Detlef Gysau

FILLERS FOR PAINTS

3rd Revised Edition
Detlef Gysau
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Fillers for Paints
Fundamentals and Applications

3rd Revised Edition
For Jacqueline and Gian-Flurin and Mica-Ladina and also Rambo and Fuchur

There is no debt more pressing than the expression of gratitude.

Marcus Tullius Cicero
Foreword

The topic of fillers for use in paints and varnishes is an old one, so one might ask why there has been no comprehensive book on the subject to date. Could it be something to do with the earlier prevailing perception of fillers as cheap materials for bulking up profits? Are fillers even worth writing about? Certainly! The sheer number of mineral end-products, the frequently underestimated effort that goes into their manufacture, the testing done to characterise their diverse properties, their wide-ranging applications – that is an awful lot of information to pack into a single work without diluting its focus.

Simply to consider the spectrum of professions involved in producing and using fillers – geologists, mineralogists, mechanical engineers, machine operators, chemists, paint and varnish specialists – highlights the extent of hidden technical activity. Fillers are instrumental in many properties of coating materials and films: their rheology, content of volatile organic compounds, solids content, brightness, opacity, reflectivity, adhesion, anti-corrosion characteristics, mechanical and chemical resistance... the list goes on. The bottom line is, proper use of fillers calls for a great deal of knowledge.

The present book sets out to convey that knowledge in a straightforward and understandable manner, without compromising scientific objectivity and rigour. Special attention has been given to clear topical division and structuring, to facilitate finding pertinent information, fast. That having been said, the gamut of available fillers is so vast that there would be insufficient space to cover all the materials out there, some of them quite exotic. Instead, this book concentrates on fillers in regular current use, with numerous figures and tables to illustrate their properties and applications. All the same, this book cannot claim to be exhaustive in scope. Readers wishing to obtain further information and details will be served by the extensive bibliographic references provided.

This book is intended for anyone who is in any way professionally involved with fillers used in coating materials. Beginners and students will gain a comprehensive overview of the field, while experienced developers will find practical details of immediate relevance to solving their everyday problems.

In 2016 I was notified that also the second edition of “Fillers for Paints” is going to be sold out soon as well. I am more than delighted to learn that also the second edition found so many new readers. The continued interest in my book is also judged by manifold feedbacks which I received since 2006. All of them expressed to me their thanks and congratulations by filling a knowledge gap in raw materials for paints.

Detlef Gysau: Fillers for Paint
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In particular, I appreciate that the book supports training for all different kind of groups, either in industry or science. The third edition allowed me to place small corrections, update market and filler data and add more sub chapters about new fillers and nevertheless an outlook about the future, for example sustainability and light weight fillers.

Detlef Gysau
Oftringen/Switzerland, January 2017
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1 Introduction

1.1 Historical overview

Paints and varnishes have a history that goes back around 100,000 years, to the time when stone age peoples applied red body-paint as part of their cultish rituals\textsuperscript{[1]}. The first paintings on cave walls date back to the late Stone Age, their origins still somewhat shrouded in mystery. Many thousands of years later, in the 4th century B.C., the intermingling of ancient Egyptian and Greek civilisations brought remarkable developmental advances through “Hagia Techné” or “Alchimia” – hallowed arts practiced by the high priests of the day. Their discoveries about the secrets of paint making remained influential well beyond the 16th century A.D. As the industrial revolution started in the 18th century, paints and varnishes came into widespread use for many different applications. Early 20th century triumphs of chemistry and technology in particular signified a clear departure from empiricism, to science.

The history of fillers can be traced back almost as far as paints and varnishes. Pigment analysis has revealed the presence of filler materials in early cave paintings\textsuperscript{[2, 3]}, the oldest identifiable specimens dating from 20,000 to 30,000 years ago, see Table 1.1 p.14. However, the first people to systematically use fillers for their cave paintings were the ancient Egyptians, and the Mediterranean cultures that succeeded them. The most frequent materials were chalk and gypsum, both white mineral fillers. Clays, or crushed mollusc shells, were also used on occasion. As history progressed, the ancient Greeks began using a mineral that was whiter still: white lead. Because of its rare occurrence in nature, they developed an intricate process to obtain the pigment synthetically. Contemporary demand for greater opacity and brightness evidently made the effort worthwhile. The Roman historians Pliny and Vitruvius respectively reported eight and five white pigments then in use, although only three were of real significance: the minerals melinum, paraetanum and cerussa (white lead).

During the period of the Roman Empire, there was a marked increase in the consumption of fillers, which were used in paints for murals, panels and frescoes. But filler production collapsed along with the Roman Empire, and artists subsequently resorted to local minerals. There were large chalk deposits in England, France, the Netherlands and Germany. Even in Spain, chalk grew prevalent under the name of Spanish white. In Italy, though, gypsum predominated. That was the situation until the 19th century, when the industrial revolution came into full swing.

The enormous increase in consumption of raw materials during the industrial revolution also brought a sustained rise in demand for fillers. Semi- and fully-automatic dress-
**Introduction**

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<th>Modern name</th>
<th>Mineral composition</th>
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<td>Cerussa (^{(1,2)})</td>
<td>White lead, Krems White, etc.</td>
<td>Basic lead carbonate, made from metallic lead and vinegar</td>
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<tr>
<td>Creta anularia (^{(1,2)})</td>
<td>Crete white</td>
<td>Chalk mixed with powdered glass</td>
</tr>
<tr>
<td>Cimolia creta (^{(1)})</td>
<td>Kimolos chalk</td>
<td>Chalk or clay-like material</td>
</tr>
<tr>
<td>Creta eretria (^{(1)})</td>
<td></td>
<td>Probably a white talc, named after a place on the southwest coast of Euboa</td>
</tr>
<tr>
<td>Creta selinusia (^{(1,2)})</td>
<td>Selinus chalk</td>
<td>Chalk or chalk clay, named after a place on Sicily</td>
</tr>
<tr>
<td>Melinum (^{(1,2)})</td>
<td>Melian white</td>
<td>Bianca San Giovannini or white clay</td>
</tr>
<tr>
<td>Paraetonium (^{(1,2)})</td>
<td>White sepiolite</td>
<td>Limestone chalk with some magnesium phosphate, silicic acid and clay, named after a place in Libya</td>
</tr>
<tr>
<td>Creta argentaria (^{(1)})</td>
<td>Argentiferous chalk</td>
<td>Chalk</td>
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\(^{(1)}\) Pliny, *Natural History*, XXXV  \(^{(2)}\) Vitruvius, *Ten Books on Architecture*, VII

**Table 1.1: Natural and synthetic white minerals used by the ancients**

**Figure 1.1: Overall European production of paints and varnishes, in millions of tons**

ing processes were developed to address this demand, as well as to meet the steadily advancing requirements of industry. High-power machinery like crushers, grinding drums and classifiers came into use. The end of the Second World War brought even greater demand for fillers, which was a motor for further modernisation by the filler industry. The resulting technical developments led to ever-finer natural fillers and tailor-made synthetic fillers, some with surface coatings, see Figure 1.1 p.14.

1.2 Filler market

The market often underrates fillers, on account of their relatively low price compared to the other raw materials used for making paints and varnishes. Overall Global and European show a continuous growth since 1997. Once believing the prognosis for the global paint and coatings market, then the number will almost double from 1997 to 2018 to approx. 47 Mio tons. Despite the growth for the production in Europe, its global share drops from 32.0 % in 1997 versus a much stronger growth in emerging markets such as Asia to 23 % in 2018.

If one compares the four million-plus tons of fillers consumed in 2003 with the quantity of paints and varnishes produced in that year, their 42 percent statistical share makes it clear that fillers are the dominant class of raw materials used in paint and varnish production, see Figure 1.2 p.15.

The chart of mineral fillers in current use reveals another dominance: natural calcium carbonate is the basis for three quarters of all the fillers used in paints and varnishes. Carbonate fillers together have an 85 percent aggregate share. This profile of mineral filler consumption is essentially repeated on other continents as well, see Figure 1.3, p. 16.

An analysis of application areas reveals that most fillers go into architectural paints, in particular emulsion paints. This group of paint systems is far and away the largest, at around 60 percent of overall paint and varnish production. Empirically speaking, classical and contemporary coating systems both tend to use considerably less fillers, or indeed dispense with them altogether. These systems generally are formulated below the critical pigment volume concentration (CPVC), which necessitate a higher proportion of pigments in order to achieve sufficient opacity.
1.3 Definition of fillers and pigments

There are numerous differences in the properties of fillers and pigments. Yet they can also overlap, depending on the application. Therefore, it is important to draw a clear distinction between these two groups of raw materials. Help is provided by the sets of standard specifications published by the German standards institution (DIN)\(^{[4, 5]}\), the European Committee for Standardisation (CEN) and the International Organisation for Standardisation (ISO)\(^{[6]}\).

According to DIN 55943, EN 971-1 and ISO 3262 part 1, “a filler is a substance consisting of particles which is practically insoluble in the application medium and is used to increase volume or to improve technical properties and/or to influence optical properties.” The standards discourage the use of terms like “extender”, “extender pigment”, or “pigment extender”, instead stating that “on this basis, whether a substance should be regarded as a filler or a pigment is determined by its application.”

Pigments are defined in the German standards DIN 55943 and DIN 55945: “A pigment is a substance consisting of particles which is practically insoluble in the application medium and is used as a colorant or by virtue of its corrosion-inhibiting or magnetic properties.” Pigments may be described more precisely, for example as inorganic or organic pigments, coloured pigments, white pigments, effect pigments, anti-corrosion pigments, magnetic pigments, etc. depending on their chemical composition, optical or other technical properties.

![Figure 1.3: Percent share of fillers in Europe, categorised by mineral](image-url)
Definition of fillers and pigments

Practically speaking, material constants like the refractive index often determine whether a substance is acting as a pigment or a filler. This is usually apparent from the optical effect of the substance as a component of the coating material. If the substance helps to increase opacity, then it has the characteristics of a pigment. If it behaves transparently, though, it is considered to be a filler. In general, materials with a high refractive index \((\geq 1.7)\) are pigments. All other mineral materials with a similar refractive index, like organic polymers, belong in the category of fillers.

### 1.4 Classification of fillers

Given the diversity of mineral fillers, it is helpful to divide them into various categories. Categories like carbonates, silicates, silicas (silicon dioxides), sulphates, oxides and organic
fillers include well known as well as more obscure materials. In addition to this type of categorisation, fillers are also grouped according to their natural versus synthetic origin.

Not all of the fillers listed in Table 1.2 are (as yet) industrially significant. Although they have been listed here for the sake of completeness, they will not be covered in subsequent chapters of this book.

1.5 References

Detlef Gysau, Omya International AG, has been engaged in the development of hydro-fillers for the automotive industry at Akzo Coatings in Stuttgart, after his apprenticeship of a paint laboratory assistant (1985–88). During his studies he joined the industrial research centre of Rohm and Haas, Philadelphia and the R+D lab for photo initiators at Ciba-Geigy, Basel. 1996 he acquired his engineer degree in the fields of paints, lacquers and plastics (M.Eng.) at the University of Applied Science in Stuttgart. Today, he is employed at Omya International and led for 14 years the Applied Technology Services for Paints, Coatings & Adhesives (ATS-PCA) with global responsibility for development and technical service. In 2010 Detlef Gysau finished his Executive MBA in General Management at the University of St. Gallen, Switzerland and changed to Omya’s Group Function Sales & Marketing. Here he held positions as Marketing Strategy Manager, Head of Product Management and actually Head of Innovation & Technical Marketing in the Segment Construction.
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