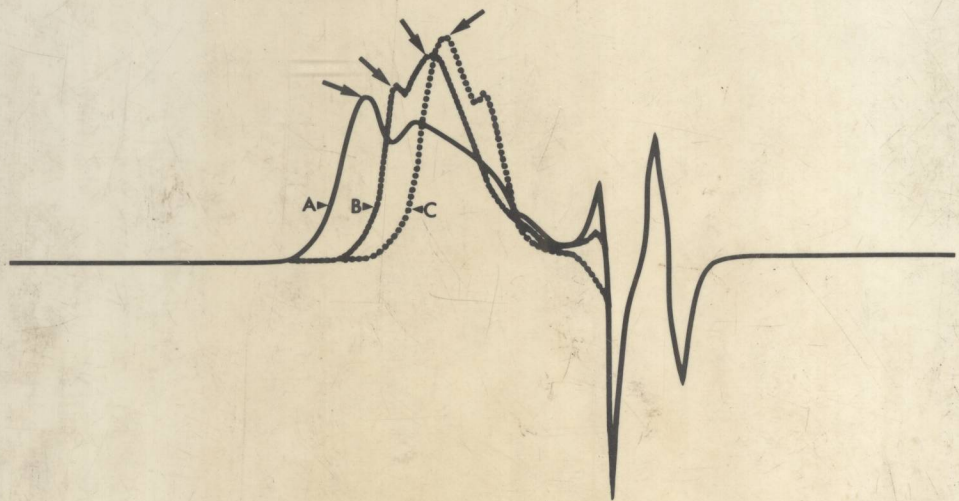


Books in Soils and the Environment

# High Solids Alkyd Resins



Krister Holmberg

# **High Solids Alkyd Resins**

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# Preface

High solids coatings are not new. Vegetable oils, especially linseed oil, have a long tradition both as high solids binders and as reactive solvents for other binders. In earlier days, however, a low solvent emission was not an important matter for the coatings industry. As new vehicles were developed that performed better but had a higher solvent demand, the industry rapidly switched to these.

During the last 10 to 20 years great pressure has been placed on the paint formulator to reduce the emission of organic solvents. "High solids" is an expression that has become known to everyone in the field. The goal to reduce the amount of volatile components in formulations is common with almost all types of paints and lacquers, air-drying as well as enamels. The same trend can be found almost everywhere where organic solvents are being used.

For alkyd-based paints there are two main alternatives to reduced levels of volatile organic solvents: high solids and water-reducible systems. This volume deals with high solids. The pre-

dominant aim of this monograph is to cover the chemistry, as opposed to the technology, of high solids compositions. This means that emphasis is put on the binder component and, to a lesser extent, on the solvent. Formulations of high solids surface coatings are only dealt with in passing. Appropriate formulations are usually available from the raw material suppliers.

Factors controlling the viscosity and, consequently, the solids contents of alkyd resins are discussed in relative detail. Different approaches mentioned in the literature to preparing high solids alkyds are described. Since the solids content of the binder is intimately linked to the choice of solvent, Chapter 4 is devoted to this subject.

Alkyd resins for stoving are generally combined with amino resins, usually melamine- or urea-formaldehyde condensates. Melamine resins are preferred in high solids formulations. Systems of this type are discussed in Chapter 5.

The topic of high solids alkyds would not be complete unless a chapter dealing with reactive solvents for these binders were included. The emphasis in Chapter 6 is on newer developments in the area. The traditional system of this type, i.e., styrene-unsaturated polyester, is also described.

*Krister Holmberg*

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# 1

## Introduction

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## 1.1 THE MEANING OF HIGH SOLIDS

High solids coatings is only one of several approaches to solventless or solvent-free paints. The move toward a higher nonvolatile content for paints and lacquers can be said to have been initiated in 1966 by the well-known "Rule 66" of California, which regulates the emission levels of photochemically reactive solvents in paint formulations. However, it is only during the last decade that paints with a considerably higher solids content have entered the market.

Strictly speaking, the term "high solids" refers to coatings with more than 80% nonvolatiles by volume. In practice, paints with 70% and even 60% volume solids are usually included in the high solids category. However, since the higher level is necessary for exemption under air pollution legislation, this is the goal that the industry is striving for.

Because the solvent is the component of a paint formulation with the lowest density, the 80% volume figure corresponds to 85-88% weight solids. Thus, to fulfill the strict demand of a high solids formulation, only 12-15 g of solvent (the exact amount depending mainly on the type and amount of pigment used) can be employed. Achieving this level without affecting drying and film properties in a negative way places extreme demands on the binder, as well as on the solvent.

Throughout the book, the term "high solids" is used in a free sense and is not restricted to formulations having 80% or more nonvolatiles by volume.

## 1.2 DRIVING FORCES

The main driving forces for the reduction of solvents in paints and lacquers are

- air pollution control
- control of indoor emission of solvents
- energy savings
- materials savings
- time savings

The last three points refer to the evaporation of solvent during the drying and curing operations. Even if a considerable amount of resources were wasted in these processes, the pollution aspects, exterior and interior, are by far the most important driving forces for the development of high solids paints. In the following, air pollution regulations will be briefly discussed. The reader is referred to Ref. 1 for a more comprehensive review of the air pollution regulations in the United States and in various European countries.

The objective of Rule 66 of California was to control the emission level of "photochemically reactive" solvents. Major emphasis was given to aromatic solvents and to some ketones. As a consequence, the concept of so-called exempt solvents was born and rapidly used in many types of paints.

It gradually became clear, however, that a division of solvents into these two categories is not adequate. Harmless organic compounds can, for instance, become irritants by reactions in the atmosphere induced by ultraviolet light.

In accordance with this view the U.S. Environmental Protection Agency (EPA) has enforced the concept of Volatile Organic Compounds (VOC) as its measure of emission control. All

components in a paint—not only solvents—are defined as volatile if the vapor pressure exceeds 13.3 Pa (0.1 mm Hg) at 25°C. (There are still exceptions, discussed later.)

The amount of solvent emitted during the coating process depends not only on the solids content of the paint but also on the efficiency of the application process. In the EPA guidelines, as well as in the Clean Air Act of 1977, *total* emission of volatile compounds is discussed, including application losses.

The VOC requirements of paints also vary from industry to industry and depend on whether the coatings are stoved or air dried at temperatures below 90°C. For baking enamels with stoving temperatures above 90°C, lower VOC values are required.

The VOC of a paint is measured on the paint as it is being used, according to the expression

$$\text{VOC} = \rho \frac{100 - \text{NV}_s}{100}$$

where  $\rho$  = density of the paint in kg/m<sup>3</sup> (or g/l)

$\text{NV}_s$  = % nonvolatile by weight

The VOC value is then obtained in kg/m<sup>3</sup> (or g/l).

Also in the EPA guidelines two solvents, dichloromethane and 1,1,1-trichloroethane, have been exempted from control. These two chlorinated solvents are considered to have negligible photochemical reactivity in the troposphere and no significant impact in the stratosphere. This has led to an increased use of these two solvents in high solids and radiation curing systems.

In Europe many countries have differentiated the solvents according to their harmfulness. West Germany is the forerunner in this respect with its Federal Emission Law of 1974. The volatile emissions are divided into three classes, with Class I com-

pounds having extremely low emission limits. Most of the commonly used paint solvents belong to Classes II or III. The limits for each class have gradually been reduced since the law was issued and some solvents have been reclassified. Most West European countries have regulations or recommendations which basically follow either the United States or West Germany. The situation is very complex, however, and many countries have regional air pollution regulations.

### 1.3 EMERGING TECHNOLOGIES

The high solids concept is not the only development line being pursued in order to reduce the amount of organic solvent in paints and lacquers. A number of new technologies, all derived from the demand to reduce or eliminate the organic solvent from the coating system, have become established on the market today. The most important of these, apart from high solids coatings, are powder coatings, waterborne coatings, radiation curable coatings, and reactive diluent systems. Each one of these will be discussed briefly later.

#### 1.3.1 Powder Coatings

Powder coatings may be regarded as the ultimate form of high solids systems. They have been on the market for about two decades by now, but their breakthrough, which has been predicted is yet to be seen. Powder coatings are today being used in applications such as household products, electrical devices, and in the automotive industry. Besides the very low emission of volatile compounds, powder coatings have a number of advantages, such as high application efficiency, low energy consumption, and low labor and clean-up costs.

Powder coatings may be based on either thermoplastic or thermosetting polymers. The former are mainly applied by a fluid-bed process, and no chemical curing process takes place after application. The thermosetting polymers are normally applied by electrostatic spray processes, and the material undergoes polymerization on heating after application.

Representative examples of thermoplastic and thermosetting polymers are as follows:

Thermoplastic	Thermosetting
Polyesters	Polyesters
Polyamides	Polyacrylates
Polyolefins	Epoxy resins
Cellulose esters	

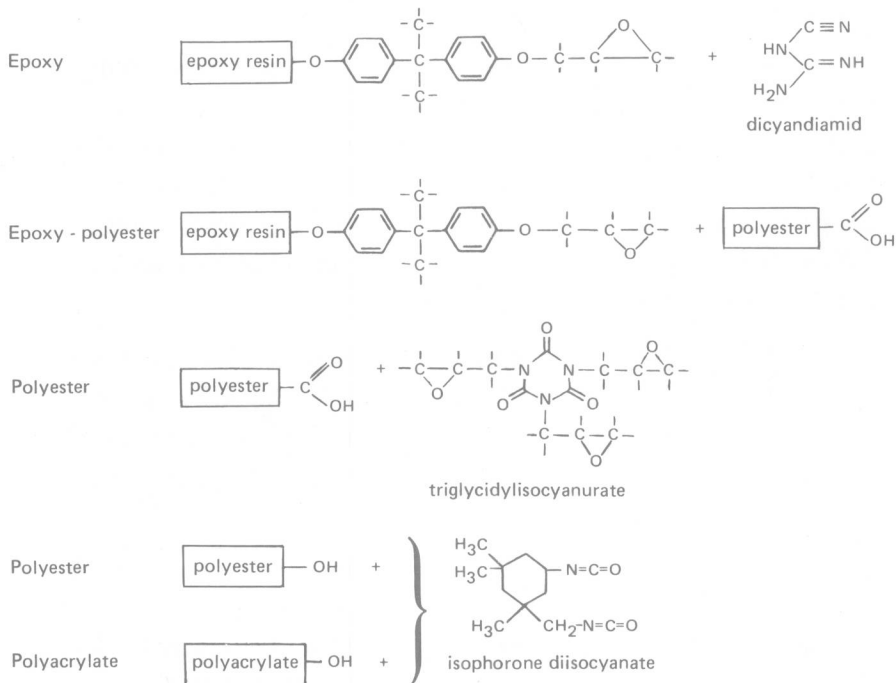
High quality finishes are obtained with thermosetting two-component systems. The curing conditions are typically 15 min at 140-160°C, and application by modern high voltage powder guns can give relatively thick, smooth films even on irregular surfaces. Oversprayed powder can be recovered to a large extent and reused. The waste in powder coating operations is, therefore, very small.

The main curing reactions taking place with thermosetting powder coatings are given in Figure 1.1. In the majority of powder coating compositions epoxy resins are involved either as the main component or as the cross-linker.

References 2-5 give deeper descriptions of the area.

### 1.3.2 Waterborne Coatings

Waterborne coatings may be subdivided into two major groups, aqueous dispersions having a particle size in the range of 0.1-3

Main PolymerCuring Reaction

**Figure 1.1** Powder coatings systems.

$\mu\text{m}$  and water reducible coatings with a particle size below  $0.01 \mu\text{m}$ . Coating systems of intermediate particle size ( $0.01\text{--}0.1 \mu\text{m}$ ) have also been described, for instance in the context of micro-emulsions of alkyds, but they seem not to have reached the market on a larger scale yet.

Aqueous dispersions or latexes are composed of polymer particles dispersed in water and stabilized with surfactants. Both thermoplastic and thermosetting systems of this type are so well established on the market that they, as a group, can hardly be included within the concept of emerging technologies. However, new advanced fields are being developed within the frame-

work of aqueous dispersions. Polyurethane dispersions [5] are probably the best example of this.

Water-reducible coatings are usually made by employing polymers possessing either carboxylic or amino groups that are partially or fully neutralized with base or acid, respectively. Carboxyl-containing alkyds and acrylics neutralized with amines are the prime examples of this class of coatings. A water-miscible solvent (coupling solvent) must usually be added as well, and, in practice, the VOC may be rather high.

Water-reducible resins have an established position in electrodeposition coating compositions. These can be either anionic, e.g., polybutadiene adducts containing 5-25% maleic anhydride and often modified with phenolic resin, or cationic, e.g., amino functional epoxy resins.

Introduction of polyglycol ether chains into the alkyd or polyacrylate resin molecule is an alternate way of introducing a certain water solubility. This has been suggested as a way to eliminate the use of volatile amines and coupling solvents [6]. Water sensitivity of the cured film and poor adhesion to many substrates are, however, severe drawbacks of this approach.

Water-reducible coatings are reviewed in Ref. 4.

### 1.3.3 Radiation Curable Coatings

Radiation-curable coatings comprise ultraviolet (UV), electron beam (EB), infrared (IR), and microwave cured systems. Only UV and EB curing seem to be of commercial importance for paints and lacquers today. It should be noted, however, that IR curing is being used on a large scale in the related paper-coating process.

The energy input and the type of curing mechanism for the various processes are shown in Table 1.1.

**Table 1.1** Energy Input and Curing Mechanisms for Various Radiation Curing Processes

Source	Energy (ev)	Curing Mechanism
Electron beam	$10^5$	Ionization excitation
Ultraviolet	5	Electronic excitation
Microwave	$10^{-3}$	Thermal
Infrared	$10^{-1}$	Thermal

UV curing systems is by far the most common of the radiation processes. The main components of such a system are the following:

1. A low-molecular resin containing olefinic bonds.
2. A reactive solvent, also containing unsaturated groups.
3. A photoinitiator.

Originally, unsaturated polyesters were used as the polymer in UV curing systems. However, these systems have a relatively low curing rate and are of limited use today. Instead, acrylate-based prepolymers are widely used. These may either be polyacrylate resins or some other polymer, e.g., alkyd, epoxy, or polyurethane, modified with acrylate groups. Acrylated polyesters, prepared by esterification of free hydroxyl groups of the polymer with acrylic acid, have gained widespread use.

Acrylic esters are normally used for the reactive solvent. Mixtures of monofunctional and di- or polyfunctional monomers are frequently employed. Acrylated polyols, e.g., trimethylolpropane triacrylate and pentaerythritol triacrylate, have been found to be particularly effective in combination with a number of polymers [7]. Styrene is used as the main monomer in combination with nonmodified unsaturated polyesters.



The role of the photoinitiator is to generate active species through light absorption. These species subsequently disintegrate to radicals and ions, which bring about the polymerization in the system. Acetophenones, benzophenones, benzil derivatives, and benzoin ethers are the most commonly used initiators.

UV curing systems have an established position in wood coatings. They have reached a commercial position in a number of other areas as well, but a major breakthrough has not yet occurred. Problems such as oxygen inhibition, light absorption, and scattering by pigments and the toxicity of the monomers seem to be severe drawbacks for the technique in the future.

References 4 and 8 are review articles on radiation curable coatings.

#### 1.3.4 Reactive Diluent Systems

UV curing systems may be regarded as a good example of reactive diluent systems. However, by convention only thermally cured systems are included in this category, and systems cured by irradiation are normally dealt with separately.

Reactive diluent systems are closely related to high solids systems, and the subject is treated in Chapter 6. The reactive diluent concept should probably not be regarded as a development line of its own, but could be viewed as an integrated part of the development of high solids systems. A small amount of reactive solvent as part of the total volume of solvent is a way of further increasing the nonvolatile content of a high solids formulation.

For high solids alkyds the concept can be used both for air-drying and stoving coatings. In the former case the diluent must contain a group capable of participating in the autoxidation process, e.g., an allyl ether function. For stoving alkyds used in