

ORGANIC COATINGS

Science and Technology, Volume 7



ORGANIC COATINGS

Science and Technology, Volume 7

edited by

Geoffrey D. Parfitt

*Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania*

Angelos V. Patsis

*Department of Chemistry
Institute in Science and Technology
State University of New York
New Paltz, New York*

Library of Congress Cataloging in Publication Data

main entry under title:

Organic Coatings, science and technology.

"Based on papers originally presented at the Ninth International Conference in Organic Coatings Science and Technology in Athens, Greece"--Pref.

1. Plastic coatings--Congresses. I. Parfitt, G. D. II. Patsis, Angelos V. III. International Conference in Organic Coatings Science and Technology (7th : 1981 : Athens, Greece) IV. Series: Organic coatings ; v. 7

TP1175.S607 1984 668.4 83-14338

ISBN 0-8247-7242-3

COPYRIGHT © 1984 by MARCEL DEKKER, INC. ALL RIGHTS RESERVED

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

This book is based on papers originally presented at the Ninth International Conference in Organic Coatings Science and Technology which was held in Athens, Greece, July 11-15, 1983. The Athens Conference is now firmly established as the premier annual scientific and technological conference on coatings in Europe. There were 19 invited and 3 contributed papers covering the range from fundamental research to applications, and including both state-of-the-art reviews and original experimentation.

In this, as in previous conferences in the series, a wide variety of topics were discussed, including new developments in the preparation and curing of polymeric resins, characterization of pigments and pigment/vehicle interactions, photodegradation of surface coatings, coating defects, and corrosion protection. These papers reflect the advances currently being made in research and development in the field of organic coatings.

We would like to express our appreciation to all those who helped in the preparation of this volume, particularly the authors.

G. D. Parfitt
A. V. Patsis

CONTRIBUTORS

T. ASAI R&D Laboratories-I, Central R&D Bureau, Nippon Steel Corporation, Kawasaki City, Kanagawa, Japan

H. ASANO R&D Laboratories-II, Central R&D Bureau, Nippon Steel Corporation, Sagamihara, Kanagawa, Japan

DAVID R. BAUER Engineering and Research Staff, Ford Motor Company, Dearborn, Michigan

JAMES R. BLEGEN Ashland Chemical Company, Dublin, Ohio

P. L. BONORA Engineering Faculty, University of Genova, Genova, Italy

E. BRAGGIO Engineering Faculty, University of Genova, Genova, Italy

P. G. CAPPELLE Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Lovain, Louvain-la-Neuve, Belgium

G. CERISOLA Engineering Faculty, University of Genova, Genova, Italy

D. T. CLARK* Department of Chemistry, University of Durham,
Durham, England

J. COLLETTE Finishes and Fabricated Products Department, Marshall
R&D Laboratory, E. I. DuPont de Nemours & Company, Inc., Philadel-
phia, Pennsylvania

B. A. COOKE Research Department, Imperial Chemical Industries,
Paints Division, Slough, England

J. DE WIT Research Department, Kunstsharsfabriek Synthese B.V.,
Bergen op Zoom, The Netherlands

ERNST HAERING Paint Research Department, BASF Farben & Fasern
AG, Cologne, Federal Republic of Germany

R. E. HARREN Research Administration Department, Rohm and Haas
Company, Spring House, Pennsylvania

HIROMICHI HIGAKI R&D Division, Asahi Glass Company, Ltd.,
Yokohama, Japan

J. W. HOOK, III Trade Sales, Coatings Research Department, Rohm
and Haas Company, Spring House, Pennsylvania

H. F. HUISMAN Technical Department, PD Magnetics B.V., Ooster-
hout, The Netherlands

ANDERS HULT Department of Polymer Technology, The Royal
Institute of Technology, Stockholm, Sweden

GEN KOJIMA R&D Division, Asahi Glass Company, Ltd., Yokohama,
Japan

M. LAZZARA Finishes and Fabricated Products Department, Experi-
mental Station Laboratory, E. I. DuPont de Nemours & Company, Inc.,
Wilmington, Delaware

S. MAEDA R&D Laboratories-I, Central R&D Bureau, Nippon Steel
Corporation, Kawasaki City, Kanagawa, Japan

KEIZO MAKUUCHI Department of Development, Takasaki Radiation
Chemistry Research Establishment, Japan Atomic Energy Research
Institute, Takasaki, Gunma, Japan

* Current affiliation: Imperial Chemical Industries PLC, New Science
Group, Runcorn, Cheshire, England

A. G. NORTH Cray Valley Products, Ltd., Farnborough, Kent,
England

H. OKADA R&D Laboratories-II, Central R&D Bureau, Nippon Steel
Corporation, Sagami-hara, Kanagawa, Japan

S. OKUDA Department of Chemical Engineering, Doshisha University,
Kamigyo-ku, Kyoto, Japan

M. H. PALM-GENNEN Groupe de Physico-Chimie Minérale et de
Catalyse, Université Catholique de Louvain, Louvain-la-Neuve,
Belgium

M. PIENS Corrosion Department, Coatings Research Institute, Limelette,
Belgium

PERCY E. PIERCE Coatings and Resins Research Center, PPG In-
dustries, Inc., Allison Park, Pennsylvania

AMLETO POLUZZI Ashland Chemical Italiana, Milano, Italy

BENGT RÅNBY Department of Polymer Technology, The Royal
Institute of Technology, Stockholm, Sweden

W. T. RAUDENBUSCH Koninklijke/Shell Laboratorium, Amsterdam,
The Netherlands

A. J. P. ROEGIES Technical Department, PD Magnetica B.V., Ooster-
hout, The Netherlands

P.G. ROUXHET Groupe de Physico-Chimie Minérale et de Catalyse,
Université Catholique de Louvain, Louvain-la-Neuve, Belgium

A. SAARNAK Scandinavian Paint and Printing Ink Research Institute,
Hørsholm, Denmark

R. M. TORRES SANCHEZ Groupe de Physico-Chimie Minérale et de
Catalyse, Université Catholique de Louvain, Louvain-la-Neuve, Belgium

CLIFFORD K. SCHOFF Coatings and Resins Research Center, PPG
Industries, Inc., Allison Park, Pennsylvania

C. SENKLER Finishes and Fabricated Products Department, Experi-
mental Station Laboratory, E. I. DuPont de Nemours & Company, Inc.,
Wilmington, Delaware

E. SIBILLE Research Department, Industrie Vernici Italiane S.p.A.,
Stabilim. di Quattordio, Quattordio (AL), Italy

W. J. J. M. SPRANGERS Technical Department, PD Magnetics B.V.,
Oosterhout, The Netherlands

R. VERBIST Corrosion Department, Coatings Research Institute,
Limelette, Belgium

J. VERECKEN Dienst Metallurgie Elektrochemie, Vrije Universiteit
Brussel, Brussels, Belgium

MASAAKI YAMABE R & D Division, Asahi Glass Company, Ltd.,
Yokohama, Japan

M. YAMAMOTO R&D Laboratories-I, Central R&D Bureau, Nippon
Steel Corporation, Kawasaki City, Kanagawa, Japan

TOYOHICO YOSHIDA Department of Coatings Technology, Institute
of Vocational Training, Sagamihara City, Kanagawa, Japan

W. ZIMMT Finishes and Fabricated Products Department, Marshall
R&D Laboratory, E. I. DuPont de Nemours & Company, Inc.,
Philadelphia, Pennsylvania

CONTENTS

Preface iii

Contributors ix

NEW ISOCYANATE-FREE TWO-COMPONENT ACRYLIC COATINGS 1
A. G. North

IMPROVEMENTS IN THE PROPERTIES OF AIR-DRYING ALKYDS BY
THE INCORPORATION OF ACRYLIC MOIETIES 13
J. de Wit

NEW FLUOROPOLYMER COATINGS 25
Masaaki Yamabe, Hiromichi Higaki and Gen Kojima

CROSSLINKING STUDIES ON POLYOL-MELAMINE RESIN
SYSTEMS 41
W. Zimmt, J. Collette, M. Lazzara and C. Senkler

A NOVEL CONCEPT FOR CROSSLINKING SURFACE COATINGS 59
W. T. Raudenbusch

- APPLICATION OF RADIATION CURABLE COATINGS ON METAL
SUBSTRATES 79
Ernst Haering
- GAS CURING OF POLYMERS: STATE-OF-THE-ART AND RECENT
INDUSTRIAL APPLICATIONS IN COATINGS 95
Amleto Poluzzi and James R. Blegen
- SYNTHESIS AND MODIFICATION OF COATINGS BY PLASMA
TECHNIQUES 113
D. T. Clark
- PHOTODEGRADATION AND PHOTOSTABILIZATION OF ORGANIC
SURFACE COATINGS 137
Bengt Rånby and Anders Hult
- MECHANISM FOR FLOW CONTROL BY DISPERSED POLYMERIC
PARTICLES IN HIGH SOLIDS PAINTS 157
David R. Bauer
- COATINGS DEFECTS: CAUSES AND ANALYSIS 173
Clifford K. Schoff and Percy E. Pierce
- ASPECTS OF METAL PRETREATMENT BEFORE PAINTING 197
B. A. Cooke
- STUDIES ON ADHESION LOSS OF CATHODIC ELECTROCOAT IN
WATER IMMERSION TEST 223
S. Maeda, T. Asai, M. Yamamoto, H. Asano, and H. Okada
- STUDY AND SELECTION OF CORROSION PROTECTIVE PAINTS
BY USE OF IMPEDANCE TECHNIQUES 249
M. Piens, R. Verbist, and J. Vereecken
- HYDROGEN EVOLUTION INDUCED DEFECTS ON PRECOATED
STEELS DURING CATHAPHORETIC ELECTRODEPOSITION 265
G. Cerisola, E. Braggio, P. L. Bonora and E. Sibille
- ON THE PERFORMANCE OF FLAKE FILLED COATINGS FOR THE
PERMEATION OF WATER 285
S. Okuda
- OPAQUE POLYMERS 299
J. W. Hook, III and R. E. Harren

RECENT ADVANCES IN THE APPLICATION OF RADIATION PROCESSING OF POLYMER LATEXES	317
Keizo Makuuchi	

X-RAY PHOTOELECTRON SPECTROSCOPY AND THE SURFACE CHEMISTRY OF PIGMENTS AND RELATED SUBSTANCES	329
P. G. Rouxhet, P. G. Cappelletti, M. H. Palm-Gennen, and R. M. Torres Sanchez	

ADSORPTION ON PIGMENT SURFACES	357
A. Saarnak	

ADSORPTION OF POLYMERS ON INORGANIC PIGMENTS FROM LOW AND MODERATELY CONCENTRATED POLYMER SOLUTIONS	375
W. J. J. M. Sprangers, H. F. Huisman and A. J. P. Roegies	

COLOR LOCUS OF PIGMENT MIXTURES—INTERPRETATION BY COEFFICIENT OF SCATTERING AND ABSORPTION	399
Toyohiko Yoshida	

backbone, high levels of crosslinking were needed to achieve maximum resistance and these then gave slow early drying due to the initial plasticizing affect of the polyisocyanate.

Against this background we carried out a long term research program whereby functional acrylic resins were crosslinked in order to capitalize on the known durability of acrylic polymers and the formulation flexibility that could be achieved in obtaining particular physical properties. The blueprint for this initial research was to develop a coating for supersonic aircraft where the requirement was for room temperature cure, the development of tough films with hardness and flexibility over a wide temperature range, resistance to a variety of materials including aircraft fuels, hydraulic liquids and de-icing chemicals, and all of these characteristics were required for coatings that had to have extended durability at altitudes up to 80,000 feet where there was high u.v. radiation and a significant ozone concentration. The final requirement was for color retention and nonembrittlement at a surface operating temperature up to 150°C.

In this work a large number of possible curing mechanisms were examined but most were rejected at an early stage. The system that was eventually chosen which met all of the requirements, consisted of an acrylic copolymer containing both epoxy and carboxy groups which could be self condensed at room temperature by addition of a tertiary amine catalyst. This product known at the time as Synocryl* 860S was successfully used for the coating of a number of military aircraft and met the specification that had been originally established. However, this coating had a major disadvantage for more general use in coatings and particularly in vehicle refinishing, in that stability of the basic copolymer was limited to three months at ambient temperature.

Of the other systems examined, that based on hydroxy functional acrylics with a polyisocyanate curing agent came very close to the 860S type in performance, so this was developed originally for high performance exterior coatings particularly for aircraft, locomotives, road and rail tankers but subsequently for commercial motor car refinishing. The first resins introduced for this purpose was Synocure* 866S and 867S and these were followed by many variants. Economics subsequently led to the development of hybrid systems consisting of acrylated polyesters and these resins typified by Synocure* 861X are now in wide use throughout the world in coatings for refinishing of motor cars and original finishings of commercial and specialist vehicles.

Characteristics of the three resins mentioned are described in Table 1.1.

The use of biuret derivatives of hexamethylene di-isocyanate or adducts of isophorone di-isocyanate has meant that volatility of isocyanate

*Registered trade name of Cray Valley Products, Ltd.

TABLE 1.1
Existing Two-Component Systems

Reference	Synocure 860S	Synocure 867S	Synocure 861X
Resin type	Acrylic	Acrylic	Acrylated polyester
Resin functionality	Carboxy and epoxy		Hydroxy
Hardener/catalyst type	Benzyl-dimethylamine		Biuret of HMDI
Resin:catalyst ratio on solids	Non critical ca 70:1	3:1	2.1
Non volatile content %	45	60	55
Solvent type	Xylene, n-Butanol	Xylene, ethyl glycol acetate	Xylene
Average viscosity poise at 25°C	15	40	20

functional material is extremely low and no hazard results. There is, however, some concern over aerosol particles which may be breathed during spraying operations particularly as some individuals are sensitive to isocyanate reactivity. Work at the Paint Research Association (1,2) has demonstrated the significance of this potential problem.

The work now described was aimed at developing a nonisocyanate vehicle refinishing system both to provide an alternative on environmental and toxicity grounds but also to establish if improved performance could be achieved in specific properties. Two potential areas of improvement over hydroxy acrylics cured with polyisocyanates are the speed of initial dry to the tape test stage and the ability to polish out coating defects.

EXPERIMENTAL

Many of the 34 systems originally examined for aircraft coating were re-examined with the benefits of twenty years of additional polymer chemistry. The combinations that showed most promise but which were finally

TABLE 1.2
Some of the Better Two-Component Systems Examined

Acrylic functionality	Component B	Cure at R.T.	Problems
N-methylol acrylamide	Mineral acids including BF_3 etherates	Excellent	Poor water resistance, and pigment flocculation
Epoxy	Acid acrylic copolymer	Fair	Compatibility
Epoxy	Amine functions acrylic copolymer	Fair	Compatibility
Epoxy	Dithiol	Fair	Odor
Acid	Tris 1 (2 methyl) aziridiny phosphine oxide	Good	Curing agent toxicity
Hydroxyl	Aluminum chelates	Poor	Exterior embrittlement
Hydroxyl	Anhydrides	Poor	Solubility and compatibility of suitable anhydrides

rejected are listed in Table 1.2 with a note on the major deficiency which caused their elimination. It should be stressed however that many of these alternative systems do have particular benefits and may well reappear at a later date for specific uses or where additional development has overcome the disadvantages. Vehicle refinishing is commonly carried out at room temperature, and at 60°C or 80°C and while the specification for this development program was cure under all three conditions there is a place for coatings which may only cure at the force dry temperatures.

By a process of elimination the curing mechanism which met most of the requirements was one which an acid functional acrylic is crosslinked with an aliphatic polyepoxide. A number of variants have been made and typical of these is the system now known as Synocure 881S (the acrylic copolymer) and 882 (the polyepoxide).

TABLE 1.3
White Gloss Finish Formulation F72572

A	Futile titanium dioxide	20.84
	Synocure 881S	59.05
	Xylene	12.22
	n-Butanol	4.08
		96.19
B	Synocure 882	3.81
		100.00
Mix parts A and B before use and thin to spray viscosity with 3:1 Xylene:n-Butanol		
	Viscosity of mixed components	4.8 poise
	Vehicle solids	41%
	Total solids at spray viscosity	40%
	Pot life at 21°C	
	Initial viscosity	0.5 poise
	7 hours	0.5 poise
	24 hours	1.0 poise
	54 hours	3.2 poise

In Table 1.3 the formulation and characteristics of a standard white gloss finish based on this system are shown, while in Table 1.4 a comparison of curing rate against the previously described acrylated polyester-isocyanate system is shown as development of drying stages, hardness and solvent resistance.

The selected system was chosen after a systematic variation of acrylic backbone monomers, type and level of the functional acid groups, and the nature and level of catalyzing groups both within the molecule and as post additions.

The other main variable examined was the choice of epoxy cross-linking agent. Terminal epoxy groups such as glycidyl ethers and esters, chain epoxy groups such as epoxidized oils, and ring epoxies such as cyclohexene oxides were examined, as were their adducts with a variety of polymers. The need for maximum exterior durability largely excluded aromatic epoxy resins. The general conclusion was, as had been established with other catalyzed systems, that a crosslinking agent of

TABLE 1.4
Curing Rate Against Acrylated Polyester-Isocyanate Control
at 21°C for White Gloss Paints

	Synocure 881-2	Acrylated polyester-isocyanate
Sand dry BS 3900	6 minutes	11 minutes
Hard dry BS 3900	12 minutes	70 minutes
Koenig hardness %		
1 day	50	30
3 days	64	70
7 days	69	82
Xylene swab-60 seconds		
1 day	Severe marking	Removal 3 seconds
3 days	Slight marking	Loss of gloss
7 days	V. slight marking	Unaffected
Petrol spot resistance		
1 day	Slight staining	Softened
2 days	V. slight staining	No effect

high functionality and low molecular weight is most effective in producing maximum cure at room temperature, presumably because of reduced steric hindrance.

During the development, film performance of all experimental resins was monitored with a series of standard tests and these are listed in Table 1.5 where performance after room temperature cure is compared with the acrylated polyester and acrylic controls.

Differences are essentially self explanatory. All were confirmed in further work on various pigmentations and in clears over both self color and metallic base coats. Humidity resistance was investigated in most detail because of observed whitening in some clear coatings. Such whitening has not been seen in either Q.U.V. or natural weathering but can occur in the BS 3900 humidity test chamber. Strangely it is not normally seen on 7 day room temperature cured panels but is present with force dried coatings cured for 30 minutes at 60°C. Weight change measurements show a gain of up to 5% with air dried coatings but a small loss of less than 1% with the force dried coatings. It is probable that effective stoichiometry is changed by the alteration in curing conditions although no other performance changes have been observed.

TABLE 1.5
Film Performance of Air Dried Coatings

White gloss at 21°C for 7 days, 50-60 μ m, abraded steel			
	881-2	Acrylated polyester -isocyanate	Acrylic isocyanate
Erickson indentation mm.	9.1	8.1	8.9
Pencil hardness	H	H	H
Mandrel bend inches	1-1/2	1	1-1/8
Cross hatch adhesion	100	100	100
Gloss 20°C	83	100	98
60°C	95	99	100
Distilled water 48 hours	V. slight blistering	Unaffected	Unaffected
40% sulphuric acid 48 hours	Unaffected	Unaffected	Unaffected
40% sodium hydroxide 48 hours	Unaffected	Unaffected	Unaffected
5% acetic acid 8 hours	Unaffected	Unaffected	Unaffected
24 hours	Blistered	Unaffected	Unaffected
Lipstick staining 4 hours	2.5	2	2
Shoe polish staining 2 hours	3	3	3
Q.U.V. resistance:			
Initial gloss 60°C	88	99	100
250 hours	94	100	98
500 hours	91	78	94
1000 hours	77	54	75
Color ΔE^a			
Initial	1.7	1.9	2.2
1000 hours Q.U.V.	1.0	1.2	2.0

^a ΔE calculated from a standard white tile.