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ROBERT D. ATHEY, JR.

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Los Gatos, California

Marcel Dekker, Inc.   New York • Basel • Hong Kong

Athey, Robert D.
Emulsion polymer technology / Robert D. Athey, Jr.
p. cm. -- (Plastics engineering ; 22)
Includes bibliographical references and indexes.
ISBN 0-8247-7850-2
1. Emulsion polymerization. 2. Polymers. I. Title. II. Series:
Plastics engineering (Marcel Dekker, Inc.) ; 22.
QD281.P6A87 1991
668.4'2--dc20 90-28413
CIP

This book is printed on acid-free paper.

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

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Preface

There is a real need for a book on emulsion polymers that speaks directly to the users (the mill engineers in paper mills, the chemists in paint or textiles plants, etc.). The need is not so much for erudition, but for simple explanation of operating mechanisms involved in the physics and chemistry of polymers and colloids as they apply to emulsion polymer manufacture and use. My own students (in the engineering extension division courses taught through the University of California at Berkeley) called my attention to the need for such a book.

Emulsion polymers or latexes are substantial commercial entities. However, the information available on these polymer systems is based on:

1. Classical reference books, at least 20 years old
2. An occasional chapter in a review book or an article in a trade magazine written for a specific industry (TAPPI, AATCC, various paint organizations, and so on)
3. Patents (often describing products that never make it to production scale)
4. Technical brochures describing products (again, specifically oriented to one industry)

This means that a paint formulator will often not know of a good textile polymer emulsion that would work well in a needed application *and* be cost-effective.

The key to finding the appropriate emulsion polymer system for a formulator is knowing how to compare compositions and properties. Our intention here is to clearly outline the various available materials, how they are made, and how their synthesis formulations and processes affect their fluid and dry film properties. We also provide some guidance on formulation with additives to make the emulsion into the desired end product.

We emphasize the similarities among the ink, paint, paper, textiles, adhesives, and rubber industries and note the differences where they are important. We look for connections between apparently unrelated facts that allow a better understanding of the emulsion polymer as both a colloidal system and a polymer system.

We do not intend this as a comprehensive review of all the literature, but as a representative sampling illustrating specific points. The information contained here is a combination of experience and the teachings of a variety of readings in colloid science, emulsion polymers, and their applications. We advise the reader that this is a brief reference, and further readings and experience will build expertise. The book may be used by the scientist/engineer in industrial practice or as a supplementary text for the advanced student in material science, polymer chemistry, or colloid science.

Recognizing that the text may include misinterpretations or be incomplete, we would appreciate readers' contributions of lore, references, reprints, and recommendations for additions, deletions, or modifications for future editions. A friend some years ago grumbled to me that a reprint I sent him meant the new edition of the book he'd just finished was out-of-date and needed a rewrite. I am not afraid of such a prospect. Current interpretation of observations is always subject to change as new evidence is gathered and we become more knowledgeable about how to conduct and interpret experiments. How can writing a general reference be any different?

We've experienced four levels of support from a variety of people over the years to help get this publication together. Thanks are offered to:

1. Barbara Hartmann, my three daughters, and Patricia Shaw for their moral support when needed
2. Fred Goetz, Ray Gates, Willem Van Essen, and Ted Herman for their professional support in setting my sights higher throughout my career
3. Professor Elizabeth Dyer, who asked me to give a talk on the first course I took on polymer science about emulsion polymerization soon after I started learning it at work (I called it a black art), and Prof. Steve Rosen, who wanted me to repeat it 15 years later (they got me thinking in the directions needed for this compilation)
4. Michael Murphy (Editor, *Metal Finishing Magazine*), Lothar Vincentz (Publisher, *Farbe Und Lack* and *European Coatings Journal*), and Maurits Dekker (Chairman, Marcel Dekker, Inc.) for their encouragement and patience with my polemics, style, and delays.

I also cannot forget the many coworkers who taught me what I needed when I needed it. The art of chemistry is really an apprenticeship, as it involves a lot

of manipulative skills and on-site observation of the process and product performance. I often cite Zimmerman, Meincke, Witt, the TAPPI and FSCT organizations, and other coworkers, but there are many more. Recognize your contribution to this effort. I continue to learn simply because you opened my eyes.

Robert D. Athey, Jr.

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Introduction

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The Common Ground

The emulsion polymer is a heterophase mixture of many ingredients. All the ingredients affect the colloidal or polymer properties (and sometimes both) and are of concern to the user who wants the adhesive to stick, the paint or coating to cure, or the dipped product to be free of holes and impermeable. The user may find this collection of information a good guide for thinking on the new better formulation to be designed, for solving the problem that crops up in production of the emulsion polymer, or in the production or use of a formulation based on the emulsion polymer.

We shall assume a basic understanding of the many concepts of the organic chemistry, electrochemistry, and colloid science that underlie the emulsion polymer theory. However, we will refer to these concepts occasionally to remind the reader of their importance, and to occasionally cull out a detail or two that will affect the formulation or performance. The necessity for this sort of examination is not immediately obvious, but we recognize how the emulsion polymer industry has grown over the past 50–60 years.

The original researchers in the industry were transplanted paint chemists, or adhesive chemists. Some were analytical chemists trying to follow the manufacture process using some of the techniques they knew from other fields. Some were physical chemists by training who tried optical, thermochemical, or electrochemical characterization techniques to make their contributions. Many were organic chemists who were brought in to do something related, and were taught emulsion polymerization so they could get new products on the market. I was initially hired to make unusual monomers, and had swamped the man making the polymers in a matter of about six months. I was then assigned to learn emulsion polymerization techniques, so I could evaluate my own monomers. In the ensuing years, I have probably worked for only one year in the area of the organic chemistry of my academic background and for more than 20 years in emulsion and polymer science. I have called myself a colloid scientist rather than an organic chemist for about 10 years.

So for many years, the makers of emulsion polymers in industrial labs were essentially formulators, using a variety of commercial products they knew as polymers, initiators, and colloidal stabilizers in a rather Edisonian approach to making a good latex. This is not bad, in any sense, as these people were smart enough to have a mental formulary library of things that worked; this formulary library grew every day. Many had good academic backgrounds that they kept updated by readings in colloid science. I have a great deal of respect for people like Russ Meincke of General Tire and Carl Zimmerman of International Latex, who could come up with new products ready for commercialization six months after they received the assignment. Their primary publications are patents, based on good analytical thinking. But these lights are hidden under bushels, compared to the more visible people in the field who publish from academic or research institute labs.

The field of industrial emulsion polymers is so broad and heterogeneous that no one discipline can be the basis for the understanding needed to make a workable product. Although my academic training was as an organic chemist, the physical and inorganic chemistry contributions to the process and products have extended my usable information base. As one cannot be a renaissance man, one must depend upon co-workers with special areas of expertise to help solve any problem that may come up. Indeed, I have called myself an experienced novice, as I visited various labs looking for a little help on my problem projects. The ideal research technique is probably to have a team of reviewers skilled in different fields look over the project results and reports to recommend new approaches for the experimentalist.

A contributing (and complicating) factor to the heterogeneity of the field of emulsion polymers is the variety of specialized applications. In some cases, the polymer is to be easily coagulated, whereas in others, the polymer should not coagulate at all. In some formulations, the polymer is used alone as a coating, in others with 10% pigment or filler, and in others with 600% pigment or filler, by weight on the dry polymer solids. We give examples in Table 1.1. Unfortunately, many of these differences in formulations are specific to different industrial applications, and the users in those differing industries do not talk to each other or read each others' technical or trade journals. It is interesting that they all use essentially the same components, albeit in different amounts. So the

Table 1.1 Industrial Formulations for Emulsion Polymer Products

Industry	Pigments and Fillers, Dry Wt.	Emulsion Polymer, Dry Wt.
Paint	up to 100	100
Paper	100	3–20[a]
Carpet	200–600	100

[a]May have other binders (starch or protein) with the latex.

mystery of the emulsion polymer deepens! This creates an opportunity for the consultant for cross-fertilization of ideas.

The wide variety of components used in each industry is an eye opener. Each industry uses what is essential to the end use, and no cognizance is given the other users in other industries, or what the other industries can teach about the usage. The typical components used by selected industries are shown in Table 1.2. Again, the mystery of the emulsion polymer deepens! Again, this creates a substantial opportunity for the consultant for cross-fertilization of ideas.

Given the difficulty of dealing with a complex set of formulation components like these, and given that a common formulation will have a dozen or more of these components, one could really be concerned with whether or not one should start at all. Indeed, some professor of engineering said many years ago that ". . . after a process or formulation has more than seven components, it is no longer capable of being rigorously modelled mathematically and controlled. Then

Table 1.2 Typical Components for Emulsion Polymer Formulations

Component	Paper Coatings	Carpet Backings	Paint
Surfactants	X	X	X
Dispersants	X		X
Thickeners	X	X	X
Defoamers	X	X	X
Biocides			X
Flame retardants		X	X
Plasticizers		X	X
Curatives	X	X	X
Reodorants		X	X
Antioxidants		X	X
UV stabilizers		X	X
Pigments		X	X
Buffer salts	X		X
pH Neutralizers	X	X	X

you are dealing with art of control, rather than engineering or science." That is perhaps an oversimplification in today's world of sophisticated statistical modeling techniques, powerful computers, and better information on what components do in formulations. However desirable process–product control modeling is, it is still not commonly done. It is a matter of economics, and only the better funded research and engineering departments of large companies in industry will even start such a statistical control program. The small ink or paint company, or the small mill (textile or paper), will more likely depend upon their local production trouble shooter to solve the problem or develop the product, from their mental formulary. Perhaps we can help in their effort with the chapters following.

We have organized the presentation here along several lines of logic. The first section deals briefly with the basic principles of colloid and polymer science, with some practical observations on latex preparation. The second section covers the common monomer systems used in making the latexes, with some guidelines as to the type of latex properties which can be expected. The third section recommends the analysis and testing schemes the producer or user may find useful in problem solving. The last section deals with additives for the formulated product, and some pitfalls in their use. We hope this integration of a common language approach to a complex industrial material set may be useful to the mill engineer, the lab person, and the formulator.