

# ORGANIC

SCIENCE AND TECHNOLOGY
THIRD EDITION

ZENO W. WICKS, JR. • FRANK N. JONES S. PETER PAPPAS • DOUGLAS A. WICKS

# Organic Coatings

#### Science and Technology

Third Edition

Zeno W. Wicks, Jr.

Frank N. Jones

Sastern Michigan University

S. Peter Pappas
Consultant

**Douglas A. Wicks** University of Southern Mississippi



A JOHN WILEY & SONS, INC., PUBLICATION

Cover: Scanning electron micrograph of alumina flakes. Courtesy of F. J. Maile, G. Pfaff, and P. Reynders, Merck KGaA, Pigments R&D. Reprinted from *Progress in Organic Coatings*, Vol. 54(1), F. J. Maile, G. Pfaff, and P. Reynders, "Effect pigments—past, present, and future," pp. 150–163, 2005, with permission from Elsevier.

Copyright © 2007 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 & 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

#### Library of Congress Cataloging-in-Publication Data:

Wicks, Zeno W.

Organic coatings: science and technology / Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas; consultant, Douglas A. Wicks.

p. cm.

Includes index.

ISBN 978-0-471-69806-7 (cloth)

1. Plastic coatings. I. Jones, Frank N., 1936 - II. Pappas, S. Peter

(Socrates Peter), 1936- III. Title.

TP1175.S6W56 2006

667'.9- -dc22

2006013297

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

#### Organic Coatings



#### THE WILEY BICENTENNIAL-KNOWLEDGE FOR GENERATIONS

ach generation has its unique needs and aspirations. When Charles Wiley first opened his small printing shop in lower Manhattan in 1807, it was a generation of boundless potential searching for an identity. And we were there, helping to define a new American literary tradition. Over half a century later, in the midst of the Second Industrial Revolution, it was a generation focused on building the future. Once again, we were there, supplying the critical scientific, technical, and engineering knowledge that helped frame the world. Throughout the 20th Century, and into the new millennium, nations began to reach out beyond their own borders and a new international community was born. Wiley was there, expanding its operations around the world to enable a global exchange of ideas, opinions, and know-how.

For 200 years, Wiley has been an integral part of each generation's journey, enabling the flow of information and understanding necessary to meet their needs and fulfill their aspirations. Today, bold new technologies are changing the way we live and learn. Wiley will be there, providing you the must-have knowledge you need to imagine new worlds, new possibilities, and new opportunities.

Generations come and go, but you can always count on Wiley to provide you the knowledge you need, when and where you need it!

WILLIAM J. PESCE

PRESIDENT AND CHIEF EXECUTIVE OFFICER

PETER BOOTH WILEY

## Preface

Significant advances have been made since the publication of the second edition of *Organic Coatings: Science and Technology*. The third edition has been completely updated. Our purpose remains the same, which is to provide a reference and textbook that interrelates coatings technology with current scientific understanding.

Entire books could be written about the subject of each chapter, and many have been. To be as comprehensive as possible in the limited space available, we have had to limit coverage of each topic and have selected references for readers seeking more detailed information. We have striven to enhance the usefulness of this edition both as a classroom textbook on coatings science, as well as a reference book, by improving the presentation of each topic. The reader will benefit from having taken college level chemistry courses through organic chemistry, but no coursework in polymer science is assumed.

Many of the chapters include brief descriptions of coatings compositions and applications, supported by references, which could be omitted or used for outside assignments, such as term papers, particularly in an advanced course. These descriptions tend to be placed in the later sections of each chapter and tend to be more prevalent in the application chapters. These compositions and applications particularly enhance the value of the volume as a reference book and self-teaching text. We understand that the second edition was used widely for this purpose. We have also defined the jargon of coatings to help newcomers to the field understand its specialized language. Although the book is written specifically about coatings, many of the principles involved apply to the related fields of printing inks, adhesives, and parts of the plastics industry.

Coatings technology evolved empirically, by trial and error. The last few decades have seen a marked increase in scientific understanding of the applicable principles, but the complexities of the field are such that the formulator's art is still essential in developing and using coatings. The need to reduce air pollution while maintaining and, preferably, improving coating performance requires radically new formulations on a short time scale. Our conviction is that increased understanding of the underlying science can help

formulators work more effectively and that an appreciation of a formulator's craft is essential for scientists working in the field.

We do not claim to provide a complete literature review on each topic, but believe that many of the key references are cited. Readers are cautioned that the quality of the literature in the coatings field is uneven. Many published papers and monographs are excellent, but some are not; unfortunately, some authors did not fully understand the complexity of the field.

Many of the chapters in this edition were reviewed by people with extensive working experience with the particular topic. These reviewers were: David Bittner, Randall Brady, Adelbert Braig, John Bright, David Cocuzzi, Nico Enthoven, Ray Fernando, Werner Funke, Loren Hill, George Pilcher, Bradley Richards, Christian Schaller, John G. Stauffer, and Peter Wolfgang. Special thanks to Clifford Schoff, who reviewed three chapters and a section of another. We acknowledge the contributions of students and staff from the Wicks and Thames/Rawlins Research Groups at the University of Southern Mississippi. Special appreciation is expressed for the assistance of Helen Rassier, Stacy Trey, and Todd Williams of the Wicks Research Group.

# Symbols and Units

A	Arrhenius preexponential term
C	concentration, weight per unit volume of solution
°C	degrees Celsius
C	concentration, moles per liter
E	modulus; relative evaporation rate
E'	storage modulus (elastic modulus)
E''	loss modulus
$E_{\rm a}$	thermal coefficient of reaction rate (Arrhenius activation energy)
F	functionality of a monomer
$\bar{F}$	average functionality of a monomer mixture
f	functionality of a polymer (resin)
$rac{f}{ar{f}_{ m n}}$	number average functionality of a polymer (resin)
G	free energy; Small's molar association constant; force applied in
	a tensile test
$G_{c}$	force to crack in a tensile test
g	gram
g	gravitational constant
H	enthalpy
h	film thickness
i	angle of incidence
K	Kelvin temperature
K	absorption coefficient

Note that all acronyms are listed in the index.

$K_{\mathrm{E}}$	Einstein (shape) constant
k	rate constant
kg	kilogram
L	liter
M	molecular weight
$ar{M}_{ m c}$	average molecular weight between cross-links
$ar{M}_{ m n}$	number average molecular weight
$ar{M}_{ m w}$	weight average molecular weight
mL	milliliter
mP·s	millipascal second = 1 centipoise
N	newton
N	number of moles; refractive index
P	vapor pressure, degree of polymerization
$ar{P}_{ ext{n}}$	number average degree of polymerization
${ar P}_{ m w}$	weight average degree of polymerization
p	extent of reaction
$p_{\rm g}$	extent of reaction at gelation onset
rg	
Pa	pascal
Pa·s	pascal second = 10 poise
PDI	polydispersity index = $\bar{M}_{\rm w}/\bar{M}_{\rm n}$
R	gas constant
r	angle of reflection or angle of refraction
S	entropy; scattering coefficient
S	second
T	temperature; time
$T_{\rm b}$	brittle-ductile transition temperature
$T_{g}$	glass transition temperature
$T_{\rm m}^{\rm s}$	melting point
tan δ	tan delta, loss tangent, $E''/E'$
V	molar volume
$V_{\rm i}$	volume fraction of internal phase
W	weight fraction
X	film thickness
X	mole fraction
X	optical path length
γ	surface tension
Ϋ́	shear rate
δ	solubility parameter; phase shift in viscoelastic deformation
3	molar absorbance; strain
η	absolute shear viscosity
$\eta_e$	external phase viscosity; extensional viscosity
$\eta_{\rm r}$	relative viscosity = $\eta/\eta_s$
$\eta_s$	viscosity of solvent
[η]	intrinsic viscosity
$[\eta]_{w}$	weight intrinsic viscosity
$[\eta]_{\theta}$	intrinsic viscosity under theta conditions
r.110	

#### SYMBOLS AND UNITS XXIII

θ	contact angle
λ	wavelength
$\nu$	kinematic viscosity; Poisson's constant
$\nu_{\rm e}$	mole of elastically effective network chains per cubic centimeter
ρ	density
σ	shear stress
$\sigma_0$	yield value
ф	packing factor
Υ	activity coefficient

### **Contents**

Pref	ace	xix
Sym	bols and Units	XX
1.	What Are Coatings?	1
	1.1. Definitions and Scope / 1	
	1.2. Composition of Coatings / 4	
	References / 6	
2.	Polymerization and Film Formation	7
	2.1. Polymers / 7	
	2.1.1. Molecular Weight / 9	
	2.1.2. Morphology / 13	
	2.2. Polymerization / 17	
	2.2.1. Chain-Growth Polymerization / 17	
	2.2.2. Step-Growth Polymerization / 23	
	2.3. Film Formation / 27	
	2.3.1. Film Formation by Solvent Evaporation from Solutions of Thermoplastic Binders / 28	
	2.3.2. Film Formation from Solutions of Thermosetting Resins / 28	
	2.3.3. Film Formation by Coalescence of Polymer Particles / 34	
	General References / 38	
	References / 39	
3.	Flow	41
	3.1. Shear Flow / 41	
	3.2. Types of Shear Flow / 42	

	3.3. Determination of Shear Viscosity / 46	
	3.3.1. Capillary Viscometers / 47	
	3.3.2. Rheometers / 48	
	3.3.3. Rotating Disk Viscometers / 49	
	3.3.4. Bubble Viscometers / 50	
	3.3.5. Efflux Cups / 50	
	3.3.6. Paddle Viscometers / 51	
	3.4. Shear Viscosity of Resin Solutions / 52	
	3.4.1. Temperature Dependence of Viscosity / 53	
	3.4.2. Dilute Polymer Solution Viscosity / 54	
	3.4.3. Concentrated Polymer Solution Viscosity / 55	
	3.5. Viscosity of Liquids with Dispersed Phases / 59	
	3.5.1. Thickeners for Latex Coatings / 62	
	3.6. Other Modes of Flow / 63	
	3.6.1. Turbulent Flow / 63	
	3.6.2. Normal Force Flow / 64	
	3.6.3. Extensional Flow / 64	
	General References / 66	
	References / 66	
	Market I December 1	-
4.	Mechanical Properties	68
	4.1. Introduction: General Comments on Testing of Coating Films / 68	
	4.2. Basic Mechanical Properties / 70	
	4.3. Formability and Flexibility / 74	
	4.3.1. Fracture Mechanics / 82	
	4.4. Abrasion and Mar Resistance / 83	
	4.4.1. Abrasion Resistance / 83	
	4.4.2. Mar Resistance / 85	
	4.5. Measurement of Mechanical Properties / 86	
	4.6.1. Field Exposure Tests / 89	
	References / 95	
5.	Exterior Durability	97
	5.1. Photoinitiated Oxidative Degradation / 97	
	5.2. Photostabilization / 100	
5.	4.6.2. Laboratory Simulation Tests / 89 4.6.3. Empirical Tests / 90 General References / 94 References / 95 Exterior Durability	97

	5.2.3. Hindered Amine Light Stabilizers / 104	
	5.2.4. Pigmentation Effects / 106	
	5.3. Degradation of Chlorinated Resins / 108	
	5.4. Hydrolytic Degradation / 109	
	5.5. Other Modes of Failure on Exterior Exposure / 111	
	5.6. Testing for Exterior Durability / 112	
	5.6.1. Accelerated Outdoor Testing / 112	
	5.6.2. Analysis of Chemical and Mechanical Changes / 114	
	5.6.3. Accelerated Weathering Devices / 116	
	General References / 118	
	References / 118	
6.	Adhesion	121
	6.1. Surface Mechanical Effects on Adhesion / 121	
	6.2. Effects of Internal Stress and Fracture Mechanics / 123	
	6.3. Relationship Between Wetting and Adhesion / 124	
	6.4. Adhesion to Metal Surfaces / 125	
	6.4.1. Surface Preparation / 126	
	6.4.2. Coating-Substrate Interaction / 128	
	6.4.3. Covalent Bonding to Glass and Metal Substrates / 130	
	6.5. Adhesion to Plastics and to Coatings / 131	
	6.6. Testing for Adhesion / 133	
	General References / 135	
	References / 135	
7.	Corrosion Protection by Coatings	137
	7.1. Corrosion of Uncoated Steel / 137	
	7.2. Corrosion Protection of Metals / 140	
	7.2.1. Passivation: Anodic Protection / 140	
	7.2.2. Cathodic Protection / 141	
	7.2.3. Barrier Protection and Inhibition / 142	
	7.3. Corrosion Protection by Intact Coatings / 142	
	7.3.1. Critical Factors / 143	
	7.3.2. Adhesion for Corrosion Protection / 144	
	7.3.3. Factors Affecting Oxygen and Water Permeability / 146	
	7.4. Corrosion Protection by Nonintact Films / 148	
	7.4.1. Minimizing Growth of Imperfections:	
	Cathodic Delamination / 149	
	7.4.2. Primers with Passivating Pigments / 149	
	7.4.3. Cathodic Protection by Zinc-Rich Primers / 151	

	7.5. Evaluation and Testing / 153 General References / 156 References / 156	
8.	Acrylic Resins  8.1. Thermoplastic Acrylic Resins / 159  8.2. Thermosetting Acrylic Resins / 160  8.2.1. Hydroxy-Functional Acrylic Resins / 160  8.2.2. Acrylics with Other Functional Groups / 165  8.3. Water-Reducible Thermosetting Acrylic Resins / 166  References / 174	159
9.	9.1. Emulsion Polymerization / 177 9.1.1. Raw Materials for Emulsion Polymerization / 178 9.1.2. Emulsion Polymerization Variables / 182 9.1.3. Sequential Polymerization / 186 9.2. Acrylic Latexes / 186 9.3. Vinyl Ester Latexes / 191 9.4. Thermosetting Latexes / 193 General References / 196 References / 196	176
10.	Polyester Resins  10.1. Hydroxy-Terminated Polyester Resins for Conventional Solids Coatings / 200  10.1.1. Selection of Polyols / 202  10.1.2. Selection of Polyacids / 204  10.2. Polyester Resins for High-Solids Coatings / 205  10.3. Carboxylic Acid—Terminated Polyester Resins / 208  10.4. Carbamate-Functional Polyester Resins / 209  10.5. Water-Reducible Polyester Resins / 209  10.6. Polyester Resins for Powder Coatings / 211  References / 211	199
11.	Amino Resins  11.1. Synthesis of Melamine-Formaldehyde Resins / 214  11.1.1. Methylolation Reaction / 215  11.1.2. Etherification Reaction / 215  11.1.3. Self-Condensation Reactions / 217  11.2. Types of MF Resins / 218	213

11.3. MF-Polyol Reactions in Coatings / 220
11.3.1. Catalysis of MF-Polyol Reactions / 222
11.3.2. Kinetics and Mechanism of MF-Polyol
Co-condensation / 224
11.3.3. Package Stability Considerations / 226
11.3.4. MF Resin Reactions with Carboxylic Acids, Urethanes,
Carbamates, and Malonate-Blocked Isocyanates / 227
11.4. Other Amino Resins / 227
11.4.1. Urea-Formaldehyde Resins / 228
11.4.2. Benzoguanamine-Formaldehyde Resins / 228
11.4.3. Glycoluril-Formaldehyde Resins / 228
11.4.4. Poly(meth)acrylamide-Formaldehyde Resins / 229
References / 229
Binders Based on Polyisocyanates: Polyurethanes 231
12.1. Reactions of Isocyanates / 232
12.2. Kinetics of Reactions of Isocyanates with Alcohols / 234
12.2.1. Noncatalyzed Reactions / 235
12.2.2. Catalysts / 237
12.2.3. Interrelationships in Catalysis / 241
12.3. Isocyanates Used in Coatings / 242
12.3.1. Aromatic Isocyanates / 242
12.3.2. Aliphatic Isocyanates / 244
12.4. Two Package Solventborne Urethane Coatings / 246
12.4.1. 2K Urea Coatings / 249
12.5. Blocked Isocyanates / 250
12.5.1. Principles of Blocking and Deblocking / 251
12.5.2. Blocking Groups / 254
12.5.3. Catalysis of Blocked Isocyanate Coatings / 258
12.6. Moisture-Curable Urethane Coatings / 259
12.7. Waterborne Urethane Coatings / 261
12.7.1. Polyurethane Dispersions / 261
12.7.2. Acrylic-Polyurethane Dispersions / 262
12.7.3. 2K Waterborne Urethanes / 264
12.8. Hydroxy-Terminated Polyurethanes / 266
References / 267
Epoxy and Phenolic Resins 271
13.1. Epoxy Resins / 271
13.1.1. Bisphenol A Epoxy Resins / 271
13.1.2. Other Epoxy Resins / 275

12.

13.

14.

15.

13.2. Epoxy-Amine Systems / 278	
13.2.1. Pot Life and Cure Time Considerations / 279	
13.2.2. Toxicity and Stoichiometric Considerations / 281	
13.2.3. Graininess and Blushing / 282	
13.2.4. $T_g$ Considerations / 283	
13.2.5. Other Formulating Considerations / 283	
13.2.6. Waterborne Epoxy-Amine Systems / 285	
13.3. Other Cross-Linking Agents for Epoxy Resins / 286	
13.3.1. Phenols / 286	
13.3.2. Carboxylic Acids and Anhydrides / 286	
13.3.3. Hydroxyl Groups / 288	
13.3.4. Mercaptans / 288	
13.3.5. Homopolymerization / 289	
13.4. Water-Reducible Epoxy Acrylic Graft Copolymers / 290	
13.5. Epoxy Resin Phosphate Esters / 290	
13.6. Phenolic Resins / 290	,
13.6.1. Resole Phenolic Resins / 291	
13.6.2. Novolac Phenolic Resins / 292	
13.6.3. Ether Derivatives of Phenolic Resins / 293	
General References / 293	
References / 293	
Drying Oils	295
14.1. Composition of Natural Oils / 295	
14.2. Autoxidation and Cross-Linking / 297	
14.2.1. Nonconjugated Drying Oils / 297	
14.2.2. Catalysis of Autoxidation and Cross-Linking / 300	
14.2.3. Conjugated Drying Oils / 301	
14.3. Synthetic and Modified Drying Oils / 302	
14.3.1. Heat-Bodied Oils, Blown Oils, and Dimer Acids / 302	
14.3.2. Varnishes / 302	
14.3.3. Synthetic Conjugated Oils / 303	
14.3.4. Esters of Higher Functionality Polyols / 303	
14.3.5. Maleated Oils / 303	
14.3.6. Vinyl-Modified Oils / 304	
General References / 305	
References / 305	
Alkyd Resins	306
15.1. Oxidizing Alkyds / 307	
15.1.1 Monobasic Acid Selection / 308	

15.1.2. Polyol Selection / 310 15.1.3. Dibasic Acid Selection / 311 15.2. High-Solids Oxidizing Alkyds / 312 15.3. Water-Reducible Alkyds / 313 15.4. Nonoxidizing Alkyds / 314 15.5. Synthetic Procedures for Alkyd Resins / 315 15.5.1. Synthesis from Oils or Fatty Acids / 315 15.5.2. Process Variations / 316 15.6. Modified Alkyds / 320 15.7. Uralkyds and Other Autoxidizable Urethanes / 320 15.7.1. Uralkyds / 320 15.7.2. Autoxidizable Polyurethane Dispersions / 322 15.8. Epoxy Esters / 322 General Reference / 324 References / 324
Silicon Derivatives 326
16.1. Silicones / 326 16.1.1. Silicone Rubbers and Resins / 327 16.1.2. Silicone-Modified Resins / 329 16.2. Reactive Silanes / 331 16.3. Orthosilicates / 333 16.3.1. Sol-Gel Coatings / 333 References / 333
Other Resins and Cross-Linkers 335
<ul> <li>17.1. Halogenated Polymers / 335</li> <li>17.1.1. Solution Grade Thermoplastic Vinyl Chloride Copolymers / 335</li> <li>17.1.2. Vinyl Chloride Dispersion Copolymers / 336</li> <li>17.1.3. Chlorinated Rubber, Chlorinated Ethylene Vinyl Acetate Copolymers, and Chlorinated Polyolefins / 336</li> <li>17.1.4. Fluorinated Polymers / 337</li> <li>17.2. Cellulose Derivatives / 338</li> <li>17.2.1. Nitrocellulose / 338</li> <li>17.2.2. Cellulose Acetobutyrate / 339</li> </ul>
17.3. Unsaturated Polyester Resins / 340
17.4. (Meth)acrylated Oligomers / 342
17.5. 2-Hydroxyalkylamide Cross-Linkers / 342
17.6. Acetoacetate Cross-Linking Systems / 343
17.7. Polyaziridine Cross-Linkers / 345

16.

17.