Additives for Waterborne Coatings

Wernfried Heilen et al.
Vincentz Network, Hannover, Germany, 222 pages
ISBN 3-86630-850-7

This book stems from the author’s long experience in developing waterborne coatings, which is considered that he lacked a book which would both explain the mode of action of water-borne additives (theory) and indicate the choice of additives to use (practice). So, together with colleagues in the raw material industry, he has written such a book himself. He has held senior positions in the additive industry (Byk Chemie, Goldschmidt and Evonik-Tego) and has numerous publications and patents to his credit.

1. Introduction

Waterborne coatings have very different properties from those of conventional solvent based systems.

• The heat of evaporation of water is high compared with that of most organic solvents. So air-dry waterborne systems dry slower at lower temperatures and high humidity. Heat-curing waterborne systems require more energy for cure than solvent systems.

• Solvent borne systems utilise a wide range of solvents and co-solvents. In contrast, the choice for co-solvents for waterborne systems are relatively limited.

• Water is strongly polar with a high surface tension. This can cause problems in both manufacture and application necessitating the use of additives.

The various additives for use in waterborne coatings are then described in Chapters 2 to 12 which is described in the text but I suspect a missed nuance concerned.

2. Wetting and Dispersing Additives

Dispersion of pigments is a demanding step in making coatings, but preventing reflocculation of the dispersed particles is even more difficult. Anionic wetting agents are satisfactory for the dispersion of inorganic pigments: organic pigments of low surface energy and high surface area require more complex additives.

The function of wetting and dispersion additives are then considered under three sections, viz. wetting, dispersion (called grinding in the text but I suspect a missed nuance in translation) and stabilisation. The latter may be electrostatic, steric or electrosteric. Modern additivmes are often electrosteric in nature.

• The different methods of stabilisation affect various coating properties e.g. viscosity, colour strength, compatibility and stability: the effect of additive addition on these properties of the formulations is considered.

To stabilise pigments, two different types of molecular segments are needed: ‘anchor’ groups with an affinity to the pigment and water-soluble side chains for steric hindrance.

The pigment affinity groups are mostly hydrophobic and the side chains hydrophilic, so wetting and dispersing agents are described as amphiphilic. Surfactants are amphiphilic but the low molecular weight of many surfactants precludes their use as pigment stabilisers.

Commercially available products are mostly polymeric.

The author then goes on to discuss the most important pigment wetting and dispersing agents, namely polyacrylate salts, fatty acid and fatty alcohol derivatives, acrylic copolymers, maleic anhydride copolymers, alkyl phenol ethoxylates (e.g. modified fatty acid ethoxylates and modified polyethylenes). These replacements were developed because alkyl phenol ethoxylates are structurally similar to oestrogen and waters polluted with them can have a disastrous effect on the capacity of female animals to produce male descendants.

The use of the various types of pigment wetting and dispersing agents are then discussed in relation to various types of coatings, viz. architectural, wood and furniture coatings, industrials and finally, inks. This section ends with the comment that the compatibility of additives, for water-borne, with the binder matrix, can only be tested in the presence of the pigment. The importance of pH in avoiding pigment shock in let-down is also stressed.

Test methods for assessing the quality of dispersion are then considered as follows. Particle size monitoring can be used to determine whether satisfactory dispersion is achieved. Fineness of grind gauges (called Grindimeters here) can be useful, but laser diffraction or ultrasound methods are more precise. These methods are expensive, however so reliable that secondary indications can be used, such as colour strength, rub-out, viscosity or zeta-potential. The latter method has its limitations and perhaps would not often be used.

The chapter ends with a brief summary and literature references.

3. Defoaming

Some of the causes of foam formation are as follows:

• Mechanical introduction of air by mixing or application processes

• Air displacement during wetting or dispersion

• Generation of gas by chemical reaction

• Rapid drying causing bubbles.

Surface active substances often promote foam stabilisation; to prevent foam formation during processing and to destroy foam already built up, defoamers or deaerators may be used.

Foam is the dispersion of a gas in a liquid or solid where the volumetric content of the gas predominates. Gas bubbles in foam are separated by liquid or solid walls; solid foams are usually created from existing liquid foams.

The presence of a gas in a liquid does not necessarily cause foam. Intensive mixing is needed for a fine distribution of the gas in the liquid and this results in new gas/liquid interfaces. In most pure liquids these interfaces are unstable and quickly collapse. However, the presence of surface active agents in the liquid will stabilise the gas as foam. Since surface active agents are invariably present in coating systems, the chance of foam formation is high.

Defoaming mechanisms are then covered in detail.

The chemistry and formation of defoamers are then described; these may be classified as silicone oils, mineral oils, vegetable oils, polar oils, molecular defoamers (gemini surfactants), hydrophobic particles, emulsifiers and solvents; defoamers may be supplied as concentrates, emulsions or solutions. A list of the major suppliers is appended.

Defoamers are then discussed in relation to the type of waterborne paint, namely, acrylic, styrene-acrylic, vinyl acetate or polyurethane. Other criteria to be considered include PVC, method of defoamer incorporation, shear forces during application and the surfactant content of the formulation. However testing under practical conditions is the ultimate way of proving whether the choice of defoamer is correct.

This chapter also includes a few useful tips. Splitting the defoamer between millbase and letdown often gives the best results and using a combination of defoamers, rather than just one. The chapter ends with a summary and eleven references.

4. Rheology Modifiers

By lowering the surface tension, rheology modifiers improve film quality, colour acceptance and wet abrasion resistance, as well as controlling rheological properties such as in-can stability, brushability, film building and sagging. They are also used to aid dispersion of pigment particles in the millbase.

The main types of rheological modifiers are:

• Synthetic thickeners such as cellulose ethers (HEC), polyurethanes (HEUR), alkali thickening acrylic emulsions (HASE) and polyethylenes

• Mineral thickeners such as bentonite, attapulgite

• Natural thickeners such a alginites, guar and xanthane gums. The first group are by far the most commonly used.

5. Substrate wetting additives

This chapter begins with a discussion of the properties of water and, in particular, the surface tension of water. Its mechanism is described and the effects of the high surface tension of water are listed. The mode of action of substrate wetting additives is then described.

The types of substrate wetting additives used in coatings are then listed and properties considered in relation to structure:

• Polyether siloxanes

• Gemini surfactants

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The first group are by far the most commonly used.

The remainder of this chapter deals with ethoxylated and hydrophobically modified urethanes (HUSUR) in detail, dealing with synthesis, properties and applications. These are Sections 4.3 to 4.3.5. Similarly, sections 4.4 to 4.4.2 deal with alkali swellable emulsions (ASE and HASE).

The chapter concludes with twenty references.

5. Substrate wetting additives

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wet and stabilise various pigments. High colour strength, gloss and transparency can be achieved at very low viscosities. Better drying times and better mechanical properties are also achieved.

Co-binders, commercially available and specified as such, do not seem to be an established feature of Australian or American paint technology. Neither our RAW MATERIALS INDEX (8th Edition) nor the US-FCTS CODING DICTIONARY (1995, 2nd edition) list co-binders as such. This does not mean that Australian or American technologies are not exploiting all available materials according to compatibility and to their own ingenuity. It is possible that our technology has not yet caught up with these European developments. Readers’ comments can eliminate both microfloom and macrofloom.

Some of the factors favouring the development of microfloom are listed; the substrate e.g. porous wood, can also play a part. A number of tests for observing or assessing the effectiveness of deaerators are described. The author concludes by expressing the hope that the mechanism of defoaming/deaeration by additives will eventually be clearly understood; and that this understanding will lead to the development of highly effective deaerators/deagglomorators. Thirteen references are given.

One interesting point raised earlier in this chapter (p117) describes the use of carbon dioxide instead of air for spray application of waterborne paints. The solution is then carbonated. Water is about 50 times that of air. The carbon dioxide microflox bubbles dissolve faster than those of air, permitting the application of microfloe-free films.

Polymer films can include a variety of compounds that have been added to improve properties and performance. Some of these additives are described below.

Wax additives

Waxes may be natural, synthetic or semi-synthetic. The natural waxes may be renewable and cheap, but other waxes, such as microfloe, are also available. Wax additives offer a range of properties, from good gloss retention and maintenance of the integrity of the coating.

10. Light stabilisers for waterborne coatings

The UV stabilisation of coatings is achieved by adding UV absorbers and radical scavengers. By absorption of incoming UV light, the chain reaction of free radicals created by UV light is stopped. Light stabilisers are described in detail in this chapter. The Taber Abraser is useful in assessing such lacquers. By adding 2% HDPE wax dispersion such a lacquer, the Taber weight loss was reduced from 30.5mg to 18.0mg (1000 cycles), a significant improvement.

Waxes are also useful in inks, can coatings, coil coatings and floor coatings. Recommendations for the appropriate wax to solve the problem are given. Water repellency and anti-blocking are also discussed.

The use of wax additives offers many possibilities for influencing coating properties, but it is important to select the right wax base and type of additive. Some waxes are meltpoint for surface protection and polarity for water repellency and anti-blocking. It is important to note that waxes and other claims that it is possible to maximise the orientation of ‘effect’ pigments through new rheology-modified wax additives.

11. In-can and dry film properties

The last half-century has seen a phenomenal increase in the use of waterborne paints, often replacing the ‘old’ and ‘rustied’ traditional drying oil based paints. Waterborne paints often provide ideal conditions for the proliferation of micro-organisms, both in the can and on the dry paint film. Hence the growth in the
6. Improving performance with co-binders

This book mostly covers additives used in small amounts, say 0.1% to 3% of the total form, such as pigments (with the following section discussing modifying formulations by adding up to 30% of a co-binder). This section discusses the use of wetting additives in various sections of the market e.g. Inks, wood finishes etc. Page on ‘tips and tricks’ follows. e.g. the order of addition in a formulation can be changed.

The chapter ends with a discussion of test methods, measurement of dynamic surface tension, measurement of dynamic surface tension and some ‘practical’ tests e.g. draw down. Six references.

1. Fluoro surfactants
2. Acetylatedenes and modifications
3. Sulfoxocarbone
4. Alkylated fatty alcohols
5. Cationic surfactants
6. Surfactants other than those above. The correct choice of additive is not easy. The next section shows a table recording the percentage of additive with the following properties: reduction of static surface tension, reduction of dynamic surface tension, rheology, tendency, and price. For example, for the best reduction of static surface tension, use ammonium salt, but the price is high. This useful table is discussed in detail and is followed by a section which considers various defects e.g. crating in relation to various additives. The next section discusses the use of wetting additives in various sections of the market e.g. industrial finishes.

2. Effective deaerators reduce droplet size during application and fewer, smaller microfoam bubbles are generated which dissolve faster.

3. By oxidising the wax at high temperature, high-boiling solvents can be achieved. This high-boiling solvent allows the formation of smaller microfoam bubbles.

4. The author concludes by expressing the hope that the study of deaeration by additives will eventually be clearly understood; and this is under way due to the development of highly effective deaerators/deagglomeration. Thirteen references are given.

5. One interesting point raised earlier in this chapter (p117) describes the use of carbon dioxide instead of air for spray application of waterborne. The solubility of carbon dioxide in water is about 50 times that of air. The carbon dioxide microfoam bubbles dissolve faster than those of air, permitting the application of microfoam-free films.

6. Polymethylene wax and microcrystalline both from natural sources are those where the monomers are emulsified in water and then polymerized (co-condensation) to produce.

7. Deaerators are partially insoluble in the medium to be deaerated, although the mechanism is not fully understood; however the following points have been made:

1. Deaerators are partially insoluble in the medium to be deaerated, although the mechanism is not fully understood; however the following points have been made:

2. The semi-synthetic waxes of most importance are the amide waxes and montan wax. The semi-synthetic waxes are obtained by oxidation and re-esterification; most importantly, the dark colour of the original montan wax is lost.

Synthetic waxes are either homo hydrocarbons or polymers or copolymers. The formation of the Fischer-Tropsch waxes produced by hydrogenating carbon monoxide in the presence of a catalyst is described. Polypropylene waxes are also homopolymer.

10. Light stabilisers for waterborne coatings

The UV stabilisation of coatings is achieved by a range of stabilisers: absorbed and radical scavengers. By absorption of incoming UV light, the active ingredients in the stabiliser preparations for waterborne coatings can be activated. The development of specific light stabiliser preparations for waterborne products has led to a range of products which allow a comparable performance of such systems, compared to their solvent-based counterparts.

Finally, tests methods and analytical determinators are discussed; a useful summation of the various testing and references is given. Twenty literature references are appended.

11. In-can and dry film pigment dispersion

The last half-century has seen a phenomenal increase in the use of waterborne paints, often replacing the ‘old’ solvent-borne paints. Waterborne paints often provide ideal conditions for the proliferation of micro-organisms. UV-activated preservatives are often used in the can and on the dry paint film. Hence the growth in the...
**BOOK REVIEW**

**Waterproofing Technologies – Envirosystems**

**Summary**

In the future, it seems that fewer microorganisms in paints will be biologically active substances will be favoured. Facades must be protected against excessive water absorption. Historical, naturally fats and oils were used for this purpose, then waxes became popular. In recent years, silicon derivatives have become major hydrophobes. The first part of this chapter describes capillary water-absorption, so how hydrophobes function. If the contact angle is greater than 90°, the substance is said to be hydrophobic; if the contact angle is greater than 140°, it is strongly hydrophobic. The advantage of silicones is that although liquid water is unable to enter the pores of silicone, cement, the pores remain permeable to air and water vapour. That is, the walls can still ‘breathe’. Silicons can be oils, fats, resins or rubbers. Linear polyiloxides (silicone oils) are resistant to UV radiation, heat and alkalis. The composition, properties and applications of the various silicones are described. Then follows a description of the waterproofing of the various architectural waterborne paints. A useful table (Table 12.3) compares the difference types of paint listing water absorption, water-vapour diffusion, dirt-pick up and contact angle. There are some noticeable differences in dirt pick up. The author concludes that, because of their high efficiency, long-term effectiveness and recoatability, polyiloxides and silicon resins have replaced other types of hydrophobic agents.

A useful appendix, 12.5, describes Künzel’s facade protection theory, formulated in the 1960’s. Two properties play an important part in this theory, viz: 1. The water absorption capacity of the substrate and; 2. The water vapour permeability of the coating.

Künzel noted the importance of a protective coating which is both moisture resistant and ‘breathable’, i.e., allowing water vapour to pass through. Two parameters are crucial to this theory, viz: 1. Water absorption coefficient (e-value) 2. Water vapour diffusion resistance (s-value)

**Surface Coatings Technology e-Learning Course**

Course prerequisites

Due to the level of technical content, the general requirement is a degree or diploma in chemistry (or equivalent qualification). However, those without a tertiary qualification may apply but must have successfully completed a secondary year 12 certificate including chemistry, and must have at least 5 years of relevant experience in the coatings or related industry.

Course structure and resources

The course syllabus comprises 49 lessons in total, structured into 6 units. All lesson content is provided via a set of two CDs.

Course fee and applications

The course fee is A$ 1,900 (for students who are not SCAA members), and A$ 1,600 for SCAA members. These prices are inclusive of GST (in Australia).

For further details and application for admission to the course, go to the course website at www.etsrelaunching.com/scaal.

**COMPANY PROFILE**

**Waterproofing Technologies**

An Australian owned and operated manufacturer of environmentally responsible, low VOC products based in St. Peters, NSW. The company pioneered its environmental approach four years ago by producing the Envirosystems range of products, which comprises specialty coatings, elastomeric and other waterproofing products, sealants and industrial flooring materials all of which have been independently certified as low VOC by the Green Building Council of Australia.

The Envirosystems product range includes high tech, fast cure spray elastomers, single pack UV stable, trafficable polyurethane waterproofing membranes, epoxies and polymer cement composites for all facets of structure repair and protection. Waterproofing Technologies compliments state-of-the-art products with experienced, technically trained personnel who are ready and able to meet the customer’s technical enquiries and specifications as required.

**Technical Director**, Bob Sun has a career spanning over 40 years with companies such as Vessey, Corda, Ameron and PPG. His wealth of knowledge regarding polyurethanes, epoxies and polymer systems in general will ensure well formulated and supported products are brought to market in a timely and professional manner.

**OBITUARY**

Peter Sawly

Passed Away 3rd February 2010

Well known N.S.W. identity, Peter Sawly, passed away on February 3rd after a brief fight with cancer. He was only 66 years old and is survived by his wife, Helen, two children and four grandchildren.

Peter was a long standing member of our association and presented a number of papers to our N.S.W. Section. He initially worked at BALM Paints on the marine coating side and eventually became National Marine Coatings Sales Manager. He subsequently moved to British Paints as National Marine Sales Manager. Then came a big change; to BASF for 11 years, selling pigments etc. to the paint and ink industries. Peter then moved back to British Paints in a technical support function. But there is more... a couple of further moves saw him finishing up at John Paints from where his family is from.

Peter will be sadly missed and fondly remembered by the industry and his SCAA associates. Our thoughts are with his family.

**Surface Coatings Technology**