

ORGANIC COATINGS

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Volume
5

edited by

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PREFACE

This publication is based on papers originally presented at the Seventh International Conference in Organic Coatings Science and Technology in Athens, Greece. With the 1981 Conference, the Athens Conference (to give it its popular name) has firmly established itself as the premier annual scientific and technological conference on coatings in Europe. The conference is modeled on the U. S. Gordon Conference. There were 21 invited and 5 short contributed papers.

The latest developments in the field of organic coatings were presented with talks in the area of binders, with special emphasis on epoxies, powder and water-soluble coatings, and pigments. The sciences of rheology and adhesion as applied to the coatings technology was also discussed. Novel, but practical coatings application techniques was the subject of some presentations.

Most of the papers presented at the conference are collected in this volume. The topics covered range from developmental efforts to fundamental research.

We would like to express our appreciation to all those who helped in preparing this volume, especially the authors.

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RECENT DEVELOPMENTS IN EPOXY RESINS

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INTRODUCTION

Superimposed on the evolutionary advancements that are intrinsic traits of the coatings industry, ecological pressures and the need to conserve energy are creating demands for major technological changes in the coatings industry. For example, the United States Environmental Protection Agency (EPA) has issued guidelines they want enacted by individual regions in the United States before December 1982, limiting the amount of solvent in industrial coatings on an industry-by-industry basis. These guidelines are summarized in Table 1.1, and as can be seen, with only a few exceptions most industries will be required to limit the volatile organic compounds emitted to 340 g/L of paint or less. The 340 g/L limit very roughly corresponds to 60%-65% volume solids, depending on the composition of the particular coating.

The model rule for marine coatings adopted by the California Air Resources Board (CARB) will eventually prohibit coatings from containing more than 295 g of volatile organic material per liter of coating as applied. The CARB model rule dealing with so called architectural coatings, which includes by CARB definition industrial maintenance coatings, proposes a 250 g/L limit. The 295 g/L and 250 g/L limits very roughly correspond to 65% and 70% volume solids, respectively. There is already much activity in at least 25 other states to adopt high solids regulations similar to the CARB model rules.

TABLE 1.1
EPA Guidelines
Recommended Limitations^a for
Various Industrial Coatings

Coating Use	Recommended Limitations	
	Volatile Organic Components g/L	Approx %v
Automobile primers	230	70-75
Automobile topcoats	340	60-65
Large appliances	340	60-65
Can coatings		
Roller coatings	340	60-65
Interior spray	500	45
Side seam spray	660	30
Coil coatings	310	65
Metal furniture	360	60
Magnetic wire insulation	200	75-80

^aRecommended limitations obtained from a publication of the United States Environmental Protection Agency. The volume percentages were estimated from the EPA recommended limitations.

It is estimated then that in the United States, the market percent for all types of industrial coatings resins going into solution coatings (coatings having less than 70% v solids) will drop during the period from 1977 to 1985 from 74% to 33%. The market for resins in all types of high solids industrial coatings (coatings having more 70% v solids) will increase in this period from 6% to 23% (Table 1.2). These changes, though spawned by government legislation to reduce solvent-vapor emissions, will certainly result in other benefits, such as lower energy consumption during curing and baking operations as well as substantially reduced solvent costs.

These pressures have not gone unnoticed by the suppliers of epoxy resins, curing agents, and manufacturers of epoxy resin coatings. Over the past 5 years, epoxy resin sales in the United States have experienced an annual growth rate of about 8%/year. In 1980, production of epoxy resins exceeded 288 million pounds and domestic sales were greater than 254 million pounds with the markets being divided almost equally between protective coatings and structural end uses [1] (Figure 1.1). Although small when compared to the volume of alkyds and polyesters used as binders by

TABLE 1.2
Technology Forecast
Industrial Coating Resins

	Percent Market Share		
	1977	1981	1985
Solution (< 70% v)	74	48	33
High solids (> 70% v)	6	16	23
Powder	3	5	6
Water-borne	14	25	31
Other (UV)	3	6	7

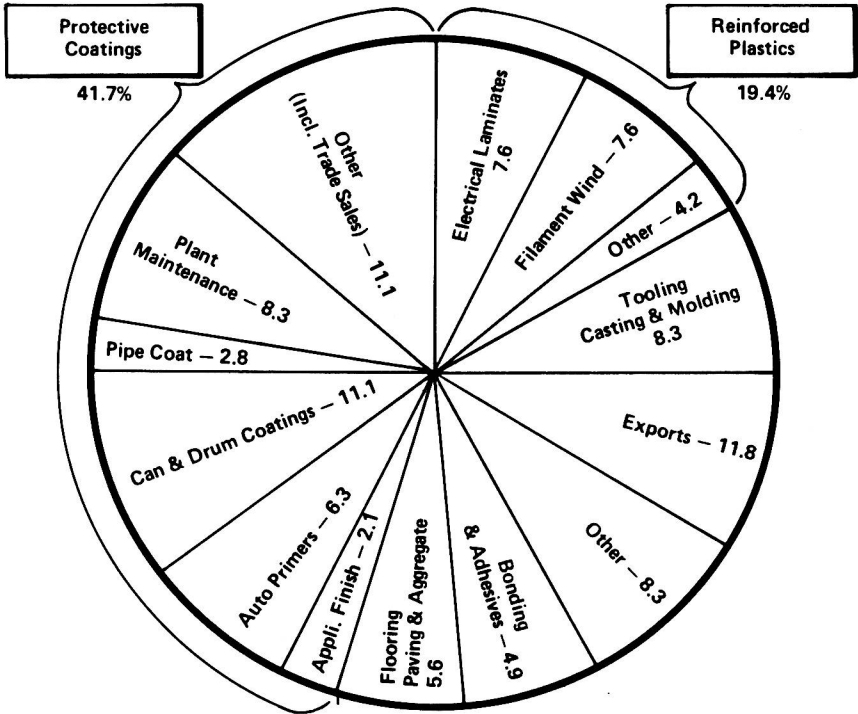


FIGURE 1.1 Epoxy resin consumption by end-use (1980).

the coatings industry in the United States, it still constitutes a significant quantity of premium high performance organic coatings. The following describes some of the recent interesting developments in epoxy resin technology that should assure continued epoxy resin usage in the premium coatings market.

WATER-BORNE EPOXY COATINGS

Water-borne coatings have always offered considerable promise as a means of obtaining ecologically compliant coatings for industrial applications. Unfortunately, they have not entirely lived up to that promise, and water-borne epoxy resin coatings have been no exception. Many attempts have been made to develop such coatings, and some of these have met with a certain amount of success for particular applications, such as electro-deposited primers, industrial maintenance coatings, and coatings for beer and beverage cans. The patents and publications dealing with new water-borne epoxy based coating resins and epoxy coatings are too numerous to deal with here in any depth. Therefore, this discussion will be limited to the approaches to water-borne epoxy finishes that are currently showing the greatest technical and commercial success.

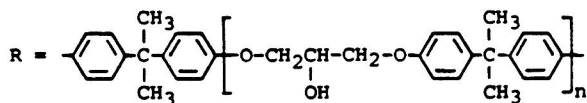
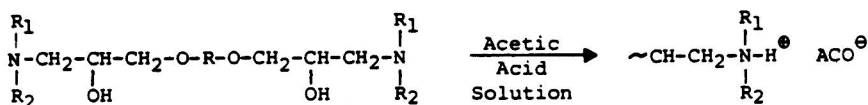
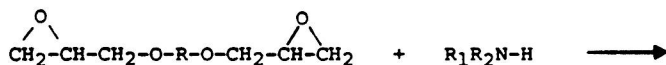
Water-Borne Baking Finishes

The application where epoxy resin based water-borne coatings probably have achieved their greatest success to date is in automotive primers applied by electrodeposition (ED). Electrodeposition of coatings using anodic systems is well established technology, having the proven advantages of efficiency of coating utilization, being essentially nonpolluting, and capable of a high degree of automation. More recently, however, cathodic systems have been replacing the anodic type because of the increased corrosion resistance obtained with cathodic coatings while retaining the advantages of the anodic process. The preferred system appears to be based on:

- (1) a hydroxyl-containing reactive product of a primary or secondary amine and a polyepoxide, which is solubilized with an acid, and
- (2) a blocked isocyanate crosslinker, which is stable at ambient temperatures in the presence of the hydroxyl-containing material but reactive with the epoxy adduct at elevated temperatures.

Even in the area of cathodic electrodeposition the literature is now extensive. The following illustrates some of the types of systems proposed for solubilizing the hydroxyl containing portion of the system. In the first example, the terminal epoxy groups of a polyglycidyl ether are reacted with a primary or secondary amine [2] to give an adduct that can be subsequently solubilized by addition of acid, such as or acetic or lactic acids.

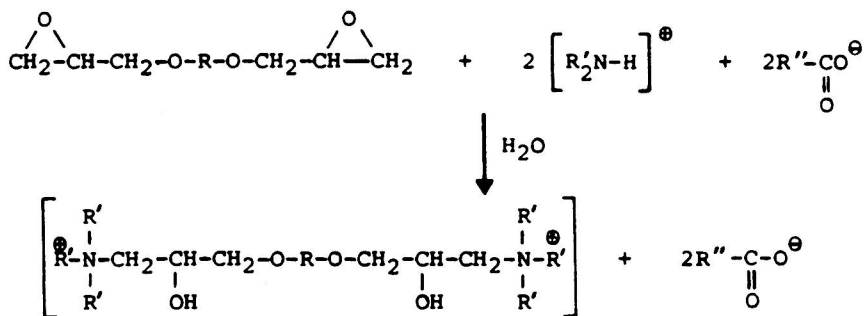
AMINE FUNCTIONAL POLYMERS

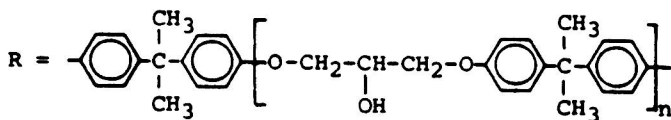


R_1 and R_2 = Hydrogen and/or Alkyl

In a second approach, the terminal epoxy groups are adducted with a tertiary amine salt or an internal zwitterion formed, for example by the reaction of a secondary amine and a conjugated unsaturated carboxylic acid [3].

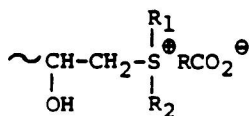
QUARTEARNARY AMMONIUM SALT PROCESS



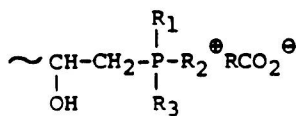


R' and R'' = Alkyl Groups

Also terminal epoxy groups of polyepoxides have been reacted with sulfides and phosphines to give products, which in the presence of an acid result in water dispersible quaternary sulfonium [4] and phosphonium salts [5], respectively.



SULFONIUM SALT



PHOSPHONIUM SALT

A unique feature of many of these cationic electrodeposition systems is that they are cured with blocked isocyanates. The cure of aminoplast resins typically used as crosslinkers in anodic systems is retarded in these cationic systems by the influence of the amine functionality. The blocked isocyanates are reported to be diurethanes from toluene diisocyanate with, for example, 2-ethylhexanol. Cure schedules for these systems range from about 45 min at 350°F to 10 min at 380°F.

Anodic electrodeposition binders have been reported with much improved corrosion resistance over the current state-of-the-art systems [6a]. Development of these improved ED binders was based on the principle that hydroxyl functionality promotes binder adhesion to the substrate, and consequently improves corrosion resistance as illustrated in Table 1.3. The data summarized in the table indicates good salt-spray resistance on bare steel is obtained with coatings containing between 200 and 400 meq hydroxyl groups per 100 g resin, and it appears that salt spray resistance is unrelated to the degree of crosslinking of the systems.

A typical approach to hydroxyl rich binders of this type is to react the terminal epoxy groups of a solid epoxy resin with stoichiometric quantities of hydroxy acids, such as lactic or dimethylol propionic acid (DMPA).