

**ENCYCLOPEDIA**  
**of**  
**EMULSION**  
**TECHNOLOGY**

Volume 2

**APPLICATIONS**

edited by

**Paul Becher**

# ENCYCLOPEDIA OF EMULSION TECHNOLOGY

VOLUME 2  
Applications

*Edited by PAUL BECHER*

*Paul Becher Associates Ltd.  
Wilmington, Delaware*

MARCEL DEKKER, INC. NEW YORK and BASEL

Library of Congress Cataloging in Publication Data

(Revised for vol. 2)

Main entry under title:

Encyclopedia of emulsion technology.

Includes bibliographical references and indexes.

Contents: v. 1. Basic theory -- v. 2. Applications of emulsions.

1. Emulsions. I. Becher, Paul.

TP156.E62 1983 660.2'94514 82-18257

ISBN 0-8247-1876-3 (v. 1)

ISBN 0-8247-1877-1 (v. 2)

COPYRIGHT © 1985 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

# ENCYCLOPEDIA OF EMULSION TECHNOLOGY

VOLUME 2

Applications

## Preface

This, the second volume of the *Encyclopedia of Emulsion Technology*, deals with applications of emulsions. As a consequence, it will no doubt seem rather more diffuse than Volume 1, with a certain degree of repetition, which was so successfully avoided in the earlier volume.

This is a simple consequence of the subject matter; we have tried to cross-reference material to other chapters in this volume and in Volume 1, but have recognized that some repetition is both inevitable and necessary.

The first chapter, by Menon and Wasan, explores the thorny problem of demulsification, which has recently been treated at book length by Lissant. Lissant's presentation, however, deals with the problem from a pragmatic point of view, while the present chapter delves more deeply into the theoretical background.

Chapter 2, by Danièle Clausse, is perhaps unique, in that it treats emulsions as an experimental tool in the investigation of phase transitions. I hope that the publication of this work will stimulate further application of this technique.

In the following chapters, specific applications are considered: to medicine (Davis, Hadgraft, and Palin); to agriculture (D. Z. Becher); and to foods. This last topic requires two chapters; the first of these, by Krog, Riisom, and Larsson, explores the preparation of a large area of food emulsions, while the second chapter on foods, by Jaynes, restricts itself to consideration of the narrow topic of emulsions stabilized by emulsions. The chapter by Breuer covers the large (and economically significant) area of cosmetics.

The final chapter, by the editor, does not precisely fit the category of applications. However, the earlier bibliographies of HLB (prepared in collaboration with William C. Griffin) were so well received and have proved so useful that an update seemed inevitable. I have received considerable help in this update, especially in the identification of earlier papers which had been missed in previous versions. There are no doubt still some gaps; if so, the editor takes responsibility. In addition, the bibliography extends

only to 1983, and I am already aware of later publications which could be usefully included. Perhaps a supplement in a later volume will rectify this.

In the following volume, further applications will be considered, and techniques in the preparation and evaluation of emulsions will be covered.

One final point: The reviews of Volume 1 have, in the main, been flattering. A few reviewers, however, have objected to the title of this work on the basis that "it is not really an encyclopedia." Those who know me realize that I tend to be fastidious on matters of usage (some of my contributors will no doubt make that "overfastidious"). According to the Oxford English Dictionary, encyclopedia is a pseudo-Greek formation (arising from a misreading of a Greek text—some things never change!). Its meaning is that of "encyclical education," and one of the OED definitions is "An elaborate and exhaustive repertory of information on all the branches of some particular art or department of knowledge." To be sure, the OED adds "esp. one arranged in alphabetical order." It is clear, however, that alphabetical ordering is not a *sine qua non*; that this work fulfills the first portion of the definition is the devout hope of the editor.

Paul Becher

## Contributors

DAVID Z. BECHER

Monsanto Agricultural Products Co., St. Louis, Missouri

PAUL BECHER

Paul Becher Associates, Ltd., Wilmington, Delaware

MIKLOS M. BREUER

The Gillette Company, Boston, Massachusetts

DANIELE CLAUSSE

Université de Technologie de Compiègne, Compiègne, France

STANLEY S. DAVIS

University of Nottingham, Nottingham, England

JONATHAN HADGRAFT

University of Nottingham, Nottingham, England

EDGAR N. JAYNES\*

General Foods Corporation, Tarrytown, New York

NIELS J. KROG

Grindsted Products A/S, Braband, Denmark

KÅRE LARSSON

Lund University Chemical Center, Lund, Sweden

VENUGOPAL B. MENON

Illinois Institute of Technology, Chicago, Illinois

KAREN J. PALIN

University of Nottingham, Nottingham, England

TOM H. RIISOM†

Grinsted Products A/S, Braband, Denmark

DARSH T. WASAN

Illinois Institute of Technology, Chicago, Illinois

---

### *Current affiliations:*

\*S. C. Johnson and Son, Inc., Racine, Wisconsin

†Danos International A.m.b.A., Viby, Denmark

## Contents

Preface	iii
Contributors	v
Contents of Volume 1: Basic Theory	ix
Contents of Volume 3: Applications/Measurements	xi
1. Demulsification Venugopal B. Menon and Darsh T. Wasan	1
2. Research Techniques Utilizing Emulsions Danièle Clausse	77
3. Medical and Pharmaceutical Applications of Emulsions Stanley S. Davis, Jonathan Hadgraft, and Karen J. Palin	159
4. Applications in Agriculture David Z. Becher	239
5. Applications in the Food Industry: I Niels J. Krog, Tom H. Riisom, and Kåre Larsson	321
6. Applications in the Food Industry: II Edgar N. Jaynes	367
7. Cosmetic Emulsions Miklos M. Breuer	385
8. Hydrophile-Lipophile Balance: An Updated Bibliography Paul Becher	425
Index	513

## Contents of Volume 1: Basic Theory

Preface

Contributors

Contents of Volume 2: Applications

Introduction

1. Liquid/Liquid Interfaces  
Tharwat F. Tadros and Brian Vincent
2. Formation of Emulsions  
Pieter Walstra
3. Emulsion Stability  
Tharwat F. Tadros and Brian Vincent
4. Microemulsions  
Stig E. Friberg and Raymond L. Venable
5. Phase Properties of Emulsions: PIT and HLB  
Kōzō Shinoda and Hironobu Kunieda
6. Emulsion Droplet Size Data  
Clyde Orr
7. Rheological Properties of Emulsions  
Philip Sherman
8. Optical Properties of Emulsions  
Raymond S. Farinato and Robert L. Rowell
9. Dielectric Properties of Emulsions and Related Systems  
Marc Clausse

Index

## Contents of Volume 3: Applications/Measurements

Preface

Contributors

Contents of Volume 1: Basic Theory

Contents of Volume 2: Applications

Applications:

1. Applications in the Petroleum Industry  
B. Davis
2. Emulsion Explosives  
H. A. Bampffield and J. Cooper

Measurements:

3. Determination of Particle Size  
C. Orr
4. Colloidal Stability in Quiescent Media  
D. H. Melik and H. S. Fogler
5. Surfactant Properties  
H. B. Klevens and S. Qutubuddin
6. Emulsion Structure by Neutron Scattering  
H. Hoffman
7. Triangular Diagrams in the Study of Emulsions  
R. Mackay
8. Glyphs in the Study of Multivariant Systems  
K. J. Lissant

Index

# 1

## Demulsification

VENUGOPAL B. MENON and DARSH T. WASAN / Illinois Institute  
of Technology, Chicago, Illinois

---

I. Introduction	1
II. Emulsion Breakdown	2
A. Creaming	3
B. Inversion	4
C. Demulsification	4
III. Factors Affecting Demulsification	15
A. Temperature	15
B. Solid particles	15
C. Continuous phase viscosity	16
D. Electrolyte	17
IV. Techniques for Demulsification	19
A. Chemical methods	20
B. Physical methods	27
References	66

### I. Introduction

Dispersion of a liquid phase into another relatively immiscible phase frequently occurs in operations involving liquid-liquid contacting. Some of these dispersions are desirable, as in the food and cosmetic industry, while there are many situations where such dispersions, or emulsions, are undesirable.

In this chapter we attempt to highlight the important factors affecting demulsification and to review some of the principal techniques available for demulsification. The reader is encouraged to refer to two excellent complementary reviews on emulsion stability and mechanisms of emulsion breakdown which were recently presented by Tadros and Vincent [1] and Carroll [2].

Macroemulsions (droplet diameters  $>1\ \mu\text{m}$ ) are thermodynamically unstable and, given sufficient time, will separate out naturally. However, it is not economically feasible to wait for nature to do the job, so techniques for accelerating the process are needed. The importance of the operation of demulsification is evident in the number and variety of industries that need to eliminate emulsions in their work.

The idea of separating oil droplets from water began with the steam engine, where the lubricating oil needed to be removed from the steam condensate. Even today one of the most common cases of undesirable emulsification is found in the petroleum industry. Because of the coexistence of oil and water in the rock strata of oil reservoirs, the crude oil pumped from oil wells contains emulsified water. It is necessary to separate the water from the oil lest the water cause foaming, corrosion of pipelines and tanks, increased coke deposition, higher power consumption, or handling problems due to the resultant increase in volume and viscosity [3].

Fuel oil-water emulsions are frequently encountered in the fuel tanks of ships. Seawater increases the corrosion of pump surfaces, destroys furnace linings, and decreases the effectiveness of the oil, thus leading to rapid pump failure [4]. Rapid demulsification of such emulsions is a matter of extreme importance.

Increased environmental consciousness has created interest in separating oil from effluent water streams, mopping up accidental spills and leaks which cause lake and river water pollution, and cleaning bilge water from ships. Separation of butter from milk, removal of rubber from latex, cleaning of light distillates, retrieval of bitumen from tar sands, phase separation at the end of liquid-liquid extraction operations, recovery of oil from streams of used cutting oil [5], etc., also involve the demulsification of emulsions. Chemical and mechanical methods have been used to coalesce and separate such emulsions.

## II. Emulsion Breakdown

The phenomenon of emulsion separation can be broadly categorized into three different processes: (1) creaming, (2) inversion, and (3) demulsification.

### A. Creaming

This is the phenomenon by which the emulsion separates into two emulsions, one richer and the other poorer in the dispersed phase. The more concentrated emulsion is commonly referred to as the *cream*. The separation of cream from unhomogenized milk is a very common example of the creaming phenomenon. Creaming does not, in the true sense, represent a breaking of the emulsion, but it is favored since it leads to the formation of larger droplets and it may be one step toward the ultimate goal of total demulsification [6].

The mechanism of creaming appears to be due to the slow sedimentation of the emulsified droplets. The velocity of sedimentation of a drop of radius  $r$  and density  $\rho_D$  in a liquid of viscosity  $\eta$  and density  $\rho_C$  is given by the Stokes equation:

$$v = \frac{2gr^2(\rho_C - \rho_D)}{9\eta} \quad (1)$$

Strictly speaking, the Stokes equation applies only to the case of rigid spheres, and therefore many modifications of the equation are available in the literature [6]. For example, the Stokes equation has been modified to give the velocity of settling for a dilute suspension of particles [7]. The equation is of the form

$$v = v_0(1 + k\phi)^{-1} \quad (2)$$

where

$k$  = constant

$\phi$  = volume fraction of the dispersed phase

$v_0$  = Stokes velocity for a simple droplet

The value of  $k$  is around 5.0 and varies with the precise distribution of particles [8].

Reddy et al. [9] have derived a general dynamic equation to describe the behavior of an emulsion where aggregation due to Brownian motion collisions, sedimentation, and creaming are occurring simultaneously. They account for sedimentation-flocculation, in which collisions occur between particles moving at different creaming rates due to particle size differences.

The creaming process can be accelerated by the use of high-speed centrifugal separators or by the addition of creaming agents. In the latter case, the creaming agents cause individual droplets to cluster. Although such clusters are different from single spherical droplets, the general implications of the Stokes relation can still be applied.

### B. Inversion

The sudden change of a water-in-oil (W/O) emulsion to an oil-in-water (O/W) emulsion and vice versa is termed *phase inversion*. This instability is dependent on a variety of factors, such as emulsifier nature and concentration, volume fractions of the two phases, and physical properties of the phases and temperature.

Shulman and Cockbain [10] have advanced a mechanism explaining the inversion process. They suggest that the globules of the dispersed phase are pushed close to one another when the oil concentration of a W/O emulsion is increased. The oil in the droplets pierces across the interfaces and coalesces to form the continuous phase, while the water in between the droplets gets trapped as dispersed droplets in the inverted emulsion [3]. Becher [11] studied the hysteresis effects of the inversion phenomenon by measuring the conductance of emulsions when the phase ratio was varied. The hysteresis effects show that the behavior of an inverted emulsion depends to some extent on its previous history.

The phase inversion temperature can be a very handy tool for predicting inversion behavior. The studies of Wellman and Tartar [12] and others [13, 14] demonstrate that inversion is strongly dependent on temperature. At low emulsifier concentrations the temperature is extremely sensitive to emulsifier concentration, but at high concentrations, the curve of the phase inversion temperature versus emulsifier concentration tends to level out (Fig. 1).

Enever [15] studied the effects of electrolyte on the inversion temperatures of emulsions. The addition of NaCl to the aqueous phase depressed the phase inversion temperatures of the emulsions. He found a linear correlation between the phase inversion temperature and the logarithm of the globule coalescence rate.

### C. Demulsification

The breakage of emulsions occurs in two stages: (1) flocculation and (2) coalescence. *Flocculation* refers to the aggregation of droplets, and *coalescence*

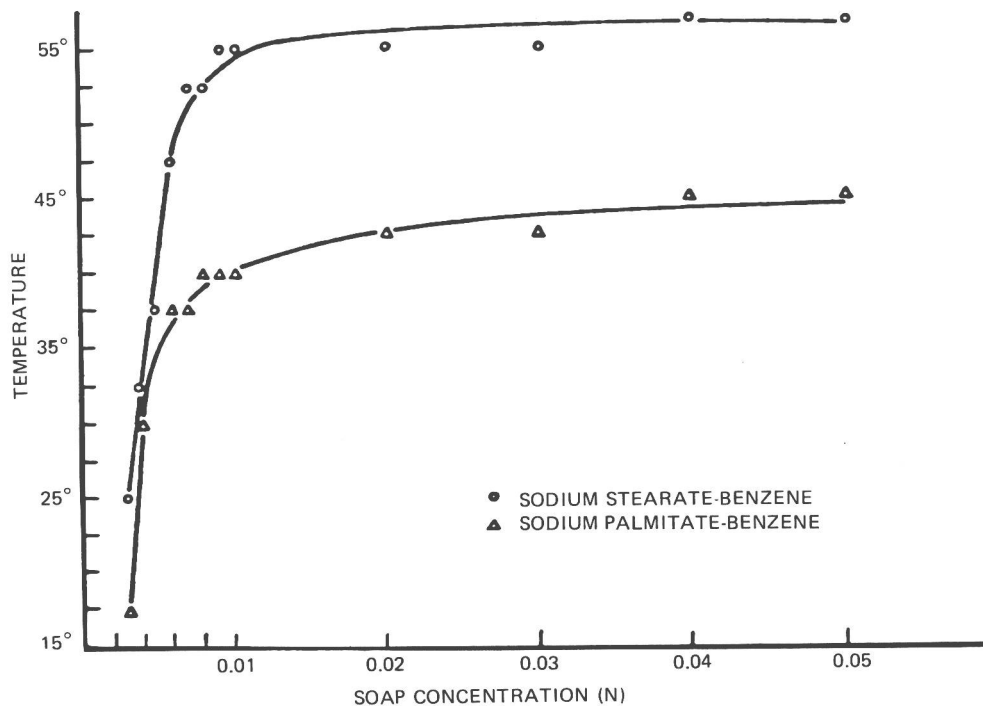


Figure 1. Temperature dependence of inversion for water-in-benzene emulsions stabilized by sodium stearate and sodium palmitate. (From Ref. 6. Copyright 1966, American Chemical Society.)

involves the approach and combination of two or more of these droplets to form a larger drop. Demulsification is affected by a multitude of factors, including dispersed phase concentration, drop interaction energy, bulk physical properties of the two phases, interfacial properties, temperature, and aging.

If the droplets of an emulsion are already coagulated into one large aggregate, the search for a kinetic expression for demulsification would involve finding a rate equation for the disappearance of the globules. In actual practice, however, only a small fraction of droplets are present in aggregates; hence one has to find rate expressions that incorporate both the rate of flocculation and the rate of coalescence.

### 1. Flocculation

The apparent stability of dispersions results from the existence of interparticle forces between dispersed droplets. These forces include electrical double-layer interactions, van der Waals-London forces, and various interactions due to the presence of adsorbed layers of dissolved species or oriented

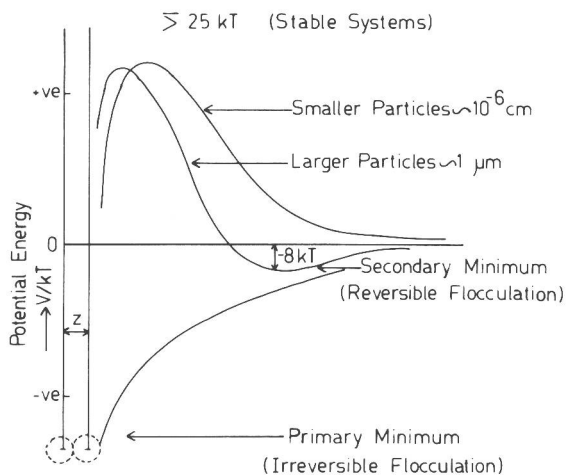


Figure 2. Characteristic interaction energy profiles according to the DLVO theory. (From Ref. 17. Copyright 1975, American Chemical Society.)

molecules [16]. A typical curve for the total interaction as a function of the separation of the particles is illustrated in Fig. 2. The theoretical models in interpreting particle forces predict the existence of a deep primary minimum at small separation and a shallow secondary minimum at large separation in the energy profile.

Flocculation is the process by which two or more droplets of the disperse phase cluster together as aggregates. This process may be either irreversible, occurring in the primary minimum, or reversible, occurring in the secondary minimum of the characteristic interaction energy profiles [17]. For the system of macroemulsions (average droplet diameter  $>1 \mu\text{m}$ ) the flocculation occurs at the secondary minimum. The first comprehensive treatment of the flocculation of dispersed systems was von Smoluchowski's work on the coagulation of hydrophobic sols [18]. Interpretations and modifications of Smoluchowski's theory can be found in the papers of van den Tempel [19] and Lawrence and Mills [20].

The rate of formation of aggregates is determined by the diffusion of the droplets through the continuous phase. The aggregation process is evidently governed by the mutual interaction forces between the droplets. Under conditions when coalescence is much more rapid than flocculation, the rate of flocculation is proportional to the square of the particle concentration,

$$-\frac{dn}{dt} = an^2 \quad (3)$$

or

$$n = \frac{n_0}{1 + an_0 t}$$

where

$n$  = number of primary particles at time  $t$

$n_0$  = number of particles at zero time

$a$  = frequency of collisions between droplets leading to the formation of aggregates.

## 2. Coalescence

As defined earlier, coalescence is the combination of two or more droplets to form a larger drop. The rate of coalescence can be expressed in terms of a simple first-order rate equation if all the globules will have flocculated in a time which is much shorter than the time scale of coalescence.

If  $K$  ( $\text{sec}^{-1}$ ) is the coalescence rate constant, then

$$-\frac{dn}{dt} = Kn \quad (4)$$

or

$$n = n_0 \exp(-Kt)$$

The above equation, first proposed by van den Tempel [19], assumes that the aggregates consist of a very large number of globules and that the coagulation is discontinued before any appreciable change in the size distribution of the drops occurs.

The rate expressions (3) and (4) represent the two ends of the coagulation spectrum, one where flocculation is rate controlling and the other where coalescence is rate controlling. When neither of the processes is rate determining, one can take recourse in a more general model which assumes that flocculation and coalescence are consecutive steps of the breakdown mechanism.

Becher [6] derives the rate expressions in terms of the two parameters  $a$  and  $K$ . His final equation is

$$n = \frac{n_0}{1 + an_0 t} + \frac{an_0^2 t}{(1 + an_0 t)^2} \left[ \frac{an_0}{K} + \left( 1 - \frac{an_0}{K} \right) e^{-Kt} \right] \quad (5)$$