Additives for Coatings

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Johan Bieleman
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Coating additives comprise an extremely important class of coating raw materials that are used for the formulation of paints and coating materials, as well as for applications closely related to coating materials.

Quality, as well as various coating-application properties are determined to a large extent by the coating additives used. Selecting the correct additives from the wide range available is therefore very important.

In practice, it rather often happens that the coating technician literally only „finds“ the right additive for the application after experimentally testing a large range of products. With this type of method, an explanation of why one additive works, and another does not, is rarely found.

The primary goal of this book is to inform the coating technician who works with the formulation and application of coating materials such as paints, varnishes, inks, and related products, about the effects that can be obtained with additives. The main classes of additives and the advantages associated with their proper application in coating materials are emphasized.

The chemical composition and basic properties of the main groups of additives, such as thickening agents, surface-active agents, surface modifiers, catalysts, biocides, etc., are explained in detail. Not only the theoretical aspects are covered, the greater part of the information is directed at practical applications and properties, such as the influence on film properties such as appearance and protection.

The book is an ideal source of information for those working as coating technicians or chemical engineers in industry and trade; however, it is also suitable for those who work in professions that deal with coatings, for instance, in schools, colleges, universities, and public institutions.

Although, in a few cases, commercial names were used to support clear information, the aim of this book is not to list or describe additives according to their trade names.

This book also does not describe all related theories and publications on coating additives in detail, without presenting connections to practical conditions.

In editing this book, I had the support of various specialists in different subjects related to coatings, and I thank them all for the professional and pleasant cooperation. My sincere thanks are particularly extended to Dr. Stoye, Dorsten, Germany, for his stimulating ideas, and to Prof. Dr. Funke, Leonberg, Germany, for his very helpful advice and corrections. A special acknowledgment goes to the management of CONDEA Servo B.V., Delden, the Netherlands, for their support and for providing the technical means.

Goor, The Netherlands
January 2000

Johan H. Bieleman
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1 Introduction

Johan Bieleman

1.1 Additives in Coating Materials

A coating material may be defined to be a product in liquid, paste, or powder form that, when applied to a substrate, forms a film which has protective, decorative, and/or other specific properties. The following main components are found in coating materials such as paints:

- binders
- pigments and extenders
- solvents
- additives

The binder determines most of the primary properties of the dried paint film, such as adhesion, various optical and mechanical properties, as well as the resistance against specific exposure conditions.

The other solid components of the paint layer, such as the pigments and extender, are fixed in the binder matrix.

The selection of the pigment determines not only the colour, but is also largely responsible for other properties such as the opacity and corrosion resistance of the paint.

Although the main contribution of the extenders is to reduce the raw-material costs of the paint formulation, they may also have some influence on various other paint properties.

The role of the solvent or diluent is, in the first place, to enable the processing of the solid or highly viscous components of the paint during manufacture, application, and film formation.

In addition to the indicated main ingredients, the additives in a paint composition have a major influence on the various paint properties. Additives may also modify the properties of the three main ingredients of a paint – binder, pigment/extender, and solvent – significantly.
1.2 Definitions

It is very difficult to give a clear and exact definition of a coating additive – they make up a very nonhomogeneous group. A wide range of additives is known, with various and widely differing functions in a coating formulation.

A possible definition is the following:

*Coating additives are any substances that are added in small quantities to a coating material to improve or to modify certain properties of the finished coating or of the coating material during its manufacture, storage, transport, or application.*

1.3 Classification According to Function

The expression “to improve or to modify certain properties” refers not only to technical properties, it also includes economical aspects such as the reduction of manufacturing costs or the pigment yield optimization.

The amount of additives in a coating formulation is seldom more than 5% by weight. The average proportion of a single additive in a formulation is usually around 1.5% of the total quantity of the coating formulation.

There is a large variety of coating additives; they are classified according to their function below.

**Thickening Agents**

These additives influence the rheological properties of a paint by increasing the viscosity.

**Surface-Active Agents**

This group is subdivided into:
- wetting and dispersing agents
- anti-foaming agents
- adhesion promoters

**Surface Modifiers**

This group is subdivided into:
- slip additives
- matting agents

**Levelling Agents and Coalescing Agents**

The group of levelling agents includes flow agents.
Catalytically Active Additives

This group includes:
- driers
- catalysts

Special-Effect Additives

The remaining additives are included in this group, e.g.:
- anti-skinning agents
- light stabilizers
- corrosion inhibitors
- biocides
- flame retardants
- photoinitiators

1.4 Quantities Used

In terms of quantities used, the catalytically active additives make up the largest product group, as seen from the relative amounts of additives used (Table 1.4-1).\footnote{11-1} Next in used quantities are the surface-active additives, followed by the thickeners. The indicated percentages are of each specific group of additives, and are based on the volume of additives used globally; there may be considerable regional variations.

Driers, used as drying catalysts in oxidatively drying paints, make up the main part of the catalytically active additives. However, the use of driers is declining: firstly, more concentrated driers are being used (less solvent), and secondly, the market share of air-drying systems is declining in favour of physically drying paints.

<table>
<thead>
<tr>
<th>Additive group</th>
<th>Usage in % of the total amount of applied additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytically active additives</td>
<td>28</td>
</tr>
<tr>
<td>Surface modifiers</td>
<td>12</td>
</tr>
<tr>
<td>Thickeners</td>
<td>16</td>
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<tr>
<td>Surface-active agents</td>
<td>19</td>
</tr>
<tr>
<td>Levelling- and coalescing agents</td>
<td>10</td>
</tr>
<tr>
<td>Special-effect additives</td>
<td>15</td>
</tr>
</tbody>
</table>
1.5 Economic Significance of Coating Additives

Although additives make up a small proportion of paint formulations, the total world consumption of additives is estimated to be more than 350,000 metric tons annually\textsuperscript{[1-2]}. The relative importance of additives is not simply expressed by total quantities or sales volumes, most important is the technical impact of the additives on the paint properties. The significance of an additive in a specific coating material is best expressed in terms of its contribution to the improvement in the quality of the paint. However, this economic contribution is not easily quantifiable into an "economic figure".

If one were to base the economic importance of additives on the raw material costs for the production of paints, it would be found to be rather moderate (Table 1.4-2)\textsuperscript{[1-3]}.

Table 1.4-2. Average contributions of the various ingredients in paints

<table>
<thead>
<tr>
<th>Paint raw material</th>
<th>Quantity in %</th>
<th>Value in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>29.5</td>
<td>31.7</td>
</tr>
<tr>
<td>Solvent</td>
<td>27.4</td>
<td>15.5</td>
</tr>
<tr>
<td>Water</td>
<td>10.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Pigments</td>
<td>18.7</td>
<td>45.9</td>
</tr>
<tr>
<td>Extenders</td>
<td>12.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Additives</td>
<td>1.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Obviously the average amount of additives in paints is rather small by weight. Additives contribute more to the total raw material costs because the various additives are more expensive than the average raw material costs of a paint.

Nevertheless, the data from Table 1.4-2 show that additives make up a very modest contribution to the total raw material costs of a coating material. The argument for the use of an additive is therefore mainly determined by the effect that the additive has on the quality of the coating material or the dried film.

References


\textsuperscript{[1-2]} Stoye-Freitag, \textit{Lackharze}, Carl Hanser Verlag, München 1996, p. 396

\textsuperscript{[1-3]} \textit{The Demand for Coating Additives}, 3rd Ed.; IRL Ltd., London 1991, p. 118–120
2 Basics

Johan Bieleman

2.1 Introduction

Coating additives are auxiliary components that are used in the formulation of surface-coating materials such as paints and lacquers and are typically added in small quantities in order to realize certain desired properties during production, storage, application, or exposure of the coating (see Section 1.2). Other main components of coatings are binders, pigments/extenders and solvents. Clearly, there are several different application purposes for additives, and additives indeed make up quite a non-homogeneous group. Coating additives may differ significantly from each other regarding their chemical compositions and functions. The only common factors for the different additive groups are that they are by definition “added in small quantities” and that the purpose of their application is “to realize certain desired properties”.

From this it is quite clear that there are no general characteristic physical and chemical properties for all additives and the various different groups of coating additives will therefore have to be considered separately. In this chapter some basic functional properties of coating additives will be explained in relation to typical applications.

2.2 Interactions

Coating additives are utilized to further modify the characteristic properties imparted by the main components of the coating material, namely the binder, pigment and solvent. Characteristic for additives is, furthermore, that these ingredients can be directed in such a way that, ideally, they develop their effect at certain predicted places within the coating formulation or layer. Indeed, one of the targets in developing additives is to devise the additives in such a way that the additive molecules are concentrated in the varnish right where they can fulfill their desired purpose (Fig. 2.2-1).

Typical characteristics of additives which are of great technical significance:

- surface activity
- vapour pressure
- solubility parameter
- chemical stability
The importance of these characteristics will be demonstrated by the following examples.

**Surface Activity**

Molecules can be tailor-made through chemical modifications so that they have a higher affinity for certain selected interfaces. This may be achieved, for instance, in the case of fatty alcohols, by introducing negatively charged groups such as carboxylates, sulphates, or phosphates. This chemical modification of the fatty alcohol results in improved adsorption on the surfaces of base pigments (covalent bonding forces).

**Vapour Pressure**

In practice, methyl ethyl ketoxime is the main additive used as anti-skinning agent in oxidative drying alkyd paints. This oxime is a good ligand for certain metals, and it complexes drying catalysts such as cobalt driers, which are typically used in these paints. In contrast to the free drier, the cobalt oxime complex has no catalytic effect on the drying rate. When the paint is applied, the surface area is increased considerably. Because methyl ethyl ketoxime has a high vapour pressure, it evaporates soon after the coating has been applied, releasing the catalyst so that it can be active (see Section 8.1.5.2).

**Solubility**

Defoaming and anti-foaming agents should be effective at the liquid/air interface. Defoaming and anti-foaming agents are usually poorly soluble in the liquid phase. As soon as the paint is applied, the defoaming agent separates and floats as a very
thin layer on top of the paint layer, resulting in a higher concentration of the de-foaming agent at the liquid/air interface.

Chemical Stability

Limited chemical stability at higher temperatures of, for example, certain blocked acid catalysts causes the release of the acid at higher temperatures, thus effecting acid-catalysed curing of paints and coatings.

2.3 Chemical Composition

The different additives vary significantly with regard to their chemical compositions. Some additives have clearly defined compositions, being made up of compounds such as oximes, silicones, cellulose-ether or metal soaps; other additives are very complex preparations made up of different components.

Some additives consist of natural products (for example lecithin) or modified or prepared natural products (such as cellulose derivatives). However, the majority of the additives are based on synthetic products.

2.4 Effectiveness of Additives

The characteristic properties as well as the field of application of most additives can be clearly defined, for example, with defoaming agents. However, additives often do not have only a single function, but have several additional effects. Sometimes this multiple effectiveness is desired: wetting agents that cause better pigment wetting, resulting in better adhesion of the coating layer onto the substrate, also improve flow and levelling. Anti-skinning agents may have the additional desired side effect of functioning as flow agent.

But negative side effects may also occur: thickeners may affect the gloss of the coating layer and work as a kind of matting agent, pigment dispersing agents may operate as polymerization catalysts under storage conditions.

Many of these phenomena are the result of interactions between the various ingredients of the complicated coating formulation, to this is added the complicating factor of the complex composition of the additives themselves.
2.5 Applications

Usually additives are selected according to the following criteria:

- functionality
- availability
- compatibility
- price/performance relationship

The functionality is related to the composition as well as the usage levels and recommended application.

Additives are often used as "problem solvers", i.e., they are selected to solve, for instance, an actual production or application problem and are therefore needed immediately. The availability of the additive is in such a case decisive.

Compatibility is a very important criterion as well. In practice different additives are used in the same formulation. Here some effects could be mutually neutralized. A good example is certain dispersing agents that can influence the effectiveness of the associative thickener negatively. The effectiveness and efficiency of an additive can be influenced by physical or chemical interactions with other ingredients of the coating formulation during storage of the paint product. A good understanding of the characteristic properties of all the ingredients in the particular coating formulation reduces the risk of being confronted with such unwanted interactions.

The sequence of addition of the raw materials can be very important, especially with regard to the additives. Some additives are typically added before the dispersing process, for example, dispersing agents, thickeners, bactericides, or the additives are added during the let-down stage of the coating-production process.

The dosage of some additives is critical; because of the complexity of a coating formulation, it is necessary to determine the optimal quantity empirically for each formulation individually.

As additives are substances which are only added in small quantities, the impact on the total raw material costs is relatively minor, the decisive factor is whether the desired improvement is obtained or not.

References

3 Thickeners

Johan Bieleman

3.0 Basics

3.0.1 Introduction

Thickeners are used in coating materials and paints to impart the required rheological characteristics to the system. The rheological properties of a coating material influence its storage, processing, as well as application performance. Thickeners are usually added before the dispersing stage of the production process – the type and amount are adjusted to the dispersing equipment – to optimize the flow behaviour of the ground paste. If the pigments are dispersed in a medium which is too thin, turbulent flow behaviour results, which leads to a great loss in supplied energy, so that it is not used optimally during dispersing.

For storage, the viscosity of the paint should be high enough to prevent sedimentation of heavy pigment particles. The viscosity can be adjusted in a similar way to influence several application characteristics such as the flow, levelling, sag resistance, brushability, as well as film thickness and opacity. There are several possible ways in which the rheology can be adjusted. By adding a thickener the viscosity can be increased. In practice, organic as well as inorganic thickeners are used.

To understand how these coating-material thickeners function, some rheological basic knowledge is necessary, and therefore, first of all, a few rheological terms will be explained.

3.0.2 Rheology and Viscosity

The definition of rheology is “the science of the deformation and flow behaviour of matter under the influence of external forces”. Put differently, it is the study of viscosity under a wide range of conditions. The literal translation of the term “rheos”, of Greek origin, is “flowing”. The term viscosity refers to the resistance of a liquid against deformation, small resistance corresponds to low viscosity, and large resistance corresponds to high viscosity.
Flow

The flow of liquids may be subdivided into two types: laminar and turbulent flow.

Laminar flow is the flow of infinite, thin, parallel layers of liquid films — from which a liquid may be considered to be made up of — which occurs in such a way that no mixing occurs.\textsuperscript{[3-3]} It is easy to describe laminar flow mathematically, provided that no turbulent flow arises.

Turbulent flow is accompanied by eddy currents in sheared material and occurs at relatively high rates of shear, for both plastic and Newtonian systems. With turbulent flow a great part of the energy, supplied to the system to make flow possible, gets lost so that it can not be used for the actual aim, to get a flow, as with laminar flow.

During production, as well as during application, the flow in coating materials is mainly laminar.

Shear Stress, Shear Rate, and Viscosity

To illustrate rheological dimensions, the two-plate-model is often used (Fig. 3.0-1). A liquid has an external force ($F$) acting on its surface (with an area $A$, in $m^2$). The external force pulls on the top layer of the liquid, with the pulling action defined as the shear stress ($\tau$), equal to $F/A$ (N m$^{-2}$). The direction of the applied force is parallel to the boundary surfaces of the films. The shear stress is the force with which two related liquid films are moved in relation to one another.\textsuperscript{[3-1]}

\begin{equation}
\text{shear stress } \tau = \frac{\text{force } F}{\text{surface } A} \text{ in [Pa]} = \frac{[N]}{[m^2]}
\end{equation}

![Figure 3.0-1. The two-plate model](image)

When a force is applied to the upper layer of a liquid, this layer is pushed in the direction of the force. As the top layer moves under the applied shear stress, the layer directly beneath it is pushed along as well. This second layer, in its turn, will push the third layer along, the third will affect the fourth in the same one, and so on. The bottom layer, however, is held in place against the container. The resulting shear gradient, or shear rate, $D$, is defined by the following equation, where the thickness of the liquid is $h$ and the velocity of the top layer is $v$.

\begin{equation}
\text{shear rate } D = \frac{\text{velocity } v}{\text{distance } h} \text{ in [s}^{-1}\text{]} 
\end{equation}