in the development of hydro-aluminum flakes, were pigments that were fully encapsulated to give a greatly increased protection. There were two types. The first of these was chromium encapsulated,[d] encapsulated with insoluble chromium III. Second was acrylic encapsulated,[e] encapsulated with a thermosetting acrylic polymer.

The chromium encapsulated[d] and acrylic encapsulated[e] have outstandingly improved gassing stability. Both types have been used for many years in the more demanding coating applications, such as automotive.

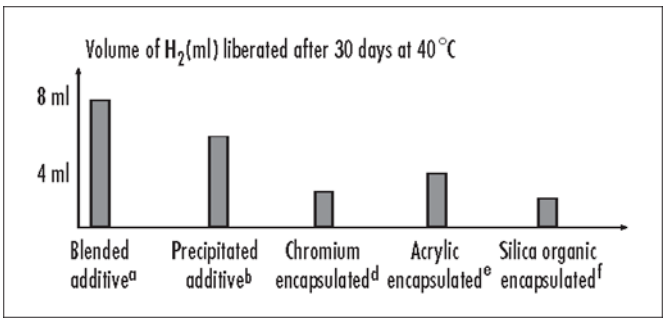
In the most recent development, silica organic encapsulated,[f] encapsulation technology has been carried a step further. Aluminium flakes already encapsulated with silica are then given a further organic coating.

The acrylic encapsulatede and silica organic encapsulatedf do not contain heavy metal and, therefore, are environmentally friendly.

Each new development was made to improve gassing stability, or environmental friendliness, as stated earlier.

The results can be put into perspective by determining the amount of gas generated by these differently stabilised aluminum pigments in the same paint formulation. To illustrate this, a worst case scenario was chosen, an automotive paint formulation which would be described as 'aggressive', see Figure 1.

Figure 1: Gassing of stabilised aluminiums in automotive paint (worst case scenario)



It has to be pointed out that gassing stability depends strongly on the paint and can vary from one system to another. Frequently the author has observed that minor changes in the paint formulation can mean the difference between gassing and no gassing.

Six different technologies have been described that protect flake pigments from gassing in water-based formulations and some of their properties have been indicated. These can be applied to many of the flake pigment grades available in the Company's wide solvent-based range. Although not commercially practical, it is possible technically for certain flake pigment grades to be available in all six. As a guide for selection and availability, Table 1 indicates for these six 'water-based' technologies, appropriate application areas and generic flake grades available.

Formulation recommendations

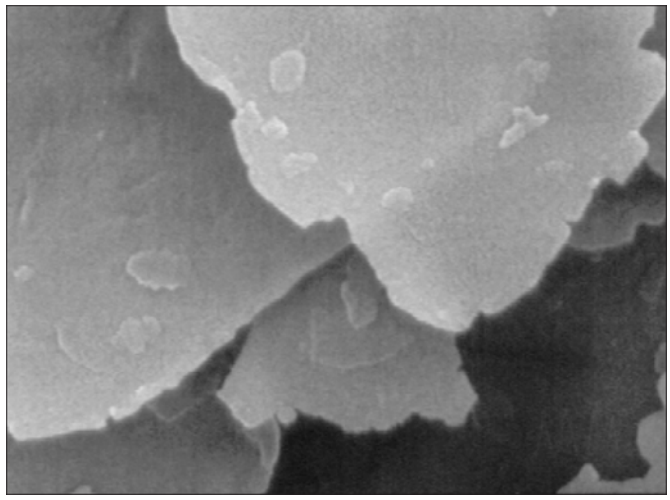
In the complexity of a water-based paint system containing aluminum pigments, each component can contribute to a tendency to gas or not to gas. To optimise optical, technological and gassing properties, all raw materials, resins, pigments and additives need to be considered, also manufacturing techniques. The following points are the most important aspects:

Incorporation of metal flake pigments

Inappropriate incorporation of metal flake pigments into binders, (using too high shear force), can have an adverse effect on the optical properties.

High shear will damage the aluminum flake in two ways. Firstly, it can bend the flake particle, thereby reducing its brilliance and secondly, it can strip the protective coating from its surface, which can result in gassing. The Photograhs 1, 2 and 3 illustrate these effects.

Photograph 1: The aluminum flake was incorporated gently and no damage can be seen



There are several things to consider for a proper incorporation of metal flake pigments.

Preparation of aluminium flake pre-dispersion

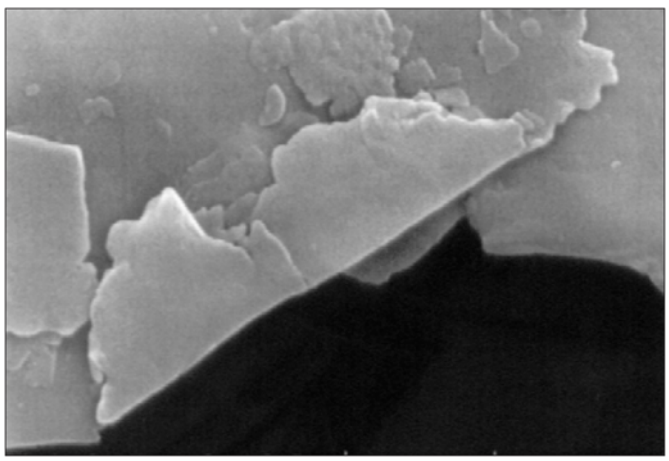
All aluminum pastes need to be pre-dispersed in an appropriate solvent to produce a pigment slurry. The slurry should be incorporated into the paint system only after all other components that need higher shear. The slurry is best incorporated using the lowest rate of shear necessary, and as near as possible to the end of the manufacturing process.

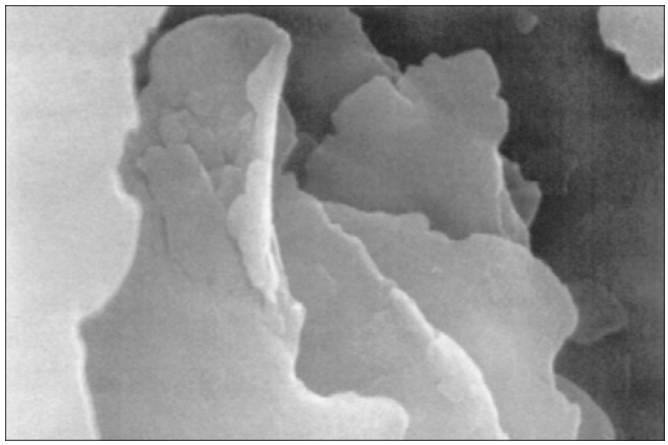
The author recommends preparing a slurry of 1:1 metal flake pigment paste: solvent. The solvents which are most favoured for water-based systems are butyl glycol, methoxypropyl acetate etc. Since most water-based formulations contain some organic solvent, the author recommends using these solvents for the pigment slurry. An advantage when using solvents is that the use of wetting agents is frequently unnecessary.

Table 1: Guide for selection and availability of hydro flake pigments

	Main use	As leafing type	As non leafing type	With aluminum	With gold bronze
Blended additive[a]	general industry/maintenance, decorative, hammer finish paints, roof coating	✗	✗	✗	
Precipitated additive[b]	OEM finishes, general industry/maintenance, decorative, ink industry, (Precipitated Additive[b] WH is typically used in inks)	✗	✗	✗	
Pre-dispersed concentrates[c]	general industry/maintenance, decorative	✗	✗	✗	✗
Chromium encapsulated[d]	automotive finishes (OEM + repair), aerosol sprays		✗	✗	
Acrylic encapsulated[e]	OEM paints, general industry/maintenance with excellent water/chemical stability		✗	✗	
Silica organic encapsulated[f]	automotive finishes (OEM + repair)		✗	✗	
Semi-oxidised aluminium flakes[g]	automotive finishes		✗	✗	

Photographs 2 and 3: The flakes were over-processed at too high shear forces, resulting in bent edges, or perforated flakes, leaving the aluminum flake unprotected from gassing





Usage of appropriate solvent grades of the chosen aluminium flake technology

It is inherent in the philosophy of modern water-based coatings that the lowest VOC levels should be aimed for. Therefore, formulators may wish to work with additive technology[a,b] W grades, which contain a water/mineral spirit mixture or water only.

Precipated additivesb W is an important, truly solvent free, water-based aluminium flake technology. Water, however, with its high surface tension, is not an ideal medium for wetting the aluminum pigments. In some cases, it may become difficult to convert the water-containing additive technologya,b W grades, into a pigment slurry.

Therefore, Eckart offer a choice of aluminum pastes that already contain selected solvents for improved dispersibility: These are the blended additivea and precipitated additive,b BG and PM grades. The encapsulated technologies can also be offered in a choice of solvents: chromium encapsulatedd PM, (methoxypropanol) and silica organic encapsulatedf IL, (iso propanol) are good examples

Wetting agents

In many cases it is advisable to add wetting agents to the metal-flake slurry in order to assist the wetting-out of the flakes. This certainly is recommended when using additive technologya,b W grades, when the use of wetting agents1-7 has also avoided harsh dispersion and subsequent reduced gassing stability.

Pre-dispersed concentrates

To avoid preparing a slurry, Eckart offers metal flake pigments as pre-dispersed concentrates.c These liquid concentrates are pourable and very easy to use. They can be added to the paint as a last step of the production process. Frequently they result in a better dispersion than when starting from slurry, which can result in use of lower levels of metal pigment.

Binder systems

If the paint is formulated with emulsions, some perform very well in terms of gassing stability, while others are more aggressive and do not.

Some acrylic emulsions8,9 have been shown to be quite gentle to the aluminium flake pigments and therefore cause less gassing than other binders.

The same is true of some resin solutions, eg certain water-dilutable alkyd resins10 were found to be ideal binders for metal pigments.

pH value and neutralisation

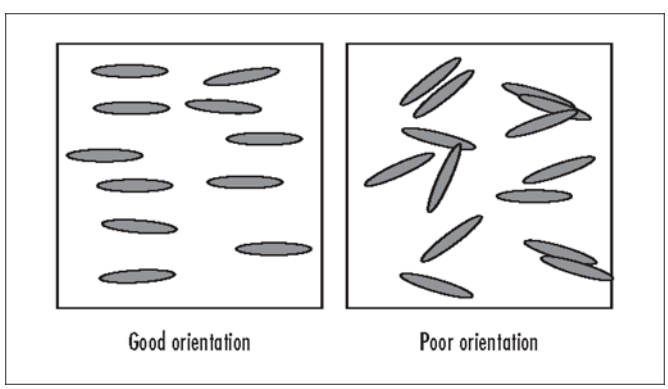
If water-soluble resins are being used, the neutralising agent should not be too basic eg ammonia should be avoided, because it is prone to react with the aluminum. Preferably, the pH value should be adjusted with amines like DMEA and TEA. Also 2 amino-2-methyl-1-propanol,11 can be used, which has the added advantage that it has anti-corrosive properties. Also, in some cases it can replace a wetting agent.

In general, owing to the different gassing stability of the different stabilisation systems, pH should be adjusted carefully. Additive technologiesa,b and pre-dispersed concentratesc are recommended if the pH does not exceed 8-8.5, while the encapsulated technologiesd,e,f can tolerate a pH of 9 – 9.5. To keep them in solution, most of the available resins do not require higher pH values than this.

Orientation

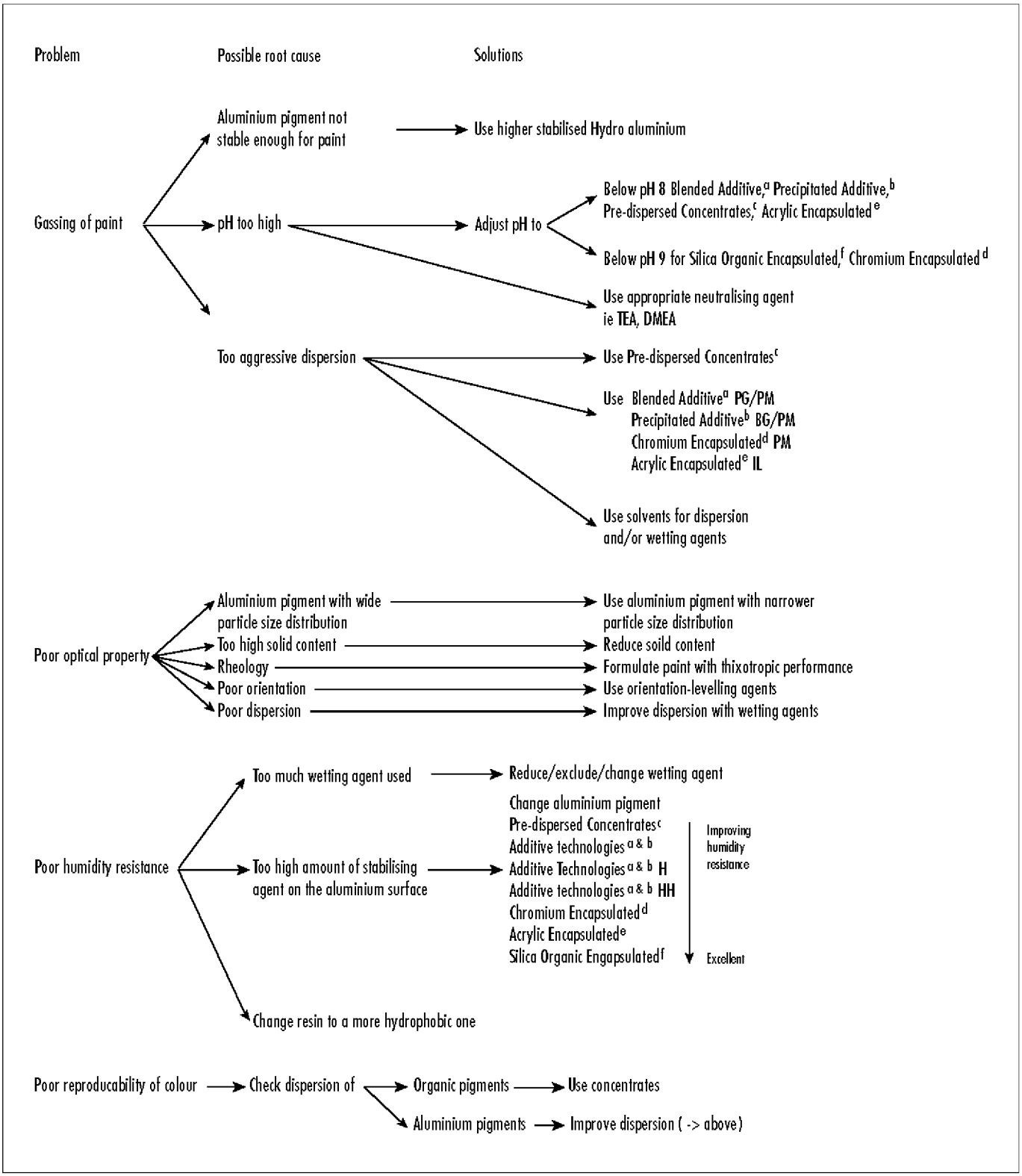
Orientation of the metal flake pigments is a very important aspect of metal effect coatings. Poor orientation will reduce the brilliance, as well as the flop effect. The better the flakes are aligned parallel to the substrate, the better the metallic effect, see Figure 2.

Figure 2: Orientation of the metal flake pigments



In solvent-based paints the orientation of the metallic flakes can be influenced strongly by the addition of special additives, eg cellulose-aceto-butyrates.12

Table 2: Flow chart for finding solutions to some common problems found when combining aluminium flake pigments with aqueous binders.



In aqueous paints the orientation of metal flakes is, in general, inferior to that in solvent-based paints. To improve this orientation in aqueous paints, polyethylene wax dispersions13,14 can be added.

Also, the rheology of the paint system plays an important role in assisting the orientation of the flakes. Improved orientation is, in general, achieved by adding components that confer a slight thixotropy. Thixotropes,15,16,17 must be mentioned in this connection. Care must be taken when using these. See the recommendations for anti-settling agents.

Anti-settling

Most paints contain additives that function as anti-settling agents. Since these components normally require a high level of shear to be dispersed adequately in the paint, they must be incorporated before the aluminium slurry is added.

If not, the flake pigments may be damaged, resulting in a loss of brightness and increased gassing. This was described earlier.

Transparent iron oxides

Silica organic encapsulation,[f] after its introduction, was quite often found to give good gassing stability in formulations using transparent iron oxides. These are popular in modern automotive paints but, in combination with aluminium flake pigments, had critically reduced gassing stability.

Miscellaneous

Some of the additives tested have been found to improve even further gassing stability. Here must be mentioned, wetting agents,[5&7] and an anti-settling agent.[18]

Problem solving

Additional information will be found in Table 2, Flow chart for finding solutions to some common problems found when combining aluminium flake pigments, with aqueous binders.

Other metallic pigments for water-based coatings

Aluminum pigments, with their characteristic flop effect, are not the only ones that can be used for metallic effect paints.

Gold bronze flake pigments, based on copper and brass, are now available to the water-based paint formulator, in a recently developed water-compatible form. The easy to handle gold bronze pre-dispersed concentratesc include leafing grades for decorative and general industrial aqueous finishes and also silica encapsulated bronze pigments. The silica encapsulated, 'resist' non-leafing grades, have longer term tarnishing stability, higher heat resistance and much better outdoor durability.

Also recently introduced, are champagne coloured semi-oxidised aluminium flakes.[g] These are extremely gassing stable, owing to the aluminum-oxide layer. In most cases they can be used in aqueous paints without any additional stabilisation. Supplied as a 65% paste in methoxypropanol they are easy to disperse.

For very aggressive binders there is an additionally stabilised version, semi-oxidised aluminium flake,[g] Hydro PM, which offers unique gassing stability.

Conclusion

In a continuous effort to improve the performance characteristics of metallic pigments for aqueous coatings, a wide variety of 'water friendly', metal flake pigments are now available. They have been carefully designed to meet the individual needs of different paint markets.

Eckart is in a position to tailor-make metal flake pigments for the individual cases, for individual industries. Water-based coatings formulators can now combine the most suitable stabilised metallic pigment with a well-adjusted formulation. Now water-based, gassing-resistant, coatings, are a reality.

Additional information for selecting and getting the best use from Metal Flake Pigments, will be found in Tables 1 and 2.

Acknowledgements

Finally, the author would like to acknowledge the assistance of Mr Henning Bunge, (Eckart-America), for help with translation from the German original and Mr Robert J Lewis, (Eckart-UK) for help with presentation for English publication.

Recommendations

Wetting agents[1-7]

1. Disperbyk 192 (Byk-Chemie)
2. Efka LP 4540 (Efka Chemicals)
3. Efka LP 9002 (Efka Chemicals)
4. Solsperse 27000 (Zeneca)
5. Strodex MOK 90 (Dexter)
6. Surfynol 104 (Air Products)
7. Tego Disperse 720 W (Tego Chemie)

Acrylic emulsions[8,9]

8. Joncryl (Johnson Polymer)
9. Zinpol (Worlee Chemie)

Water-dilutable alkyd resins[10]

10. Reshydrol (Vianova Resins)

pH adjustment additive[11]

11. 2 amino-2-methyl-1-propanol, (AMP), (Angus Chemicals)

Orientation additives[12-17]

Cellulose-aceto-butyrates[12]

12. CAB 381, (Eastman Chemicals)

Polyethylene wax dispersions[13,14]

13. Ultralube (Surface Chemie)
14. Cerafak (Byk-Cera)

Thixotropes[15-17]

15. Bentone, (Kronos)
16. Optigel, (Süd Chemie)
17. Laponite, (Laporte)

Anti-settling agent[18]

18. Aerosil R 972, (Degussa)

Eckart product names

a. Blended Additive, (Stapa Hydrolac).
b. Precipitated Additive, (Stapa Hydroxal).
c. Pre-dispersed Concentrates, (Rotovario Aqua).
d. Chromium Encapsulated, (Stapa Hydrolux).
e. Acrylic Encapsulated, (Stapa Hydromer).
f. Silica Organic Encapsulated, (Stapa Hydrolan).
g. Semi-oxidised aluminium flakes, (Stapa Aloxal & Stapa Aloxal, Hydro PM).

W Water
BG Butyl Glycol
PM Methoxy Propanol
IL Iso Propanol

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