COATINGS TECHNOLOGY Fundamentals, Testing, and Processing Techniques

EDITED BY Arthur A. Tracton



COATINGS TECHNOLOGY FUNDAMENTALS, TESTING, AND PROCESSING TECHNIQUES

COATINGS TECHNOLOGY FUNDAMENTALS, TESTING, AND PROCESSING TECHNIQUES

Edited by Arthur A. Tracton



CRC Press is an imprint of the Taylor & Francis Group, an informa business The material was previously published in *Coatings Technology Handbook, Third Edition* © Taylor and Francis Group 2006.

CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

© 2007 by Taylor & Francis Group, LLC CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works Printed in the United States of America on acid-free paper 10 9 8 7 6 5 4 3 2 1

International Standard Book Number-10: 1-4200-4406-0 (Hardcover) International Standard Book Number-13: 978-1-4200-4406-5 (Hardcover)

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

No part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http:// www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC) 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data Tracton, Arthur A. Coatings technology : fundamentals, testing, and processing techniques / Arthur A. Tracton. p. cm. Originally published under title: Coatings technology handbook. ISBN 1-4200-4406-0 (hardcover) 1. Coating processes--Handbooks, manuals, etc. I. Tracton, Arthur A. Coatings technology handbook. II. Title. TP156.C57C62 2006b 667'.9--dc22 2006b

Visit the Taylor & Francis Web site at http://www.taylorandfrancis.com

and the CRC Press Web site at http://www.crcpress.com

Preface

The coatings world is continually changing by adding new material to the treasury of the old material. However, the fundamentals of coatings and inks are the beginning of the experience. Included in the fundamentals are the concepts of testing (what to test and how to test it), design of experiments to maximize investigation and physical and chemical properties. Once these aspects have been determined, the next step is processing techniques.

Each industry has its own use for coatings and inks. Based on the substrate, each industry has a different approach or method of applying the materials to the substrate. The application method dictates the physical and chemical properties used. Variations are even seen in one industry between applying equipment.

The direction of this book is to acquaint the reader with some of the many aspects of the coating and inks industries. When you know the fundamentals of testing and processing techniques, you can adapt to most situations.

Arthur A. Tracton

Contributors

Harold Van Aken GretagMacbeth New Windsor, New York

Walter Alina

General Magnaplate Corporation Linden, New Jersey

Mark J. Anderson Stat-Ease, Inc. Minneapolis, Minnesota

Brian E. Aufderheide W. H. Brady Company Milwaukee, Wisconsin

Deepak G. Bhat

GTE Valenite Corporation Troy, Michigan

Donald L. Brebner

E. I. du Pont de Nemours & Company Wilmington, Delaware

Patrick Brennan

Q-Panel Lab Products Cleveland, Ohio

George E. F. Brewer George E. F. Brewer Coating Consultants Birmingham, Michigan **Naomi Luft Cameron** Datek Information Services Newtonville, Massachusetts

Robert W. Carpenter Windsor Plastics, Inc. Evansville, Indiana

Chi-Ming Chan Raychem Corporation Menlo Park, California

Carl A. Dahlquist 3M Company St. Paul, Minnesota

David R. Day Micromet Instruments, Inc. Cambridge, Massachusetts

Arnold H. Deutchman BeamAlloy Corporation Dublin, Ohio

Eric T. Everett Q-Panel Lab Products Cleveland, Ohio

Carol Fedor Q-Panel Lab Products Cleveland, Ohio

K. B. Gilleo Sheldahl, Inc. Northfield, Minnesota **William S. Gilman** Gilman & Associates South Plainfield, New Jersey

F. A. Goossens Stork Brabant Boxmeer, The Netherlands

Douglas Grossman Q-Panel Lab Products Cleveland, Ohio

William F. Harrington, Jr. Uniroyal Adhesives and Sealants Company, Inc. Mishawaka, Indiana

Herman Hockmeyer Hockmeyer Equipment Corporation Elizabeth City, North Carolina

Stephen L. Kaplan Plasma Science, Inc. Belmont, California

Douglas S. Kendall

National Enforcement Investigations Center U.S. Environmental Protection Agency Denver Federal Center Denver, Colorado Artur Koch Ahlbrandt System GmbH

John Lind Graphic Arts Technical Foundation Pittsburgh, Pennsylvania

H. Thomas Lindland Flynn Burner Corporation New Rochelle, New York

Harry G. Lippert Extrusion Dies, Inc. Chippewa Falls, Wisconsin

Donald M. MacLeod Industry Tech Oldsmar, Florida

John A. McClenathan IMD Corporation Birmingham, Alabama

Frederic S. McIntyre Acumeter Laboratories, Inc. Marlborough, Massachusetts

Timothy B. McSweeney Screen Printing Association International Fairfax, Virginia

R. Milker Lohmann GmbH Neuwied, Germany Wayne E. Mozer Oxford Analytical, Inc. Andover, Massachusetts

Richard Neumann Windmöller & Hölscher Lengerich/Westfalen, Germany

Michael O'Mary The Armoloy Corporation DeKalb, Illinois

Robert J. Partyka BeamAlloy Corporation Dublin, Ohio

John A. Pasquale III Liberty Machine Company Paterson, New Jersey

Patrick Patton Q-Panel Lab Products Cleveland, Ohio

Lindas Pranevicius Vytautas Magnus University Kaunas, Lithuania

H. Randhawa Vac-Tec Systems, Inc. Boulder, Colorado

Richard Rathmell Consultant Londonderry, New Hampshire **Peter W. Rose** Plasma Science, Inc. Belmont, California

D. Satas Satas & Associates Warwick, Rhode Island

John Stack National Institute for Occupational Safety & Health National Personal Protective Technology Laboratory Pittsburgh, Pennsylvania

Steve Stalker ITW Industrial Finishing Glendale Heights, Illinois

Arthur A. Tracton Consultant Bridgewater, New Jersey

A. Vakelis Lithuanian Academy of Sciences Vilnius, Lithuania

Subbu Venkatraman Raychem Corporation Menlo Park, California

Patrick J. Whitcomb Stat-Ease, Inc. Minneapolis, Minnesota

Ulrich Zorll Forschungsinstitut für Pigmente and Lacke Stuttgart, Germany

Contents

I Fundamentals and Testing

1	Rheology and Surface Chemistry
2	Coating Rheology
3	Leveling
4	Structure–Property Relationships in Polymers
5	The Theory of Adhesion
6	Adhesion Testing
7	Coating Calculations
8	Infrared Spectroscopy of Coatings
9	Thermal Analysis for Coatings Characterizations
10	Color Measurement for the Coatings Industry
11	The Use of X-Ray Fluorescence for Coat Weight Determinations
12	Sunlight, Ultraviolet, and Accelerated Weathering
13	Cure Monitoring: Microdielectric Techniques
14	Test Panels

15	Design of Experiments for Coatings
16	Top 10 Reasons Not to Base Service Life Predictions upon Accelerated Lab Light Stability Tests <i>Eric T. Everett</i>
17	Under What Regulation?
18	Fade Resistance of Lithographic Inks — A New Path Forward: Real World Exposures in Florida and Arizona Compared to Accelerated Xenon Arc Exposures

II Coating and Processing Techniques

19	Wire-Wound Rod Coating
20	Slot Die Coating for Low Viscosity Fluids
21	Extrusion Coating with Acid Copolymers and Lonomers
22	Porous Roll Coater
23	Rotary Screen Coating
24	Screen Printing
25	Flexography
26	Ink-Jet Printing
27	Electrodeposition of Polymers
28	Electroless Plating
29	The Electrolizing Thin, Dense, Chromium Process

*Deceased.

30	The Armoloy Chromium Process
31	Sputtered Thin Film Coatings
32	Vapor Deposition Coating Technologies
33	Cathodic Arc Plasma Deposition
34	Industrial Diamond and Diamondlike Films
35	Tribological Synergistic Coatings
36	Chemical Vapor Deposition
37	Solvent Vapor Emission Control
38	Surface Treatment of Plastics
39	Flame Surface Treatment
40	Plasma Surface Treatment
41	Surface Pretreatment of Polymer Webs by Fluorine
42	Calendering of Magnetic Media
43	Embossing
44	In-Mold Finishing
45	HVLP: The Science of High-Volume, Low-Pressure Finishing
46	A Practical Guide to High-Speed Dispersion
Index	

Ι

Fundamentals and Testing

1 Rheology and Surface Chemistry

1.1 Introduction 1-1 1.2 Rheology 1-2 Types of Viscosity Behavior • Temperature Effects • Solvent 1-2 Effects • Viscosity Measurement • Yield Value 1.3 Surface Chemistry 1-8 Surface Tension • Measuring Surface Tension • Wetting • 1-12 Surfactants • Leveling 1.4 Summary 1-12 References 1-12 Bibliography 1-12

K. B. Gilleo Sheldahl, Inc.

1.1 Introduction

A basic understanding of rheology and surface chemistry, two primary sciences of liquid flow and solid–liquid interaction, is necessary for understanding coating and printing processes and materials. A generally qualitative treatment of these subjects will suffice to provide the insight needed to use and apply coatings and inks and to help solve the problems associated with their use.

Rheology, in the broadest sense, is the study of the physical behavior of all materials when placed under stress. Four general categories are recognized: elasticity, plasticity, rigidity, and viscosity. Our concern here is with liquids and pastes. The scope of rheology of fluids encompasses the changes in the shape of a liquid as physical force is applied and removed. Viscosity is a key rheological property of coatings and inks. Viscosity is simply the resistance of the ink to flow — the ratio of shear stress to shear rate.

Throughout coating and printing processes, mechanical forces of various types and quantities are exerted. The amount of shear force directly affects the viscosity value for non-Newtonian fluids. Most coatings undergo some degree of "shear thinning" phenomenon when worked by mixing or running on a coater. Heavy inks are especially prone to shear thinning. As shear rate is increased, the viscosity drops, in some cases, dramatically.

This seems simple enough except for two other effects. One is called the yield point. This is the shear rate required to cause flow. Ketchup often refuses to flow until a little extra shear force is applied. Then it often flows too freely. Once the yield point has been exceeded the solidlike behavior vanishes. The loose network structure is broken up. Inks also display this yield point property, but to a lesser degree. Yield point is one of the most important ink properties.

Yield value, an important, but often ignored attribute of liquids, will also be discussed. We must examine rheology as a dynamic variable and explore how it changes throughout the coating process. The mutual interaction, in which the coating process alters viscosity and rheology affects the process, will be a key concept in our discussions of coating technology. The second factor is time dependency. Some inks change viscosity over time even though a constant shear rate is being applied. This means that viscosity can be dependent on the amount of mechanical force applied and on the length of time. When shearing forces are removed, the ink will return to the initial viscosity. That rate of return is another important ink property. It can vary from seconds to hours.

Rheology goes far beyond the familiar snapshot view of viscosity at a single shear rate, which is often reported by ink vendors. It deals with the changes in viscosity as different levels of force are applied, as temperature is varied, and as solvents and additives come into play. Brookfield viscometer readings, although valuable, do not show the full picture for non-Newtonian liquids.

Surface chemistry describes wetting (and dewetting) phenomena resulting from mutual attractions between ink molecules, as well as intramolecular attractions between ink and the substrate surface. The relative strengths of these molecular interactions determine a number of ink performance parameters. Good print definition, adhesion, and a smooth ink surface all require the right surface chemistry. Bubble formation and related film formation defects also have their basis in surface chemistry.

Surface chemistry, for our purposes, deals with the attractive forces liquid molecules exhibit for each other and for the substrate. We will focus on the wetting phenomenon and relate it to coating processes and problems. It will be seen that an understanding of wetting and dewetting will help elucidate many of the anomalies seen in coating and printing.

The two sciences of rheology and surface tension, taken together, provide the tools required for handling the increasingly complex technology of coating. It is necessary to combine rheology and surface chemistry into a unified topic to better understand inks and the screen printing process. We will cover this unification in a straightforward and semiqualitative manner. One benefit will be the discovery that printing and coating problems often blamed on rheology have their basis in surface chemistry. We will further find that coating leveling is influenced by both rheology and surface chemistry.

1.2 Rheology

Rheology, the science of flow and deformation, is critical to the understanding of coating use, application, and quality control. Viscosity, the resistance to flow, is the most important rheological characteristic of liquids and therefore of coatings and inks. Even more significant is the way in which viscosity changes during coating and printing. Newtonian fluids, like solvents, have an absolute viscosity that is unaltered by the application of mechanical shear. However, virtually all coatings show a significant change in viscosity as different forces are applied. We will look at the apparent viscosity of coatings and inks and discover how these force-induced changes during processing are a necessary part of the application process.

Viscosity, the resistance of a liquid to flow, is a key property describing the behavior of liquids subjected to forces such as mixing. Other important forces are gravity, surface tension, and shear associated with the method of applying the material. Viscosity is simply the ratio of shear stress to shear rate (Equation 1.3). A high viscosity liquid requires considerable force (work) to produce a change in shape. For example, high viscosity coatings are not as easily pumped as are the low viscosity counterparts. High viscosity coatings also take longer to flow out when applied.

Shear rate, D =
$$\frac{\text{velocity}}{\text{thickness}}(\text{sec}^{-1})$$
 (1.1)

Shear stress,
$$\tau = \frac{\text{force}}{\text{area}} (\text{dynes/cm}^2)$$
 (1.2)

Viscosity,
$$\eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{D} (\text{dynes} \cdot \text{sec/cm}^2)$$
 (1.3)

Liquid	Viscosity (cP)
Acetone	0.32
Chloroform	0.58
Toulene	0.59
Water, standard 2(20°C)	1.0000
Cyclohexane	1.0
Ethyl alcohol	1.2
Turpentine	1.5
Mercury, metal	1.6
Creosote	12.0
Sulfuric acid	25.4
Lindseed oil	33.1
Olive oil	84.0
Castor oil	986.0
Glycerine	1490.0
Venice turpentine	130,000.0

TABLE 1.1 Viscosities of Common Industrial Liquids

Values are for approximately 20°C.

Source: From Handbook of Chemistry and Physics, 64th ed., CRC Press, Boca Raton, FL, 1984.1

As indicated above, shear stress, the force per unit area applied to a liquid, is typically in dynes per square centimeter, the force per unit area. Shear rate is in reciprocal seconds (sec-1), the amount of mechanical energy applied to the liquid. Applying Equation 1.3, the viscosity unit becomes dyne-seconds per square centimeter or poise (P). For low viscosity fluids like water (~0.01 P), the poise unit is rather small, and the more common centipoise (0.01 P) is used. Since 100 centipoise = 1 poise, water has a cP for graphics and as high as 50,000 cP for some highly loaded polymer thick film (PTF) inks and adhesives. Viscosity is expressed in pascal-seconds (Pa·sec) in the international system of units (SI: 1 Pa·sec = 1000 cP). Viscosity values of common industrial liquids are provided in Table 1.1.

viscosity of about 1 centipoise (cP). Screen inks are much more viscous and range from 1000 to 10,000 Viscosity is rather a simple concept. Thin, or low viscosity liquids flow easily, while high viscosity ones move with much resistance. The ideal, or Newtonian, case has been assumed. With Newtonian fluids,

viscosity is constant over any region of shear. Very few liquids are truly Newtonian. More typically, liquids drop in viscosity as shear or work is applied. The phenomenon was identified above as shear thinning. It is, therefore, necessary to specify exactly the conditions under which a viscosity value is measured. Time must also be considered in addition to shear stress. A liquid can be affected by the amount of time that force is applied. A shear-thinned liquid will tend to return to its initial viscosity over time. Therefore, time under shearing action and time at rest are necessary quantifiers if viscosity is to be accurately reported.

It should be apparent that we are really dealing with a viscosity curve, not a fixed point. The necessity of dealing with viscosity curves is even more pronounced in plastic decorating. A particular material will experience a variety of different shear stresses. For example, a coating may be mixed at relatively low shear stress of 10 to 20 cP, pumped through a spray gun line at 1000 cP, sprayed through an airless gun orifice at extreme pressure exceeding 106 cP, and finally allowed to flow out on the substrate under mild forces of gravity (minor) and surface tension. It is very likely that the material will have a different viscosity at each stage. In fact, a good product should change in viscosity under applications processing.

1.2.1 Types of Viscosity Behavior

Plasticity 1.2.1.1

Rheologically speaking, plastic fluids behave more like plastic solids until a specific minimum force is applied to overcome the yield point. Gels, sols, and ketchup are extreme examples. Once the yield point has been reached, the liquid begins to approach Newtonian behavior as shear rate is increased. Figure 1.1



FIGURE 1.1 Shear stress-shear rate curves.

shows the shear stress-shear rate curve and the yield point. Although plastic behavior is of questionable value to ketchup, it has some benefit in inks and paints. Actually, it is the yield point phenomenon that is of practical value. No-drip paints are an excellent example of the usefulness of yield point. After the brush stroke force has been removed, the paint's viscosity builds quickly until flow stops. Dripping is prevented because the yield point exceeds the force of gravity.

Ink bleed in a printing ink, the tendency to flow beyond the printed boundaries, is controlled by yield point. Inks with a high yield point will not bleed, but their flow out may be poor. A very low yield point will provide excellent flow out, but bleed may be excessive. Just the right yield point provides the needed flow out and leveling without excessive bleed. Both polymer binders and fillers can account for the yield point phenomenon. At rest, polymer chains are randomly oriented and offer more resistance to flow. Application of shear force straightens the chains in the direction of flow, reducing resistance. Solid fillers can form loose molecular attraction structures, which break down quickly under shear.

1.2.1.2 Pseudoplasticity

Like plastic-behaving materials, pseudoplastic liquids drop in viscosity as force is applied. There is no yield point, however. The more energy applied, the greater the thinning. When shear rate is reduced, the viscosity increases at the same rate by which the force is diminished. There is no hysteresis; the shear stress–shear rate curve is the same in both directions as was seen in Figure 1.1. Figure 1.2 compares pseudoplastic behavior using viscosity–shear rate curves.

Many coatings exhibit this kind of behavior, but with time dependency. There is a pronounced delay in viscosity increase after force has been removed. This form of pseudoplasticity with a hysteresis loop is called thixotropy. Pseudoplasticity is generally a useful property for coatings and inks. However, thixotropy is even more useful.

1.2.1.2.1 Thixotropy

Thixotropy is a special case of pseudoplasticity. The material undergoes "shear thinning"; but as shear forces are reduced, viscosity increases at a lesser rate to produce a hysteresis loop. Thixotropy is very common and very useful. Dripless house paints owe their driplessness to thixotropy. The paint begins as a moderately viscous material that stays on the brush. It quickly drops in viscosity under the shear stress of brushing for easy, smooth application. A return to higher viscosity, when shearing action stops, prevents dripping and sagging.

Screen printing inks also benefit from thixotropy. The relatively high viscosity screen ink drops abruptly in viscosity under the high shear stress associated with being forced through a fine mesh screen. The



FIGURE 1.2 Viscosity shear rate curves.

momentary low viscosity permits the printed ink dots to merge together into a solid, continuous film. Viscosity returns to a higher range before the ink can "bleed" beyond the intended boundaries.

Thixotropic materials yield individual hysteresis loops. Shear stress lowers viscosity to a point at which higher force produces no further change. As energy input to the liquid is reduced, viscosity begins to build again, but more slowly than it initially dropped. It is not necessary to know the shape of the viscosity loop, but merely to realize that such a response is common in decorating inks, paints, and coatings.

The presence in decorating vehicles of pigments, flatting agents, and other solid fillers usually produces or increases thixotropic behavior. More highly loaded materials, such as inks, are often highly thixotropic. Thixotropic agents, consisting of flat, platelet structures, can be added to liquids to adjust thixotropy. A loose, interconnecting network forms between the platelets to produce the viscosity increase. Shearing breaks down the network, resulting in the viscosity drop.

Mixing and other high shear forces rapidly reduce viscosity. However, thixotropic inks continue to thin down while undergoing shearing, even if the shear stress is constant. This can be seen with a Brookfield viscometer, where measured viscosity continues to drop while the spindle turns at constant rpms. When the ink is left motionless, viscosity builds back to the initial value. This can occur slowly or rapidly. Curves of various shapes are possible, but they will all display a hysteresis loop. In fact, this hysteresis curve is used to detect thixotropy (see Figure 1.3). The rate of viscosity change is an important characteristic of an ink which is examined later as we take an ink step by step through screen printing. Thixotropy is very important to proper ink behavior, and the changing viscosity attribute makes screen printing possible.

1.2.1.2.2 Dilatancy

Liquids that show an increase in viscosity as shear is applied are called dilatants. Very few liquids possess this property. Dilatant behavior should not be confused with the common viscosity build, which occurs when inks and coatings lose solvent. For example, a solvent-borne coating applied by a roll coater will show a viscosity increase as the run progresses. The rotating roller serves as a solvent evaporator, increasing the coating's solids content and, therefore, the viscosity. True dilatancy occurs independently of solvent loss.

1.2.1.2.3 Rheoplexy

Sounding more like a disease than a property, rheoplexy is the exact opposite of thixotropy. It is the timedependent form of dilatancy where mixing causes shear thickening. Figure 1.3 showed the hysteresis loop. Rheoplexy is fortunately rare, because it is totally useless as a characteristic for screen print inks.



Rate (sec. -1)



1.2.2 Temperature Effects

Viscosity is strongly affected by temperature. Measurements should be taken at the same temperature (typically 23°C). A viscosity value is incomplete without a temperature notation.

Although each liquid is affected differently by a temperature change, the change per degree is usually a constant for a particular material. The subject of temperature effects has been covered thoroughly elsewhere.² It will suffice to say that a coating's viscosity may be reduced by heating, a principle used in many coating application systems.

Viscosity reduction by heating may also be used after a material has been applied. Preheating of ultraviolet (UV)-curable coatings just prior to UV exposure is often advantageous for leveling out these sometimes viscous materials.

1.2.3 Solvent Effects

Higher resin solids produce higher solution viscosity, while solvent addition reduces viscosity. It is important to note that viscosity changes are much more pronounced in the case of soluble resins (polymers) than for insoluble pigments or plastic particles. For example, although a coating may be highly viscous at 50% solids, a plastisol suspension (plastic particles in liquid plasticizer) may have medium viscosity at 80% solids. Different solvents will produce various degrees of viscosity reduction depending on whether they are true solvents, latent solvents, or nonsolvents. This subject has been treated extensively elsewhere.^{2,3}

1.2.4 Viscosity Measurement

Many instruments are available. A rheometer is capable of accurately measuring viscosities through a wide range of shear stress. Much simpler equipment is typically used in the plastic decorating industry. As indicated previously, perhaps the most common device is the Brookfield viscometer, in which an electric motor is coupled to an immersion spindle through a tensiometer. The spindle is rotated in the liquid to be measured. The higher the viscosity (resistance to flow), the larger is the reading on the tensiometer. Several spindle diameters are available, and a number of rotational speeds may be selected. Viscosity must be reported along with spindle size and rotational speed and temperature.

					Consisten	су			
		Watery			Medium			Heavy	
Poise:	0.1	0.5	1.0	2.5	5.0	10	50	100	150
Centipoise:	10	50	100	250	500	1,000	5,000	10,000	15,000
Viscosity device									
Fisher #1	20								
Fisher #2		24	50						
Ford #4 cup	5	22	34	67					
Parlin #10	11	17	25	55					
Parlin #15				12	25	47	232	465	697
Saybolt	60	260	530	1,240	2,480	4,600	23,500	46,500	69,500
Zahn #1	30	60							
Zahn #2	16	24	37	85					
Zahn #3			12	29	57				
Zahn #4			10	21	37				

TABLE 1.2	Viscosity	Conversions ^a

^a Liquids are at 25°C. Values are in seconds for liquids with specific gravity of approximately 1.0. *Source*: Binks Inc., ITW Industrial Finishing, 195 International Boulevard, Glendale Heights, IL 60134.

The Brookfield instrument is a good tool for incoming quality control. Although certainly not a replacement for the rheometer, the viscometer may be used to estimate viscosity change with shear. Viscosity readings are taken at different rpms and then compared. A highly thixotropic material will be easily identified.

An even simpler viscosity device is the flow cup, a simple container with an opening at the bottom. The Ford cup and the Zahn cup are very common in the plastic painting and coating field. The Ford cup, the more accurate of the two, is supported on a stand. Once filled, the bottom orifice is unstoppered and the time for the liquid to flow out is recorded. Unlike the Brookfield, which yields a value in centipoise, the cup gives only a flow time. Relative flow times reflect different relative viscosities. Interconversion charts permit Ford and other cup values to be converted to centipoise (Table 1.2).

The Zahn cup is dipped in a liquid sample by means of its handle and quickly withdrawn, whereupon time to empty is recorded. The Zahn type of device is commonly used on line, primarily as a checking device for familiar materials.

1.2.5 Yield Value

The yield value is the shear stress in a viscosity measurement, but one taken at very low shear. The yield value is the minimum shear stress, applied to a liquid, that produces flow. As force is gradually applied, a liquid undergoes deformation without flowing. In essence, the liquid is behaving as if it were an elastic solid. Below the yield value, viscosity approaches infinity. At a critical force input (the yield value) flow commences.

The yield value is important in understanding the behavior of decorating liquids after they have been deposited onto the substrate. Shear stress, acting on a deposited coating or ink, is very low. Although gravity exerts force on the liquid, surface tension is considerably more important.

If the yield value is greater than shear stress, flow will not occur. The liquid will behave as if it were a solid. In this situation, what you deposit is what you get. Coatings that refuse to level, even though the apparent viscosity is low, probably have a relatively high yield value. As we will see in the next section, surface tension forces, although alterable, cannot be changed enough to overcome a high yield value. Unfortunately, a high yield value may be an intrinsic property of the decorative material. Under these circumstances, changing the material application method may be the only remedy.

Although a high yield value can make a coating unusable, the property can be desirable for printing inks. Once an ink has been deposited, it should remain where placed. Too low a yield value can allow an ink to flow out, producing poor, irregular edge definition. An ink with too high a value may flow out

poorly. As pigments tend to increase yield value, color inks are not a problem. Clear protective inks can be a problem, especially when a thick film is deposited, as in screen printing. When it is not practical to increase yield value, wettability can sometimes be favorably altered through surface tension modification. Increasing surface tension will inhibit flow and therefore ink or coating bleed.

1.3 Surface Chemistry

Surface chemistry is the science that deals with the interface of two materials. The interface may exist between any forms of matter, including a gas phase. For the purpose of understanding the interfacial interaction of decorative liquid materials, we need only analyze the liquid–solid interaction. Although there is a surface interaction between a liquid coating and the air surrounding it, the effect is small and may be ignored.

1.3.1 Surface Tension

All liquids are made up of submicroscopic combinations of atoms called molecules (a very few liquids are made up of uncombined atoms). All molecules that are close to one another exert attractive forces. It is these mutual attractions that produce the universal property called surface tension. The units are force per unit length: dynes per centimeter.

A drop of liquid suspended in space quickly assumes a spherical shape. As surface molecules are pulled toward those directly beneath them, a minimum surface area (sphere) results. The spherical form is the result of an uneven distribution of force; molecules within the droplet are attracted from all directions, while those at the surface are pulled only toward molecules below them. All liquids attempt to form a minimum surface sphere. A number of counterforces come into play, however. A liquid placed on a solid provides a liquid–solid interface. This type of interface is critically important to the plastic decorator, as liquid molecules are attracted not only to each other (intramolecular attraction) but also to any solid surface (intermolecular attraction) with which they come in contact. We need only concern ourselves with these two interactions; intra- and intermolecular. A fundamental understanding of this interfacial interaction will permit the decorator to optimize materials and processes.

1.3.2 Measuring Surface Tension

Every liquid has a specific surface tension value. Liquids with high surface tensions, such as water (73 dynes/cm), demonstrate a high intramolecular attraction and a strong tendency to bead up (form spheres). Liquids with low values have a weak tendency toward sphere formation that is easily overcome by countering forces.

A variety of methods are available for measuring liquid surface tension. Table 1.3 gives values for common solvents. Methods are also available for determining the surface tension of solids, which is usually referred to as surface energy. Table 1.4 gives surface energy values for plastics. We need be concerned only with ways of estimating surface tension and with techniques for determining relative differences.

1.3.3 Wetting

A liquid placed on a flat, horizontal solid surface either will wet and flow out, or it will dewet to form a semispherical drop. An in-between state may also occur in which the liquid neither recedes nor advances but remains stationary. The angle that the droplet or edge of the liquid makes with the solid plane is called the *contact angle* (Figure 1.4).

A nonwetting condition exists when the contact angle exceeds 0° — that is, when the angle is measurable. The liquid's intramolecular attraction is greater than its attraction for the solid surface. The liquid surface tension value is higher than the solid's surface energy. A wetting condition occurs when the contact angle is 0° . The liquid's edge continues to advance, even though the rate may be slow for

Liquid	Surface Tension (dynes/cm)
SF ₆	5.6
Trifluoroacetic acid	15.6
Heptane	22.1
Methanol	24.0
Acetone	26.3
Dimethylformamide (DMF)	36.8
Dimethyl sulfoxide (DMSO)	43.5
Ethylene glycol	48.4
Formamide	59.1
Glycerol	63.1
Diiodomethane	70.2
Water	72.8
Mercury, metal	490.6

TABLE 1.3 Surface Tension of Liquids

Source: From Dean, J., Ed., Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1985.⁴

Polymer	Surface Tension (dynes/cm)
Polyperfluoropropylene	16
Polytetrafluoroethylene (Teflon)	18.5
Polydimethyliloxane	24
Polyethylene	31
Polystyrene	34
Polymethylmethacrylate (acrylic)	39
Polyvinyl chloride (PVC)	40
Polyethylene terephthalate (polyester)	43
Polyhexamethylene adipate (nylon)	46

Source: From Bikales, N.M., *Adhesion and* Bonding, Wiley-Interscience, New York, 1971.⁵



FIGURE 1.4 Contact angle.

high viscosity materials. The intermolecular (solid–liquid) attraction is greater in this case. The surface energy of the solid is higher than the liquid's surface tension.

Measuring the contact angle is a simple technique for determining the relative difference between the two surface tensions. A high contact angle signifies a large departure, while a small angle suggests that the two values are close, but not equal.

Surface Tension	Castor Oil	Toluene	Heptane	FC48/FC77
15 dynes/cm				0/100
17				100/100
19				100/0
22			100	
22.4	12.0	49.2	38.8	
24.5	55.2	25.0	19.8	
27	74.2	14.4	11.4	
30	0	100.0	0	
32.5	88.0	4.5	3.5	
35	100.0			
63	(100 glycerol)			
72.8	(100 water)			

TABLE 1.5 Surface Tension Test Kit

Mixtures are in weight percent.

Source: Various sources and tests by author.

One can estimate liquid surface tension by applying drops of the liquid onto smooth surfaces of known values until a wetting just occurs, signifying that the two surface tensions are equal. Conversely, the surface energy of a solid may be estimated by applying drops of standard surface tension liquids until wetting is achieved. A surface tension kit can be made up from simple mixtures for testing surfaces. Table 1.5 provides formulas.

Low energy surfaces are difficult to wet and can give poor results for coating, painting, and printing. The standard surface tension kit may be used to estimate the surface energy of a plastic to be decorated. If the particular plastic shows a much lower value than that reported in Table 1.4, contamination is suspected. Mold release agents, unless specially made compatible for decorating materials, can greatly lower surface energy of a plastic part, making it uncoatable.

1.3.4 Surfactants

Agents that alter interfacial interactions are called surfactants. The surfactant possesses two different chemical groups, one compatible with the liquid to be modified, and the other having a lower surface tension. For example, the surface tension of an epoxy may be reduced by adding a surfactant with an alcohol group (epoxy-compatible) at one end and a fluorochemical group at the other. The alcohol group will associate with the epoxy resin, presenting the incompatible fluorochemical "tail" to the surface. The epoxy coating will behave as if it were a low surface tension fluorochemical. The addition of a small amount of surfactant will permit the epoxy coating to wet difficult, low energy surfaces, even oil-contaminated plastic.

Surfactants efficiently lower the surface tension of inks, coatings, and paints. Typically, 1% or less is sufficient. When dewetting occurs because of intrinsically low surface energy of the substrate, use of surfactants, also called wetting agents, is indicated. These materials are not a substitute for good house-keeping and proper parts preparation. Contamination can cause adhesion failure later.

Fluorochemicals, silicones, and hydrocarbons are common categories of surfactants. Fluorochemicals have the lowest surface tension of any material and are the most efficient wetting agents. Silicones are next in efficacy and are lower in cost. Certain types of silicone, however, can become airborne, causing contamination of the substrate.

Although it may be desirable to lower the surface tension of a coating, the opposite is true for the substrate. The very agent that helps the decorating material renders the substrate useless. Silicone contamination will produce the notorious dewetting defect called "fish-eyes."

Coatings, paints, and inks, once modified with surfactants, are usually permanently changed, even after curing. Their low surface energy will make them difficult to wet over if, for example, it is necessary to apply a top coat. There are several options for overcoming this problem. The best practice is to use the smallest amount of the least potent surfactant that will do the job. Start with the hydrocarbon class. Also make sure that the substrate is clean to begin with.

Another possibility is to use reactive surfactants. Agents possessing a functional group that can react with coating or binder are rendered less active after curing. Once the surfactant has completed the role of wetting agent, it is no longer needed. One other approach is to add surfactant to the second material to be applied. Often the same surfactant will work, especially at a slightly higher loading.

1.3.5 Leveling

Leveling depends on both rheology and surface chemistry. It is a more complex phenomenon and a more difficult one to control. Coatings applied by spraying, dipping, roll coating, and most other methods are often not smooth enough for aesthetic appeal. Splatters, runs, ridges, and other topological defects require that the liquid material level out. It is therefore important to understand the dynamics of leveling.

We will first assume that proper wetting has been achieved, by wetting agents if necessary. Important parameters affecting leveling are viscosity, surface tension, yield value, coating thickness, and the degree of wet coating irregularity. Several workers have developed empirical relationships to describe leveling. The leveling equation (Equation 1.4) is quite useful.⁶

$$a_t = a_0 \frac{\exp(\operatorname{const} \sigma h^3 t)}{3\lambda^4 \eta}$$
(1.4)

where

 a_t = amplitude (height) of coating ridge

 σ = the surface tension of the coating

 η = coating viscosity

h = coating thickness or height

- t = the time for leveling
- λ = wavelength or distance between ridges

Equation 1.4 shows that leveling is improved by one or more of the following:

- 1. Longer time (t)
- 2. Higher surface tension of coating (σ)
- 3. Lower viscosity (η)
- 4. Greater coating thickness (h)
- 5. Small repeating distance between ridges (λ)

Note that *h*, the coating thickness, is raised to the third power. Doubling the thickness provides an eightfold (2^3) improvement in leveling. Also note that λ , wavelength between ridges, is raised to the fourth power. This means that ridges that are very far apart create a very difficult leveling situation.

Earlier, it was pointed out that a high yield value could prevent leveling. The shear stress on a wet coating must be greater than the yield value for leveling to take place. Equation 1.5 shows the relationship between various parameters and shear stress.⁷

$$T_{\rm max} = \frac{4\pi^3 \sigma ah}{\lambda^3} \quad \text{or} \quad D(\text{coating ridge depth}) = \frac{\tau \lambda^3}{4\pi^3 \sigma h} \tag{1.5}$$

where

 σ = surface tension of coating

a = amplitude of coating ridge

h = coating height

 λ = coating ridge wavelength

Because Equation 1.5 deals with force, the time factor and the viscosity value drop out. It is seen that increasing surface tension and coating thickness produce the maximum shear stress. Coating defect height (*a*) increases shear, while wavelength (λ) strongly reduces it. If coating ridges cannot be avoided, higher, more closely packed ones are preferable.

When the yield value is higher than the maximum shear (T_{max}) , leveling will not occur. Extending leveling time and reducing viscosity will not help to overcome the yield value barrier, because these terms are not in the shear equation. Increasing surface tension and coating thickness are options, but there are practical limits.

As yield value is usually affected by shear (thixotropy), coating application rate and premixing conditions may be important. Higher roller speed (for roll coaters) and higher spray pressure (for spray guns) can drop the yield value temporarily. It should be apparent that best leveling is not achieved by lowest surface tension. Although good wetting may require a reduction in surface tension, higher surface tension promotes leveling. This is one more reason to use the minimum effective level of surfactant.

1.4 Summary

A comprehension of the basic principles that describe and predict liquid flow and interfacial interactions is important for the effective formulation and the efficient application of coatings and related materials. The theoretical tools for managing the technology of coatings are rheology, the science of flow and deformation, considered with surface chemistry, and the science of wetting and dewetting phenomena. Viewing such rheology properties as viscosity in terms of their time dependency adds the necessary dimension for practical application of theory to practice. Such important coating attributes as leveling are affected by both viscosity and surface tension. Knowing the interrelationships allows the coating specialist to make adjustments and take corrective actions with confidence.

References

- 1. Handbook of Chemistry and Physics, 64th ed. Boca Raton, FL: CRC Press, 1984.
- 2. Temple C. Patton, Paint Flow and Pigment Dispersion, 2nd ed. New York: Wiley, 1979.
- 3. Charles R. Martens, Technology of Paint, Varnish and Lacquers. New York: Krieger Pub. Co., 1974.
- 4. Dean, J., Ed., Lange's Handbook of Chemistry, 13th ed. New York: McGraw-Hill, 1985.
- 5. Norbert M. Bikales, Adhesion and Bonding. New York: Wiley-Interscience, 1971.
- 6. S. Orchard, Appl. Sci. Res., A11, 451 (1962).
- 7. N. D. P. Smith, S. E. Orchard, and A. J. Rhind-Tutt, "The physics of brush marks," *JOCCA*, 44, 618–633, September (1961).

Bibliography

Bikales, N. M., *Adhesion and Bonding*. New York: Wiley-Interscience, 1971. Martens, C. R., *Technology of Paint, Varnish and Lacquers*. New York: Krieger Pub. Co., 1974. Nylen, P. and S. Sunderland, *Modern Surface Coatings*. New York: Wiley, 1965. Patton, T. C., *Paint Flow and Pigment Dispersion*, 2nd ed. New York: Wiley-Interscience, 1979.

2

Coating Rheology

	2.1	Introduction	2- 1
	2.2	Definitions and Measurement Techniques Surface Tension • Viscosity • Thixotropy • Dilatancy • Yield Stress • Elasticity	2- 1
Chi-Ming Chan Raychem Corporation	2.3	Rheological Phenomena in Coating Wetting • Coalescence • Sagging and Slumping • Leveling • Viscosity Changes after Application • Edge and Corner Effects • Depressions: Bernard Cells and Craters	2- 5
Subbu Venkatraman	Ackn	owledgments	2- 13
Raychem Corporation	Refei	rences	2- 13

2.1 Introduction

Depending on the nature of the starting material, coatings can be broadly classified into solvent-borne and powder coatings. The solvent-borne coatings include both solutions (high and low solid contents) and suspensions or dispersions. Methods of application and the markets for these coatings are listed in Table 2.1.

2.2 Definitions and Measurement Techniques

2.2.1 Surface Tension

Surface tension is defined as the excess force per unit length at the surface; it is reckoned as positive if it acts in such a direction as to contract the surface.^{1,6} The tendency of a system to decrease its surface area is the result of the excess surface energy, because the surface atoms are subjected to a different environment as compared to those in the bulk. Surface tension of liquids and polymer melts can be measured by methods such as capillary tube,¹ Du Nuoy ring,^{2,7} Wilhelmy plate,^{3,8} and pendent drop.^{4,5} We shall focus our discussion on two methods: the capillary-height and pendant-drop methods.

The capillary-height method is the most suitable for low viscosity liquids because the system takes a long time to reach equilibrium for high viscosity liquids. It is reported that as many as 4 days are needed to attain equilibrium for a polystyrene melt at 200°C.⁵ Figure 2.1 illustrates the capillary-height method. At equilibrium, the force exerted on the meniscus periphery due to the surface tension must be balanced by the weight of the liquid column. Neglecting the weight of the liquid above the meniscus, an approximate equation can be written as follows:

$$\Delta \rho g h = 2\gamma \frac{\cos \theta}{r} \tag{2.1}$$

where $\Delta \rho$ is the density difference between the liquid and air, g is the gravitational constant, h is the height of the liquid column, γ is the surface tension, θ is the contact angle, and r is the radius of the

Coating Type	Method of Application	Market
Solvent-borne	Brushing, rolling Spraying Spin-coating Electrodeposition	Consumer paints Automotive, industrial Microelectronics Automotive, industrial
Powder	Electrostatic	Automotive, industrial

 TABLE 2.1
 Application Methods and Markets for Solvent-Borne and Powder Coatings



FIGURE 2.1 The capillary method.

capillary. In practice, it is difficult to measure accurately a vertical contact angle and a known and uniform radius. For a more accurate determination of the surface tension, various methods are available to calculate the weight of the liquid above the meniscus.

The pendant-drop method is a very versatile technique to measure the surface tension of liquids and also the interfacial tension between two liquids. Andreas et al.⁹ used this method to measure the surface tension of various organic liquids. Wu¹⁰ and Roe¹¹ have applied this method extensively to measure the surface and interfacial tensions of many polymer liquids and melts.

The experimental setup shown in Figure 2.2 consists of a light source, a pendant-drop cell, and a syringe assembly in a constant-temperature chamber, as well as a photomicrographic arrangement. A typical shape of a pendant drop is shown in Figure 2.3. The surface tension of the liquid is given by⁹



FIGURE 2.2 Experimental setup for the pendant-drop method.



FIGURE 2.3 Typical pendant-drop profile.

$$\gamma = \Delta \rho g \frac{d_e}{H} \tag{2.2}$$

where d_e is the maximum (equatorial) diameter of the pendant drop, and H is a correction factor that depends on the shape of the drop; H is related to a measurable shape-dependent factor S, which is defined by

$$S = \frac{d_s}{d_e} \tag{2.3}$$

where d_s is the diameter of the pendant drop in a selected plant at a distance d_e from the apex of the drop (see Figure 2.3). Tables showing the values of 1/H as a function of S are available.^{12–14}

Recently there have been a number of significant improvements in both data acquisition and analysis of the pendant-drop profiles.^{15–17} The photographic recording and measurement of the pendant drop are replaced by direct digitization of a video image. The ability to measure the entire drop profile has led to the development of new algorithms for the drop-profile analysis.^{16,17}

2.2.2 Viscosity

The shear viscosity is defined as the ratio of the shear to the shear strain rate, at the strain rate of interest. Although the viscosity is usually quoted as a number without reference to the strain rate, it is really a function of strain rate. The strain rate dependence and, in certain situations, the time dependence, of the viscosity need to be determined if a meaningful correlation is to be made with coating phenomena. In the case of coatings, the shear strain rate range of interest extends from about a few thousand reciprocal seconds (during spraying, for instance) down to a hundredth of a reciprocal second (following application).

A variety of techniques is available to measure viscosity of coating formulations. Some of them are listed in Table 2.2.¹⁸ Instruments with a single or undefined strain rate should be avoided in the study

Name of Instrument	Geometries Available	Shear-Rate Range	Modes Available
Weissenberg Rheogoniometer	Couette, cone and plate, parallel plate	Broad	Steady shear, oscillatory
Rheometrics Mechanical Spectrometer	Couette, plate and cone, parallel plate	Broad	Steady shear, oscillatory
Carri-Med Controlled Stress Rheometer (CSR)	Couette, parallel plate	Fixed stress	Creep and recovery, oscillatory
Rheo-Tech Viscoelastic Rheometer (VER)	Cone and plate	Fixed stress	Oscillatory, creep and recovery
Contraves Rheomat 115	Cone and plate, couette	Broad	Steady shear
Rheometrics Stress Rheometer	Cone and plate	Fixed stress	Oscillatory, creep and recovery
Haake Rotovisco	Couette, cone and plate	Broad	Steady state
Shirley-Ferranti	Cone and plate	Broad	Steady shear
ICI Rotothinner	Couette	Single high rate	Steady shear
Brookfield Cone and Plate	Cone and plate	Medium to high	Steady
Brookfield Spindle	Undefined	Undefined	Steady shear
Gardner-Holdt	Rising bubble	Undefined	
Cannon-Ubbelohde	Poiseuille	Limited range, high end	Shear
Brushometer	Couette	High end only, single	Steady shear

TABLE 2.2 Some Commercially Available Rheological Instrumentation

of coating rheology. If meaningful correlations are to be made with coating phenomena, the viscosity must be measured over a wide range of strain rates.

The most acceptable technique for determining the strain-rate dependence of the viscosity is the use of the constant rate-of-strain experiment in torsion. This can be done in either a cone-and-plate (for low rates) or a concentric cylinder geometry (for higher rates). However, the oscillatory, or dynamic measurement, is also commonly employed for the same purpose. It is assumed that the shear strain rate and the frequency are equivalent quantities, and the complex viscosity is equal to the steady state constant rate viscosity (i.e., the Cox–Merz rule is valid). The applicability of the Cox–Merz rule, however, is by no means universal, and its validity must be demonstrated before the dynamic measurements can be substituted for the steady-state ones. The capillary technique, as employed in several commercial instruments, is not suitable for coating studies in general, because it is more suitable for measuring viscosity at higher strain rates.

2.2.3 Thixotropy

Thixotropy is a much abused term in the coatings industry. In the review, we shall define the phenomenon of thixotropy as the particular case of the time dependence of the viscosity, that is, its decrease during a constant rate-of-strain experiment. This time dependence manifests itself in hysteresis in experiments involving increasing and decreasing rates of strain. The area under the hysteresis loop has been used as a quantitative estimate of thixotropy, although its validity is still a matter of debate.^{18,19} Another attempt at quantifying thixotropy²⁰ involves the measurement of a peak stress (σ_p) and a stress at a long time (σ^{∞}) in a constant rate-of-strain experiment. In this instance, the thixotropy index β is defined as follows:

$$\beta = \sigma_p - \sigma \frac{\infty}{\sigma_p} \tag{2.4}$$

The utility of these different definitions is still unclear, and their correlation to coating phenomena is even less certain.

In a purely phenomenological sense, thixotropy can be studied by monitoring the time-dependence of the viscosity, at constant rates of strain. Quantification of the property is, however, rather arbitrary. The coefficient of thixotropy, β , appears to be the most reasonable, and is measurable in torsional rheometers such as those mentioned in Table 2.2. It should be noted that this index, as defined above, increases with increase in the rate of strain. In addition, the thixotropic behavior is influenced considerably by the shear history of the material. In comparative measurements, care should be taken to ensure a similar or identical history for all samples. The phenomenon of thixotropy is also responsible for the increase in viscosity after the cessation of shear. If after a constant rate-of strain experiment, the material viscosity is monitored using a sinusoidal technique, it will be found to increase to a value characteristic of a low shear rate-of-strain measurement.

2.2.4 Dilatancy

The original definition of dilatancy,²¹ an increase in viscosity with increasing rate of strain, is still the most widely accepted one today.^{22–24} The term has been used, however, to mean the opposite of thixot-ropy.²⁵ The constant rate-of-strain experiment, outlined above for viscosity measurements, can obviously be employed to determine shear thickening, or dilatancy

2.2.5 Yield Stress

In the case of fluids, the yield stress is defined as the minimum shear stress required to initiate flow. It is also commonly referred to as the "Bingham stress," and a material that exhibits a yield stress is commonly known as a "Bingham plastic" or viscoplastic.²⁶ Though easily defined, this quantity is not as easily measured. Its importance in coating phenomena is, however, quite widely accepted.

The most direct method of measuring this stress is by creep experiments in shear. This can be accomplished in the so-called stress-controlled rheometers (see Table 2.2). The minimum stress that can be imposed on a sample varies with the type of instrument, but by the judicious use of geometry, stress (in shear) in the range of 1 to 5 dynes/cm² can be applied. This is the range of yield stresses exhibited by most paints with a low level of solids. However, the detection of flow is not straightforward. In the conventional sense, the measured strain in the sample must attain linearity in time when permanent flow occurs. This may necessitate the measurement over a long period of time.

An estimate of the yield stress may be obtained from constant rate-of-strain measurements of stress and viscosity. When the viscosity is plotted against stress, its magnitude appears to approach infinity at low stresses. The asymptote on the stress axis gives an estimate of the yield stress.

Another method used is the stress relaxation measurement after the imposition of a step strain. For materials exhibiting viscoplasticity, the stress decays to a nonzero value that is taken as the estimate of the yield stress.

2.2.6 Elasticity

Elasticity of coating materials is frequently mentioned in the literature^{18,19} as being very important in determining the coating quality, particularly of leveling. However, most of the reported measurements of elasticity are indirect, either through the first normal stress difference or through the stress relaxation measurement. Correlations are shown to exist, in paints, between high values of the first normal stress difference and the leveling ability.¹⁸ However, no satisfactory rationalization has been put forward for a cause-and-effect relationship. Also, direct measurement of the elasticity of a coating through the creep-and-recovery experiment is virtually nonexistent. We shall not discuss the role of elasticity in this chapter.

2.3 Rheological Phenomena in Coating

Coalescence, wetting, leveling, cratering, sagging, and slumping are the processes that are strongly influenced by surface tension and viscoelasticity. These, in turn, are the two important parameters that control the quality and appearance of coatings, and hence, their effects on the coating process are discussed in detail.



FIGURE 2.4 Schematic illustration of good and poor wetting.

2.3.1 Wetting

Surface tension is an important factor that determines the ability of a coating to wet and adhere to a substrate. The ability of a paint to wet a substrate has been shown to be improved by using solvents with lower surface tensions.²⁷ Wetting may be quantitatively defined by reference to a liquid drop resting in equilibrium on a solid surface (Figure 2.4). The smaller the contact angle, the better the wetting. When θ is greater than zero, the liquid wets the solid completely over the surface at a rate depending on a liquid viscosity and the solid surface roughness. The equilibrium contact angle for a liquid drop sitting an ideally smooth, homogeneous, flat, and nondeformable surface is related to various interfacial tensions by Young's equation:

$$\gamma_{\rm lv}\cos\theta = \gamma_{\rm sv} - \gamma_{\rm sl} \tag{2.5}$$

where γ_{iv} is the surface tension of the liquid in equilibrium with its own saturated vapor, γ_{sv} is the surface tension of the solid in equilibrium with the saturated vapor of the liquid, and γ_{sl} is the interfacial tension between the solid and liquid. When θ is zero and assuming γ_{sv} to be approximately equal to γ_s (which is usually a reasonable approximation), then from Equation 2.5, it can be concluded that for spontaneous wetting to occur, the surface tension of the liquid must be greater than the surface tension of the solid. It is also possible for the liquid to spread and wet a solid surface when θ is greater than zero, but this requires the application of a force to the liquid.

2.3.2 Coalescence

Coalescence is the fusing of molten particles to form a continuous film. It is the first step in powder coating. The factors that control coalescence are surface tension, radius of curvature, and viscosity of the molten powder. Figure 2.5 shows a schematic diagram of the coalescence of molten powder. Nix and Dodge²⁸ related the time of coalescence to those factors by the equation,

$$t_c = f\left(\eta \frac{R_c}{\gamma}\right) \tag{2.6}$$

where t_c is the coalescence time and R_c is the radius of the curvature (the mean particle radius). To minimize the coalescence time such that more time is available for the leveling-out stage, low viscosity, small particles, and low surface tension are desirable.

2.3.3 Sagging and Slumping

Sagging and slumping are phenomena that occur in coatings applied to inclined surfaces, in particular, to vertical surfaces. Under the influence of gravity, downward flow occurs and leads to sagging or slumping, depending on the nature of the coating fluid. In the case of purely Newtonian or shear thinning fluids, sagging (shear flow) occurs; Figure 2.6 represents "gravity-induced" flow on a vertical surface. On the other hand, a material with a yield stress exhibits slumping (plug flow and shear flow).



FIGURE 2.5 Schematization of the coalescence of molten powders.



FIGURE 2.6 Gravity-induced flow on a vertical surface.

For the case of Newtonian fluids, the physics of the phenomenon has been treated.^{29,30} The extension to other types of fluid, including shear thinning and viscoplastic fluids, has been done as well.³¹ The treatment that follows is based largely on these three sources (i.e., Refs. 29–31). The parameters of interest in the analysis are the velocity V_0 of the material in flow at the fluid–air interface and the resulting sag or slump length, S. For the general case of a power-law fluid of index n,³¹ these above quantities can be calculated:

$$V_0 = \left(\rho \frac{g}{\eta_0}\right)^{(1/n)} \frac{n}{n+1} h^{(n+1)/n}$$
(2.7)

and

$$S = V_0 t \tag{2.8}$$

where η_0 is the zero-shear viscosity and *h* is the film thickness. The special case of Newtonian fluids is obtained by putting *n* = 1 in Equation 2.8. The final sag or slump length *S* is determined by the velocity

as well as a time factor *t*, which is really a time interval for which the material remains fluid (or the time the material takes to solidify). The velocity v_0 depends inversely on the zero-shear viscosity. When all other things are equal, a shear thinning fluid (n < 1) will exhibit lower sag and slump velocities. In general, therefore, a Newtonian or a shear-thinning fluid will sag or slump under its own weight until its viscosity increased to the point at which V_0 is negligible. However, sagging might not occur at all, provided certain conditions are met. One of these is the existence of the yield stress. No sagging occurs if the yield stress (σ_y) is larger than the force due to gravity, *pgh*. However, if the coating is thick enough (large *h*), this condition may no longer be satisfied, and both sagging and slumping can occur if the film thickness is larger than h_s , which is given by

$$h_s = \frac{\sigma_y}{\rho g} \tag{2.9}$$

Between h = 0 and $h = h_s$, sagging occurs. The velocity can be obtained by substituting $(h - h_s)$ for h in Equation 2.7:

$$V_0 = \left(\frac{\rho g}{\eta_0}\right)^{1/n} \frac{n}{n+1} (h - h_s)^{(n+1)/n}$$
(2.10)

For $h > h_s$, plug flow occurs (see Figure 2.6).

Wu³¹ also found that the tendency to sag, in general, increases in the order: shear-thinning fluids < viscoplastic fluids < Newtonian fluids < shear-thickening fluids, provided that all these materials have the same zero-shear viscosity, η_0 . The significance of η_0 for viscoplastic fluids is unclear, although it is used in the equations derived by Wu.³¹

For the particular case of sprayable coatings, Wu found that a shear thinning fluid with n = 0.6, without a yield stress, can exhibit good sag control while retaining adequate sprayability.

2.3.4 Leveling

Leveling is the critical step to achieve a smooth and uniform coating. During the application of coatings, imperfections such as waves or furrows usually appear on the surface. For the coating to be acceptable, these imperfections must disappear before the wet coating (fluid) solidifies.

Surface tension has been generally recognized as the major driving force for the flow-out in coating, and the resistance to flow is the viscosity of the coating. The result of leveling is the reduction of the surface tension of the film. Figure 2.7 illustrates the leveling out of a newly formed sinusoidal surface of a continuous fused film. For a thin film with an idealized sinusoidal surface, as shown in Figure 2.7, an equation that relates leveling speed t_v with viscosity and surface tension was given by Rhodes and Orchard³²:

$$t_{\nu} = \frac{16\pi^4 h^3 \gamma}{3\gamma^3 \eta} \ln\left(\frac{a_t}{a_0}\right)$$
(2.11)

where a_t and a_0 are the final and initial amplitudes, γ is the wavelength, and h is the averaged thickness of the film. This equation is valid only when γ is greater than h. From Equation 2.11 it is clear that leveling is favored by large film thickness, small wavelength, high surface tension, and low melt viscosity.

However, the question of the relevant viscosity to be used in Equation 2.11 is not quite settled. Lin¹⁸ suggests computing the stress generated by surface tension with one of several available methods.^{33,34} Then, from a predetermined flow curve, obtain the viscosity at that shear stress; this may necessitate the measurement of viscosity at a very low strain rate. On the other hand, Wu proposed³¹ using the



FIGURE 2.7 An ideal sinusoidal surface.

zero-shear value for the viscosity in Equation 2.11. These two approaches will yield similar results, except when the material is highly sensitive to strain rate (n < 1).

When the material possesses a yield stress, the surface tension force must overcome the yield stress to initiate the flow or leveling. Thus, we replace λ in Equation 2.11 by λ' :

$$\gamma' = \gamma - \frac{\sigma_y \lambda}{8\pi^3 a_t h} \tag{2.12}$$

This equation implies that a coating fluid with low yield stress should level out quickly. This requirement for leveling is in conflict with that for low sag or slump (high yield stress). Wu³⁵ claims that a shear thinning fluid of index 0.6 exhibits the lowest sag, provided the viscosity is 50 poise at 1 reciprocal second. Because such a fluid does not have a yield stress, it should level out well. This kind of rheological behavior may be attainable in an oligomeric powder coating at temperatures close to its melting point, or in a solution coating with a high solid content. It is difficult to see how this behavior could be realized in all situations, in particular for latex dispersions that possess yield stresses.

2.3.5 Viscosity Changes after Application

After a wet or fluid coating has been applied to a substrate, its viscosity starts to increase. This increase is due to several factors; some of the more important ones are depicted in Figure 2.8. The magnitudes of the viscosity increases due to the different factors shown in Figure 2.8 are typical of a solution coating with a low solid content. The relative magnitudes will, of course, differ for solution coatings with a high solid level, as well as for powder coatings. In powder coatings, the principal increase will be due to freezing, as the temperature approaches the melting point.

The measurement of the viscosity increase is important, because it gives us in idea of how much time is available for the various phenomena to occur before solidification. The leveling and sagging phenomena discussed above can occur only as long as the material remains fluid; as the viscosity increases, these processes become less and less significant because of the decrease in the sagging velocity and leveling speed in accordance with Equations 2.7 and 2.11. In fact, using the measured time dependence of the viscosity, one can estimate the time t (time taken to solidify) to be used in Equation 2.8, as well as the time of leveling, in Equation 2.11. In general, if the viscosity is higher than approximately 100,000 P, then leveling and sagging phenomena occur to a negligible extent.

Experimentally, one can monitor the viscosity increase using an oscillatory technique (see Section 2.2.2). This method is preferred, because measurements can be made under the condition of low shear amplitude, which approximates the condition after a coating application. Also, the solidification point can be estimated from the measurement of the elastic modulus. To mimic the condition immediately



FIGURE 2.8 Schematic plot of coating viscosity during application and film formation.

after coating, the oscillatory measurement should be preceded by shearing at a fairly high rate, corresponding to the method of application.³⁶ In such an experiment, the average amplitude of the torque/ stress wave increases with time after the cessation of a ramp shear. Although it is not easy to compute the viscosity change from the amplitude change, estimating is possible.³⁷ Alternatively, one can use just the amplitude of the stress for correlation purposes. Dodge³⁶ finds a correlation between the viscosity level after application and the extent of leveling as quantified by a special technique he developed. Another method that has been used³⁸ involves rolling a sphere down a coating applied to an inclined surface. The speed of the sphere can be taken as an indicator of the viscosity, after suitable calibration with Newtonian fluids. This method can be very misleading, because the flow is not viscometric, and it is not applicable to non-Newtonian fluids. A more acceptable technique is to use a simple shear, with a plate being drawn at constant velocity over a horizontal coating.¹⁹

2.3.6 Edge and Corner Effects

When a film is applied around a corner, surface tension, which tends to minimize the surface area of the film, may cause a decrease or increase in the film thickness at the corners as shown in Figure 2.9b and Figure 2.9d, respectively. In the case of edges of coated objects, an increase in the thickness has been observed. This phenomenon is related to surface tension variation with the solvent concentration.⁴⁰ In a newly formed film, a decrease in film thickness at the edge is caused by the surface tension of the film. Consequently, the solvent evaporation is much faster at the edge of the film, because there is a larger surface area per unit volume of fluid near the edge (Figure 2.10a). As more solvent (which usually has a lower surface tension than the polymer) evaporates, a higher surface tension exists at the edge, hence causing a material transport toward the edge from regions 2 to 1 (Figure 2.10b). The newly formed surface in region 2 will have a lower surface tension due to the exposure of the underlying material,



FIGURE 2.9 (a) Newly applied thick film at a corner. (b) Decrease in the film thickness at the corner due to surface tension. (c) Newly applied thin film at a corner. (d) Increase in the film thickness at the corner due to surface tension.



FIGURE 2.10 (a) Newly formed film near an edge. (b) Flow of materials from regions 2 to 1. (c) Further flow of materials from region 2 to the surroundings.

which has a higher solvent concentration. Consequently, more materials are transported from region 2 to the surrounding areas (regions 1 and 3) because of the surface tension gradient across the regions (Figure 2.10c).

2.3.7 Depressions: Bernard Cells and Craters

Local distortions (depressions) in a coating can be caused by a surface tension gradient (due to composition variation or temperature variation). This phenomenon is known as the Maragoni effect.⁴¹ The flow of a liquid from a region of lower to higher surface tension caused by the surface tension gradient results in the formation of depressions on the liquid surface. Such depressions come in two types: Bernard cells and craters.

Bernard cells usually appear as hexagonal cells with raised edges and depressed centers.^{42–44} The increase in the polymer concentration and the cooling due to solvent evaporation cause the surface tension and surface density to exceed those of the bulk. This creates an unstable configuration, which tends to move



FIGURE 2.11 Schematic illustration of the formation of the Bernard cells due to (a) the surface tension gradient and (b) the density gradient.

into a more stable one in which the material at the surface has a lower surface tension and density. Theoretical analysis⁴⁵ has established two characteristic numbers: the Raleigh number R_a and the Marangoni number M_a , given by

$$R_a = \frac{\rho g a \tau h^4}{K \eta}$$
(2.13)

$$M_a = \frac{\tau h^2 (-d\gamma \,/\, dT)}{K\eta} \tag{2.14}$$

where ρ is the liquid density, *g* is the gravitational constant, α is the thermal expansion coefficient, τ is the temperature gradient on the liquid surface, *h* is the film thickness, *K* is the thermal diffusivity, and *T* is the temperature. If the critical Marangoni number is exceeded, the cellular convective flow is formed by the surface tension gradient. As shown in Figure 2.11a, the flow is upward and downward beneath the center depression and the raised edge, respectively. But if the critical Raleigh number is exceeded, the cellular convective flow, which is caused by density gradient, is downward and upward beneath the depression and the raised edge, respectively (Figure 2.11b). In general, the density-gradient-driven flow predominates in thicker liquid layers (>4 mm), while the surface tension gradient is the controlling force for thinner films.

Cratering is similar to the Bernard cell formation in many ways. Craters, which are circular depressions on a liquid surface, can be caused by the presence of a low surface tension component at the film surface. The spreading of this low surface tension component causes the bulk transfer of film materials, resulting in the formation of a crater. The flow q of material during crater formation is given by⁴⁶

$$q = \frac{h^2 \Delta \gamma}{2\eta} \tag{2.15}$$

where $\Delta \gamma$ is the surface tension difference between the regions of high and low surface tension. The crater depth d_c is given by⁴⁷

$$d_c = \frac{3\Delta\gamma}{\rho g h} \tag{2.16}$$

The relationship between the cratering tendency and the concentration of surfactant was investigated by Satoh and Takano.⁴⁸ Their results indicate that craters appear whenever paints contain silicon oils (a surfactant) in an amount exceeding their solubility limits.



FIGURE 2.12 The effects of surface tension and melt viscosity on coating appearance.

In the discussion above, high surface tension and low viscosity are required for good flow-out and leveling. But high surface tension can cause cratering, and excessively low viscosity would result in sagging and poor edge coverage. To obtain an optimal coating, the balance between surface tension and viscosity is important. Figure 2.12 illustrates coating performance as a function of surface tension and melt viscosity. Coating is a fairly complex process; achieving an optimal result calls for the consideration of many factors.

Acknowledgments

We are grateful to Steve Trigwell for preparing the figures.

References

- 1. A. W. Adamson, Physical Chemistry of Surfaces, 4th ed. New York: Wiley, 1982.
- 2. L. Du Nouy, J. Gen. Physiol., 1, 521 (1919).
- 3. R. H. Dettre and R. E. Johnson, Jr., J. Colloid Interface Sci., 21, 367 (1966).
- 4. D. S. Ambwani and T. Fort, Jr., Surface Colloid Sci., 11, 93 (1979).
- 5. J. R. J. Harford and E. F. T. White, Plast. Polym., 37, 53 (1969).
- 6. J. Twin, Phil. Trans., 29-30, 739 (1718).
- 7. J. W. Strutt (Lord Rayleigh), Proc. R. Soc. London, A92, 184 (1915).
- 8. S. Sugden, J. Chem. Soc., 1483 (1921).
- 9. J. M. Andreas, E. A. Hauser, and W. B. Tucker, J. Phys. Chem., 42, 1001 (1938).
- 10. S. Wu, J. Polym. Sci., C34, 19 (1971).
- 11. R. J. Roe, J. Colloid Interface Sci., 31, 228 (1969).
- 12. S. Fordham, Prac. R. Soc. London., A194, 1 (1948).
- 13. C. E. Stauffer, J. Phys. Chem., 69, 1933 (1965).
- 14. J. F. Padday and A. R. Pitt, Phil. Trans. R. Soc. London, A275, 489 (1973).
- 15. H. H. Girault, D. J. Schiffrin, and B. D. V. Smith, J. Colloid Interface Sci., 101, 257 (1984).
- 16. C. Huh and R. L. Reed, J. Colloid Interface Sci., 91, 472 (1983).

- 17. Y. Rotenberg, L. Boruvka, and A. W. Neumann, J. Colloid Interface Sci., 93, 169 (1983).
- 18. O. C. Lin, Chemtech, January 1975, p. 15.
- 19. L. Kornum, Rheol. Acta., 18, 178 (1979).
- 20. O. C. Lin, J. Apl. Polym. Sci., 19, 199 (1975).
- 21. H. Freundlich and A. D. Jones, J. Phys. Chem., 4(40), 1217 (1936).
- 22. W. H. Bauer and E. A. Collins, in *Rheology*, Vol. 4, F. Eirich, Ed. New York: Academic Press, 1967, Chapter 8.
- 23. P. S. Roller, J. Phys. Chem., 43, 457 (1939).
- S. Reiner and G. W. Scott Blair, in *Rheology*, Vol. 4, F. Eirich, Ed. New York: Academic Press, 1967, Chapter 9.
- 25. S. LeSota, Paint Varnish. Prod., 47, 60 (1957).
- R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Fluids*, Vol. 1. New York: Wiley-Interscience, 1987, p. 61.
- 27. S. J. Storfer, J. T. DiPiazza, and R. E. Moran, J. Coating Technol., 60, 37 (1988).
- 28. V. G. Nix and J. S. Dodge, J. Paint Technol., 45, 59 (1973).
- 29. T. C. Patton, Paint Flow and Pigment Dispersion, 2nd ed. New York: Wiley-Interscience, 1979.
- 30. A. G. Frederickson, *Principles and Applications of Rheology*. Englewood Cliffs, NJ: Prentice Hall, 1964.
- 31. S. Wu, J. Appl. Polym. Sci., 22, 2769 (1978).
- 32. J. F. Rhodes and S. E. Orchard, J. Appl. Sci. Res. A, 11, 451 (1962).
- 33. R. K. Waring, Rheology, 2, 307 (1931).
- 34. N. O. P. Smith, S. E. Orchard, and A. J. Rhind-Tutt, J. Oil Colour. Chem. Assoc., 44, 618 (1961).
- 35. S. Wu, J. Appl. Polym. Sci., 22, 2783 (1978).
- 36. J. S. Dodge, J. Paint Technol., 44, 72 (1972).
- 37. K. Walters and R. K. Kemp, in *Polymer Systems: Deformation and Flow.* R. E. Wetton and R. W. Wharlow, Eds. New York: Macmillan, 1967, p. 237.
- 38. A. Quach and C. M. Hansen, J. Paint Technol., 46, 592 (1974).
- 39. L. O. Kornum and H. K. Raaschou Nielsen, Progr. Org. Coatings, 8, 275 (1980).
- 40. L. Weh, Plaste Kautsch, 20, 138 (1973).
- 41. C. G. M. Marangoni, Nuovo Cimento, 2, 239 (1971).
- 42. C. M. Hansen and P. E. Pierce, Ind. Eng. Chem. Prod. Res. Dev., 12, 67 (1973).
- 43. C. M. Hansen and Pierce, Ind. Eng. Chem. Prod. Res. Dev., 13, 218 (1974).
- 44. J. N. Anand and H. J. Karma, J. Colloid Interface Sci., 31, 208 (1969).
- 45. J. R. A. Pearson, J. Fluid Mech., 4, 489 (1958).
- 46. P. Fink-Jensen, Farbe Lack, 68, 155 (1962).
- 47. A. V. Hersey, Phys. Ser., 2, 56, 204 (1939).
- 48. T. Satoh and N. Takano, Colour Mater., 47, 402 (1974).