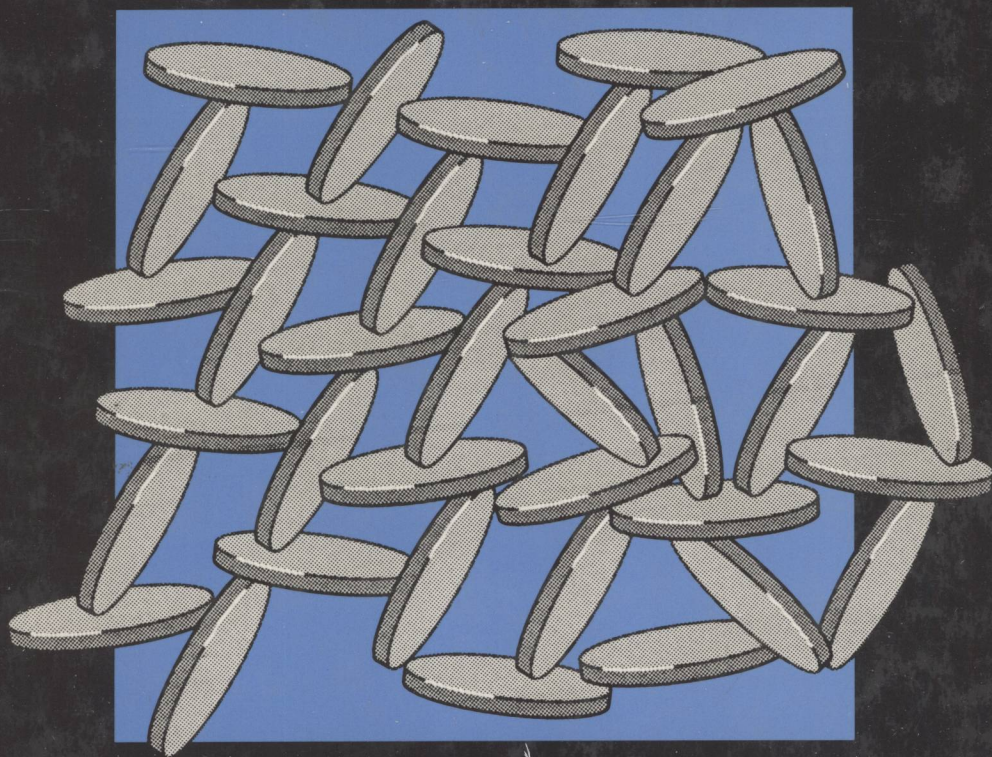


# **WATERBORNE COATINGS AND ADDITIVES**



Edited by D.R. Karsa  
and W.D. Davies

# Waterborne Coatings and Additives

Edited by

**D. R. Karsa and W. D. Davies**

*Akcros Chemicals UK Ltd, Manchester, UK*



THE ROYAL  
SOCIETY OF  
CHEMISTRY

The Proceedings of a Symposium organized by The Royal Society of Chemistry and the Society of Chemical Industry, held on 14–15 September 1994, at Manchester Conference Centre, UMIST, UK

**The cover diagram** shows the ‘house of cards’ structure formed from hectorite clay platelets during gel formation. Clays are used as thickening agents in some coatings formulations. See Figure 6 on page 223.

Special Publication No. 165

ISBN 0-85404-740-9

A catalogue record for this book is available from the British Library

© The Royal Society of Chemistry 1995

*All Rights Reserved*

*No part of this book may be reproduced or transmitted in any form or by any means – graphic, electronic, including photocopying, recording, taping, or information storage and retrieval systems – without written permission from The Royal Society of Chemistry*

Published by The Royal Society of Chemistry,  
Thomas Graham House, Science Park, Milton Road,  
Cambridge CB4 4WF, UK

Printed in Great Britain by Hartnolls Ltd., Bodmin

## Waterborne Coatings and Additives

## Preface

The paint and surface coatings industry continues to be influenced by sustained environmental pressures, in particular the reduction or elimination of volatile organic compounds (VOCs). This in turn has further accelerated the growth of waterborne formulations. Not only has the move been away from solvent to water-based coatings, but there has also been environmental pressure to eliminate coalescing solvents and glycol-based freeze-thaw stabilisers from established emulsion paints. In some instances this has led formulators to consider total reformulation of their copolymers in order to retain or optimise the film forming properties of their paint in the absence of such additives.

At the same time renewed interest has been observed in the development of water-based emulsions of high performance, film forming resins such as alkyds, epoxies, polyesters and polyurethanes.

In 1988, the North West Industrial Division of the Royal Society of Chemistry organised a two day symposium at Liverpool University on "Additives for Water-based Coatings" (RSC Special Publication No. 76, ISBN 0-85186-607-7). This present symposium, 6 years later, attempts to outline the further developments that have occurred in waterborne polymers and additives since then.

The development of anti-pollution legislation is presented and a range of water-based resins and their end-use applications are considered in depth. These include metal treatment, concrete and textile applications. Cross-linking mechanisms are also reviewed and specific papers consider amino resins, waterborne radcure coatings and water-based urethanes. The latter half of the proceedings considers a range of additives currently used in the manufacture and formulation of aqueous systems. These include biocides and foam control agents, acetylenic and polymeric surfactants, clay rheology modifiers, driers and metallic pigments.

The subject of water-based coatings and the many additives used in their formulation is too broad to cover in a single volume. However, the editors hope that this monograph will prove to be a valuable addition to current literature on this topic, suitable for both readers relatively new to the field as well as experienced workers in the coatings industry.

D.R. Karsa  
March 1995

# Contents

## Applications and Performance

Waterborne Polymers: Design for Performance <i>J.B. Clarke and E. Alston</i>	3
The Preparation and Application of Alkyd Emulsions <i>G.H. Dekker</i>	22
Structure/Property Relationships in Waterborne Epoxy Resin Emulsions <i>A. Wegmann</i>	33
Aqueous Polymeric Coatings for Textiles <i>T. Matthews</i>	46
Waterborne Maintenance Systems for Concrete and Metal Structures <i>G.A. Howarth</i>	58

## Crosslinkers

An Overview of Crosslinking in Waterborne Coatings <i>J.W. Nicholson</i>	73
Development and Application of Waterborne Radiation Curable Coatings <i>W.D. Davies and I. Hutchinson</i>	81
Chemistry of Amino Resins and Their Cross-linking Mechanisms <i>R. McD. Barrett</i>	95
Waterborne Two-pack Polyurethane Coatings for Industrial Applications <i>A. Bittner and P. Ziegler</i>	105

## Coatings and Pollution Legislation

Coatings and the Development of Air Pollution Legislation <i>S.T. Smith</i>	117
--	-----

**Additives**

Foam Control Agents for Waterborne Coatings <i>E.C.L. van Laere</i>	133
An Additives Approach to Defect Elimination in Thermoplastic Waterborne Industrial Maintenance Coatings <i>J. Schwartz, S.V. Bogar, and W.R. Dougherty</i>	142
Metallic Pigments for Waterbased Coatings <i>W. Reißer, A. Fetz, and E. Roth</i>	180
Polymeric Surfactants and Their Application in Resin Emulsification <i>A. Bouvy and A. Opstaele</i>	190
Microbiological Protection of Waterborne Paint Formulations <i>J.W. Gillatt</i>	202
Synthetic Clay Rheology Modifiers for Water Based Coatings <i>P.K. Jenness</i>	217
The Effect of Driers in Water-borne, Oxidatively Drying Surface Coatings <i>J.H. Bieleman</i>	232
A Silver Lining for Paints and Coatings - A Revolutionary Preservative System <i>K.D. Brunt</i>	243
<b>Subject Index</b>	253

## **Applications and Performance**



# Waterborne Polymers: Design for Performance

J. B. Clarke and E. Alston

ALLIED COLLOIDS LIMITED, PO BOX 38, CLECKHEATON ROAD, LOW MOOR, BRADFORD, WEST YORKSHIRE BD12 0JZ, UK

## 1. INTRODUCTION

Waterborne coatings were first introduced during the 1930's when commercial paints based on a polyvinyl acetate latex were developed in Canada.

As synthetic resin technology improved and the commercial availability of suitable monomers increased, latices based on acrylics, styrene-butadiene, styrene-acrylics, vinyl acetate - acrylics, vinyl acetate - versatate and vinyl acetate-ethylene have been specifically designed for water based coating formulations. Such formulations find wide application in a number of industries eg textile, paper, adhesives as well as paints.

Water based paints initially found their niche in the DIY field where the concepts of no solvent odours and the convenience of cleaning brushes and rollers in water were successfully marketed. The further development to replace solvent systems for the more demanding industrial applications has been somewhat retarded due to technical deficiencies in the raw materials.

However, in recent years the ever increasing legislation and attitudes towards reducing and eliminating the release of volatile chemicals into the atmosphere has put the coatings formulator under increased pressure. Whilst a number of alternative products to solvent based are available, eg powder coatings, radiation curable systems, waterborne paints retain the conventional characteristic of being liquid and can consequently be applied using existing equipment.

Fig 1 summarises UK paint sales in the period 1970-1990.

In 1970 46% of total was water based, which increased to 60% in 1990.

**Fig 1. UK Paint Sales**



A = total paint sales    B = water based

## 2. THE DESIGN OF FORMULATIONS FOR HIGH PERFORMANCE

A number of ideal requirements may be listed. (Table 1)

The quest for optimum performance relies to a large extent on the design of the base film former. However, the mixture of resin and pigment alone does not produce a coating. Other essential ingredients must be incorporated to achieve design performance. (Table 2)

Table 1Ideal Requirements for High Performance

- Elimination of all hazardous volatiles
- Elimination of unpleasant odours - not necessarily hazardous
- Ambient temperature film forming and curing
- Maximisation of resistance properties
  - water
  - alkali
  - solvents
  - heat
  - blocking
- Stable to storage conditions
- Suit the application method
- Cost effective

Table 2Essential Additives

- Pigment dispersing agent
- Thickener/rheology modifier
- Biocide
- Foam control agents
- Slip and mar additives
- Adhesion promoters

The selection and optimisation of additives is of equal importance to the selection of the main binder.

In order to exemplify designing for performance the following case study has been selected.

### 3. The design and formulation of an ambient cure wood lacquer

#### 3.1. MARKET SURVEY

Before any research project is commenced a thorough market survey of the potential for the proposal new product is essential. An ambient curing wood lacquer would find application in both industrial and retail outlets.

Table 3

#### Industrial wood finishes in Europe 1982-1992

	1982		1987		1992	
	TONS	%	TONS	%	TONS	%
Nitrocellulose	152,200	39.4	134,650	31.0	107,280	25.0
Acid-cured	132,115	34.2	150,245	34.6	122,235	28.4
Polyurethanes	30,900	8.0	66,445	15.3	91,165	21.2
Polyesters	28,975	7.5	34,750	8.0	42,350	9.9
Rad-cured	11,590	3.0	23,000	5.3	38,680	3.2
Waterborne	3,865	1.0	7,385	1.7	13,725	3.3
All others	26,665	6.9	17,800	4.1	14,115	3.3
TOTAL	386,310	100.	434,275	100.	429,550	100.

It can be seen that the demand for the more traditional resin systems is in decline to the benefit of those more environmentally acceptable. The rate of growth of waterborne systems is particularly impressive. The 1992 figures are broken down for the major European manufacturers in table 4 from which it can be seen that Germany is currently the major user of waterborne industrial wood finishes.

**Table 4. National European Demands For Industrial Wood Coatings By Type Of Resin System (1992).**

	Nitrocellulose	Polyurethanes	Acid-cured	Polyesters	Rad-cured	Waterborne	All others	Total
<b>Major Markets</b>								
France	11,830	4,440	3,450	1,430	860	865	1,775	24,650
Germany	37,825	18,690	1,006	4,450	6,140	8,365	3,470	89,000
Italy	11,800	64,125	2,565	25,650	23,650	900	135	128,250
Spain	11,430	20,300	5,485	3,680	1,830	455	2,565	45,725
United Kingdom	8,215	1,150	9,665	475	955	890	375	21,725

An assessment of the retail market for woodcare products for the whole of Europe is difficult due to the different reporting systems in the various countries but detailed figures for the U.K. market are available:-

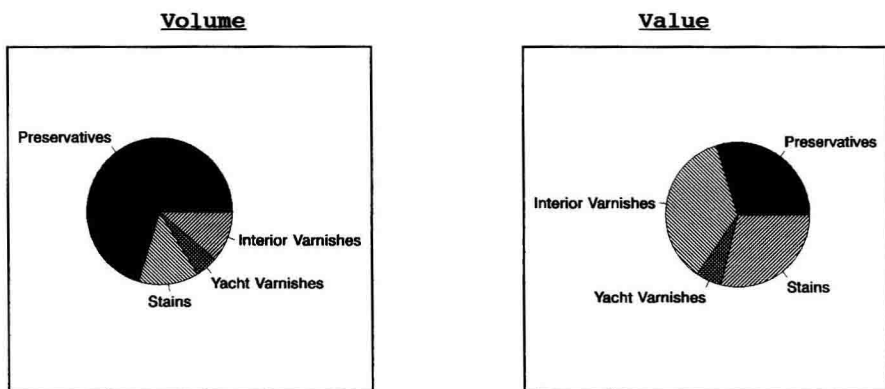
**Table 5. UK Retail Woodcare Products - Volume**

UK RETAIL VOLUME MARKET FOR WOODCARE PRODUCTS BY PRODUCT SECTOR 1989 - 1993 (MILLIONS OF LITRES)					
PRODUCT SECTOR	1989	1990	1991	1992	1993
PRESERVATIVES	17.2	18.0	20.3	19.4	21.6
VARNISHES, INTERIOR	3.6	3.5	3.7	3.9	3.7
VARNISHES, YACHT	1.4	1.5	1.4	1.3	1.3
STAINS	3.0	2.8	3.2	3.3	3.2
DYES	0.8	1.2	1.4	1.1	1.2
TOTAL	26.0	27.0	30.0	29.0	31.0

**Table 6. UK Retail Woodcare Products - Value**

UK RETAIL VALUE MARKET FOR WOODCARE PRODUCTS BY PRODUCT SECTOR 1989 - 1993 (£ MILLION)					
PRODUCT SECTOR	1989	1990	1991	1992	1993
PRESERVATIVES	22.6	24.0	25.0	26.8	24.8
VARNISHES, INTERIOR	25.4	26.0	29.5	34.7	33.8
VARNISHES, YACHT	3.9	4.0	4.8	5.9	5.7
STAINS	18.5	21.0	23.8	26.3	29.8
DYES	2.6	5.0	2.9	6.3	8.9
TOTAL	73.0	80.0	86.0	100.0	103.0

These two tables are represented graphically in Fig 2.

**Fig 2. UK Retail market for wood coating products 1993  
(% of total volume and value)**

Source: Trade and MSI estimates

Estimates show that in 1993 waterbased products counted for 55% of the market in fencing treatment, 27% of the interior varnish market and 18% of all woodstains. The latter two segments are increasing at 20% per annum currently and account for the majority of sales growth.

Users of D.I.Y. products are taking environmental issues increasingly seriously although product effectiveness and performance will still outweigh environmental concerns in the final analysis.

Leading U.K. manufacturers have introduced "solvent free" and "low odour" products and their range of waterbased alternatives to solvent based coatings has vastly increased. Although the recent U.K. recession has reduced D.I.Y activity, market sources are confident that growth in the waterbased sector will continue to improve as the overall market recovers.

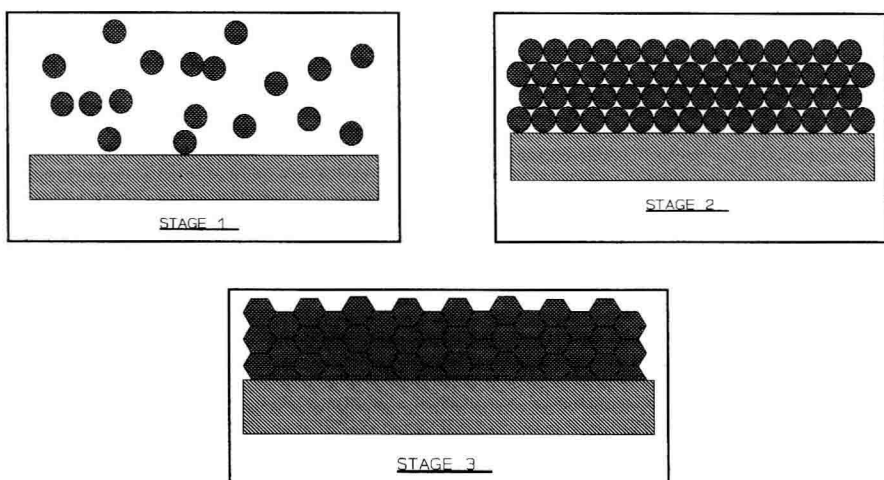
Having established a need for improvements in the performance of waterbased coatings in a growth sector of the market the next step was the design an appropriate polymer system.

### 3.2 Factors affecting the Design of an Ambient Cure Resin

The most widely used ambient temperature curable solvent based resin systems are based on convertible resins which are usually fully soluble in solvent. On drying, at ambient temperature, the simple elimination of solvent by evaporation is accompanied by a chemical conversion reaction which develops the required resistance and durability properties.

Conventional air drying latices, on the other hand, do not undergo chemical conversion during the drying process.

The first mechanistic model of the drying process of latices was published by Vanderhoff et al in 1973<sup>(1)</sup>. A three stage model was proposed (Fig 3).

**Fig 3. Film Formation From Emulsions**

In the first stage the water evaporates from the surface, gradually concentrating the system to a point where the particles begin to contact one another which leads to the second stage.

Particle coalescence then begins to take place, leading to stage 3 when the film is considered dry and fully coalesced.

The mechanism has been studied further by other workers and reported in the literature. <sup>(2,3)</sup>

The performance of conventional latices is largely governed by three factors. (Table 7)

**Table 7****Factors Governing Latex Performance**

Polymer Composition Molecular Weight Particle Size
--