Mircea Manea

HIGH SOLID BINDERS

2nd Revised Edition

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Cover: cakeio – stock.adobe.com

Bibliographische Information der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliographie; detaillierte bibliographische Daten sind im Internet über http://dnb.d-nb.de abrufbar.

Manea, Mircea
High Solid Binders, 2nd Revised Edition
Hanover: Vincentz Network, 2025
European Coatings Library

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Layout: Vincentz Network, Hanover, Germany
Printed by: Gutenberg Beuys Feindruckerei, Langenhagen, Germany

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Foreword 2nd Edition

More than 15 years have passed since the first Edition of High Solid Binders was published. There have been few publications in this field since then, but attention is currently focused on bio-based and renewable products. Nevertheless, high solid resins remain a mature technology with growing market share. The reasons why high solid binder technology remains an important approach in the coatings industry are:

- Wide range of application methods
- Wide range of curing chemistries that can be used
- Wide range of monomer choice
- Wide range of polymers and synthetic chemistries that can be used
- Wide range of solvents, including non-VOCs, that can be used
- Wide range of coating formulations
- Wide range of renewable raw materials that can be used
- Very good substitute for powder coatings where large objects need to be coated

The book also discusses the parameters that influence solids content and performance, with a particular focus on those that pull in opposite directions.

This edition contains the main chapters from the first publication, along with new chapters on silanes, polyurea, ketimines and Michael addition chemistry. There are also applied processes for acrylic resins that produce binders with a very low molecular weight that can be used at room temperature (SGO, CSTR).

The author hopes that the increased interest in high solid resins, as well as the wide range of available raw materials and curing chemistries, will attract a large readership to the new edition of High Solid Resins and Coatings.

Malmo, Sweden, March 2025
Mircea Manea

Foreword 1st Edition

Water-borne, UV curing, powder coatings and high solids are modern coatings technologies complying with new regulations and standards.

High solids represent an interesting group of coatings, as the environmental pressure and legislations are a daily concern. They impart the benefits of the solvent-borne coatings with low environmental impact. High solid coatings have been a central preoccupation of science engineers for a very long time and are in many cases the best option for applications where only solvent-borne coatings may be used. In these cases, the employment of this technology should and will make a difference.

Although several approaches have been made, no solution to solve all problems generated by high solids has been found. A relatively long history and extensive literature is presently dealing with this subject but only offering solutions for particular cases. With respect to water availability and secondary pollution in terms of disposal, energy costs, versatility and latitude of applications, high solid technology is by far more recommendable compared to any other emerging technology. Regarding the market and academic interest for certain issues related to the coatings industry, one may observe that some topics pop up from time to time.

The present book gives an overview of binder categories and the possibilities of transferring them into high solid binders. It is meant to encourage the activity and development in high solid technology, offering broad latitude of choices and angles to tackle the technological and environmental problems and to exhaust the subject without any ambition.

This book addresses chemists involved in binder development, being merely a review of the instruments available in terms of chemistry, and design of modern compliant film forming polymers. Also paint and coatings chemists are targeted for a better understanding of chemistry and processes involved in film forming.

The author believes that a picture can say more than a thousand words; therefore, a large part of the present book is composed in the form of chemical reactions. The state of the art offers a multitude of possibilities and opportunities in binder formulation, exemplified by description and chemical reactions which hopefully will capture the reader's interest.

Malmo, Sweden, August 2008
Mircea Manea

Contents

1 General considerations

1.1 Introduction

Coatings have been used since the early days of human history. Defined as any liquefiable material designed for application to a substrate in a thin layer, they are further converted into a solid film after application. The main drivers behind the development of coating materials are their decorative and aesthetic function, along with the later development of the requirement for functional protective and signalling properties. Although the use of coatings may be regarded as unnatural as they reduce entropy, they are part of daily life. The history of coatings goes back over 25,000 years to cave paintings. The Bible describes the use of pitch to coat and protect Noah's Ark, and archaeological findings in the Middle East confirm the use of lime, silica, copper, and iron oxides to produce a variety of colours. The coating described in the Bible may be the world's first High Solid coating. In Asia, clear coatings were made using resins from insect secretions and tree sap.

Coatings add value to objects, protecting them and extending their lifespan. Coatings are generally produced from four groups of raw materials: binders, pigments, solvents and additives. Once applied, the coating begins to lose its solvent, leaving behind a hard, solid film made up of the remaining materials (binders, pigments and additives) that serves an aesthetic and protective function.

This book investigates possible strategies for reducing, minimising and eliminating solvents from coating formulations to minimise the environmental impact of coatings.

1.2 Coatings

Coatings are always present in modern society. They have many applications, including decorative, protective and functional purposes, and are used to treat many kinds of surfaces. The role that coatings fulfil depends on the area in which they are used, and they can combine different properties.

Environmental awareness has a strong impact on the composition and performance of coatings in modern society.

The main issue is emissions from coating systems. Consequently, great attention is paid to the volatile content of coatings. There has been a continuous preoccupation with

Mircea Manea: High Solid Binders

tackling the problem of volatile organic compounds in coatings. Development and trends have brought new systems to market that comply with the new requirements.

Solvent-free coatings have been developed, offering the benefits of high build-up in a single application, minimal surface defects due to the absence of solvents, excellent heat and chemical resistance, and lower overall application costs. However, development in this area has had to address certain drawbacks, such as poor impact resistance and flexibility, as well as short pot life. These issues have been tackled through new application techniques, where components are blended in the correct proportions during application, and through the development of new curing agents that provide better mechanical properties and a longer pot life.

High solids coatings resemble solventless coatings, but contain less than 30 % solvent and may also contain reactive diluters, low-molecular-weight multifunctional resins, or backbone structures containing moieties other than bisphenol A.

Powder coatings were developed in the mid-1950s [1, 2] and, despite slow market penetration during the 1960s using the fluidised bed process, are currently experiencing rapid growth. Following the breakthrough of the electrostatic spraying application method, powder coatings have been regarded as a fusion coating process, offering a range of significant advantages over traditional coating technologies, including 100 % non-volatile content, the elimination of the need for thinning or dilution, and the absence of solvents or other pollutants during application or curing. Furthermore, the application procedure is easier, and phenomena such as running, dripping and sagging, which are encountered with liquid coatings, do not occur. Other significant benefits include a low rejection rate, a tough, abrasion-resistant film, and a high reclaim rate by collecting and reusing the oversprayed coating.

Liquid low-emission coatings essentially comprise two categories: water-borne coatings and UV-curing coatings.

Water-borne coatings have developed significantly in recent years, although the basic principles were established in the late 1940s. Reviews of acrylic dispersion applications on different substrates list a series of properties that make these systems suitable for coating applications, thereby explaining the market growth.

Furthermore, UV-curing systems are growing in popularity as a high-speed, high-performance, low-energy application for coatings and inks, especially for wood substrates.

1.3 Quick guide to coatings

A quick guide to coatings schematically categorization can be done as in the Figure 1.1.

Interest in clean coating technology has led to the development and growth of the market share for water-borne, UV and powder coatings over the past few years. This approach has yielded a technology that is less polluting. While solvent-borne coatings offer

excellent performance, their significant solvent content raises concerns regarding environmental impact, toxicity and flammability. This has led to the development of alternative systems such as powder coatings, high solids, radiation-curable coatings and water-borne coatings. However, solvent-borne coatings continue to coexist with these emerging technologies, as illustrated by the increasing interest in them.
The perfect coating must respond to a series of demands, such as:
- workable
- good mechanical and chemical properties
- storage stability and long pot-life
- rapid curing ("curing on the whistle")

Recently these demands have increased by the ecological interest and constraints applied to this market segment:
- low energy consuming
- less pollutant
- chemistry based on renewable raw materials

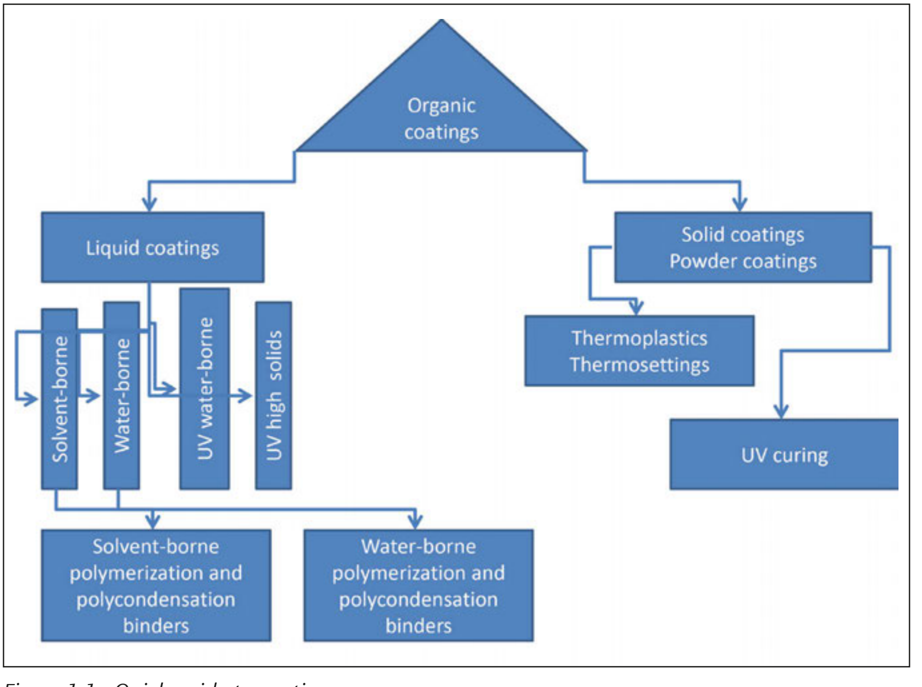

Figure 1.1: Quick guide to coatings

Table 1.1: Different principles of coatings

Function	Layer in the coating system	Purpose	Environmental compatibility	Chemistry of the film forming agent	Curing conditions
Clear coat	Primer	Car paint	Water-borne	Alkyd paint	Baking
Metallic paint	Surfacer	Decora-tive paint	Solvent-borne	Acrylic paint	Oxidative curing
Solid paint	Topcoat	Industrial paint	Radiation curing	Cellulose derivatives	Physical curing
		Wood paint	High solids	Polyurethane	Radiation curing
			Powder paint		Urethane curing

These demands are leading constantly to a green chemistry and to a higher non-volatile content. Coatings can be divided in accordance with different principles (Table 1.1).

The selection of the coating system must be in direct accordance with the specific technical, decorative and functional requirements, as well as the application conditions, substrate and curing process. All of these requirements converge to achieve optimum performance.

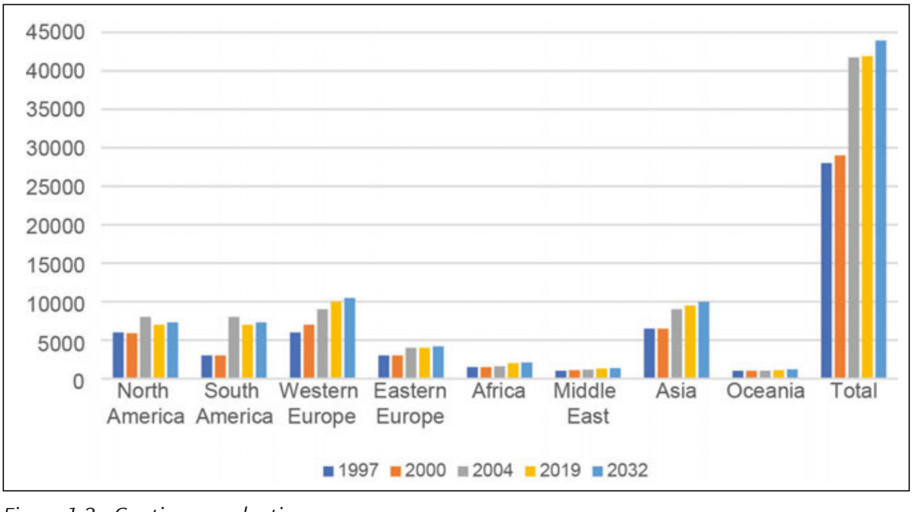

Figure 1.2: Coatings production summary

1.4 Coatings global market

Coatings, as ubiquitous part of the modern society, are manufactured at a level higher than 40 million tons per year. In the Figure 1.2, a summary of the geographical coatings production is presented. [177, 319, 326, 327]

The production volume of coatings is considered to be mature in areas such as North America, Japan and Western Europe, and is generally considered to be a reflection of the health of the economy. In other regions, such as the Asia-Pacific area, Eastern Europe, and South America, the coatings industry is still growing strongly, with an expected growth of 10–15 %, mostly due to economic growth in China.

Figure 1.3 shows the market structure as it was in 2023, and it is strongly influenced by geography. However, there is a declining trend for solvent-borne coatings, while radiation curing, powder and water-borne coatings are still pioneering. Despite their long history, high solids coatings still present strong potential and are able to take shares in the solvent-borne segment.

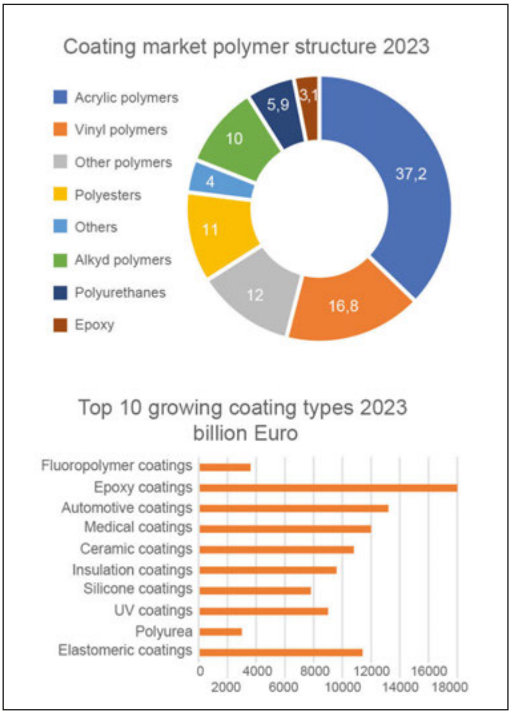

Figure 1.3: Coatings market structure

2 Environmental awareness

2.1 Environmental concerns

Air and water pollution has progressed over the last few decades from being an art to a science. This turn has evolved in both fundamental and applied research. Pollution today is regarded as a multidisciplinary approach that is directly related to the quality of life. While water pollution today mainly relates to secondary pollutants such as nutrients and refractory organics, air pollution is mainly dealing with harmful emissions.

The concept of air pollution has evolved over time. Three historical events had a considerable impact on raising awareness of air pollution:

- Week-long air stagnation in the Meuse Valley in Belgium in 1930, leading to the death of 60 people and respiratory problems for a large number of others.
- Air stagnation in Donora, Pennsylvania in 1948, resulting in nearly 7000 illness cases and 20 deaths.
- Four-day "killer fog" in London, England in 1952, resulting in 4000 deaths.

Air pollution is defined as any atmospheric condition in which substances are present in concentrations high enough above normal ambient levels to generate measurable effects in humans, animals, vegetation, or materials, or to produce an objectionable effect on the natural balance of any ecosystem.

The definition would comprehend any substance: solid, liquid or gas, which is generated in an anthropogenic activity or by natural sources that may as well affect the global climate or global ecosystem by a greenhouse effect or by an ozone depleting property.

Although these episodes were dramatised, they increased awareness of the acute health effects of high concentrations of air pollutants, and concerns have been raised over the longer-term chronic effects. This led to the introduction of a package of the original six criteria pollutants, as defined in the 1970s.

- sulfur dioxide [7446-09-5], SO_2
- nitrogen dioxide [10102-44-0], NO_2
- ozone (qv) [10028-15-6], O_3, also known as phytotoxins
- carbon monoxide (qv) [630-08-0], CO
- suspended particulates; and
- non-methane hydrocarbons, NMHC

Later a new concept was introduced, usually referred to as the maximum incremental reactivity (MIR). Species of volatile organic compounds that can combine with nitrogen oxides (NO_x) and under the sunlight energy are able to form ozone. The impact of a given VOC on formation of ground-level ozone is sometimes referred to as “reactivity”.

Similarly, owing to increased public awareness of water pollution, stringent waste-disposal regulations have been introduced, and the best available technology (BAT) had to be implemented to industrial wastewater treatment by the mid-1980s.

The NMHC are presently referred to as Volatile Organic Compounds, VOC. A source of VOC is the coating industry.

Environmental awareness and attention are presently mostly related to the release of carbon trapped for millions of years as coal and oil in the Earth crust into the atmosphere as carbon dioxide. The mass balance is still the same, but the partition of components drastically changed for the last 500 years.

The awareness of the impact of coatings on the environment has grown almost at the same speed as the market request and coatings production. The driver as finding less polluting solutions has increased along with the environmental concerns in general. This phenomenon has developed on both individual levels as well as through serious commitment and governmental regulations. [3, 4, 5].

Historically, it looks like the trend for higher non-volatile content in coatings has been initiated by the well-known “Rule 66” of California, on the emission level of photo chemically reactive solvents in paint formulations.These drivers, expressed as controlled emissions, environmental concerns, governmental regulations have inspired the development of coating industry in finding compliant solutions.

2.2 VOC regulations

Coatings are complex systems containing binders, pigments, additives, solvents, diluents, thinners. Binders, pigments and the largest number of additives are constituents of the solid matter of the coating system and are non-evaporating or non-volatile.

The volatile portion of coatings consists of water, solvents, diluents and reducers, which are removed by evaporation during application and drying. Most solvents, thinners and diluents contain VOCs.

By VOC it is understood any compound containing carbon that can participate in atmospheric photochemical reactions. In general, concerns relating to the concept of VOCs in coatings refer to any organic compound that does not remain in the coating film after the drying process. This comprises the entire volatile part of the coating, unless any specifically exempted compounds are listed. As VOCs are defined as carbon-containing compounds that participate in atmospheric photochemical processes, the list of chemicals is not definitive and is constantly under review and being updated.

Table 2.1: MIR values for some solvents

Solvent	MIR gram basis	MIR mole basis
Dimethyl carbonate	0.055	4.95
Ethane	0.26	7.8
Acetone	0.35	20.3
Methyl acetate	0.067	5.2
Propylene carbonate	0.27	27.56
Benzo trifluoride	0.28	40.91

There are thousands of individual species of VOC chemicals that can combine nitrogen oxides (NO_x) and the energy from sunlight to form ozone. The impact of a given VOC on formation of ground-level ozone is sometimes referred to as its "reactivity." It is generally understood that not all VOCs are equal in their effects on ground-level ozone formation. Some VOCs react extremely slowly and changes in their emissions have limited effects on ozone pollution episodes. Some VOCs form ozone faster, or they may form more ozone than other VOCs. Others not only form ozone themselves, but also enhance ozone formation from other VOCs. By distinguishing between more reactive and less reactive VOCs, it should however be possible to decrease ozone concentrations further or more efficiently than by controlling all VOCs equally. Assigning a value to the reactivity of a compound is a complex undertaking. Reactivity is not simply a property of the compound itself; it is a property of both the compound and the environment in which the compound is found. The reactivity of a single compound varies with VOC-NO_x ratios, meteorological conditions, the mix of other VOCs in the atmosphere, and the time interval of interest. Designing an effective regulation that takes account of these interactions is difficult and implementing and enforcing such a regulation carries the extra burden of characterizing and tracking the full chemical composition of VOC emissions. For a better understanding of VOCs an estimation scale has been implemented: MIR.

Maximum incremental reactivity (MIR) scale is designed using certain assumptions about meteorological and environmental conditions where ozone production is most sensitive to changes in hydrocarbon emissions and, therefore, is intended to represent conditions where VOC emission controls will be most effective. The MIR scale is expressed as grams of ozone formed per gram of organic compound reacted. Each compound is assigned an individual MIR value, which enables the reactivities of different compounds to be compared quantitatively. Individual MIR values now exist for many commonly used compounds, and a list of these individual values comprises a scale. Some MIR values are listed in Table 2.1.

2.3 Estimation of VOC emissions

The determination of the VOC content in a coating is simply done by the mass balance approach. The VOC content is generally available in the manufacturer's specification or material safety data sheet, in form of % by weight (*bw*) or volume (*bV*). In such cases the VOC can be calculated for each ingredient in the coating as Equation 2.1:

Equation 2.1:
$$\frac{g_{VOC}}{l_{coating}} = \frac{\%bw_{VOC}}{100} \cdot density$$

where density is given in g/l, and % is given in parts by weight (Equation 2.2)

Equation 2.2:
$$\frac{g_{VOC_i}}{l_{coating}} = \%bV \cdot density$$

where the density is given in g/l and the % of VOC_i is given in % by volume for component *i*. Hence the total VOC is the sum of all VOC components (Equation 2.3):

Equation 2.3:
$$Total\ \frac{g_{VOC}}{l_{coating}} = \sum_{1}^{n} VOC_i$$

The VOC regulations and targets differ from country to country. Below is given the EPA classification for coatings and the EPA target for United States of America [320].

2.4 Selected U.S. coating regulations by region

Table 2.2 presents the American regulation for different areas and coatings category.

2.5 Environmental targets in Europe

In Europe the targets are as follows and the strategy is a two-step process with toll gates scheduled for 2007 and 2010 (Table 2.3):

2.6 Non-VOC solvents

Some solvents are considered non-VOC. However, there are limitations when using them but solvents as dimethyl carbonate, diethyl carbonate, etc. are interesting in coatings (Table 2.4) and are very good solvents allowing a large latitude of combinations.

Table 2.2: VOC targets for North America. Values are given in g/l

Product sub-category	Cur-rent target	DE,NY, PA,VA 2005	SCAQMD 2002 July	SCAQMD 2008	Bay area 2004	OTC 2005	SCAQMD 2006 July	CARB 2004
Gloss, 70+at60°	380	250	150			250	50	250
Non-flat, 5-7at60°	380	150	150		150	150	50	150
Flat, 15at85º, 5at60º	250	100	100	50	100	100		100
Stain, does not conceal grain	550	250	250		250	250		250
Quick dry enamel, 70+gloss, 8 h dry hard	450	250	250		250	250	50	250
Quick dry primer, dry like enamel	450	200	200		200	200	100	350
Primer and undercoats	350	200	200		200	200	100	200
Floor, opaque	400	250	100		250	250	50	250
Varnish, clear wood finish	450	350	350		350	350		350
Industrial maintenance, wood or metal, primer, mid-and top-coat, industri-al use only	450	340	250		250	340		250
Rust preventive, metal only	400		400		400	400	100	400
Dry gog	400	400	400			400		400
Sanding sealer	550	350			350	350		350
Specialty primer, stain block type	-	350	350			350	100	350

Values are given in g/l

Table 2.3: VOC targets for Europe. Values are given in g/l

Product subcategory	**Technology**	**Phase I from 1.1.2007**	**Phase II from 1.1.2010**
Interior matt walls and ceilings (gloss <25 at 60°)	WB SB	75 400	30 30
Interior glossy walls and ceilings (gloss >25 at 60°)	WB SB	150 400	100 100
Interior/exterior trim and cladding paints for wood and metal	WB SB	150 400	130 300
Interior/exterior trim varnishes and wood stains, including opaque wood stains	WB SB	150 500	130 400
Interior and exterior minimally build wood stains	WB SB	150 700	130 700
Exterior walls of mineral substrate	WB SB	75 450	40 430
Primers	WB SB	50 450	30 350
Binding primers	WB SB	50 450	30 350
One-pack performance coatings	WB SB	140 600	140 500
Two-pack reactive performance coatings for specific applications such as floors	WB SB	140 550	140 500
Multicolored coatings	WB SB	150 400	100 100
Decorative effect coatings	WB SB	300 500	200 200

WB = water-borne
SB = solvent-borne

2.7 Categories of industrial surface coatings operation

An "in use" classification for coating categories for different application areas is presented by EPA (Table 2.5) for the United States. For the European Community, the product groups are listed in Table 2.3 along with the environmental targets.