Second Edition

Handbook for CRITICAL CLEANING
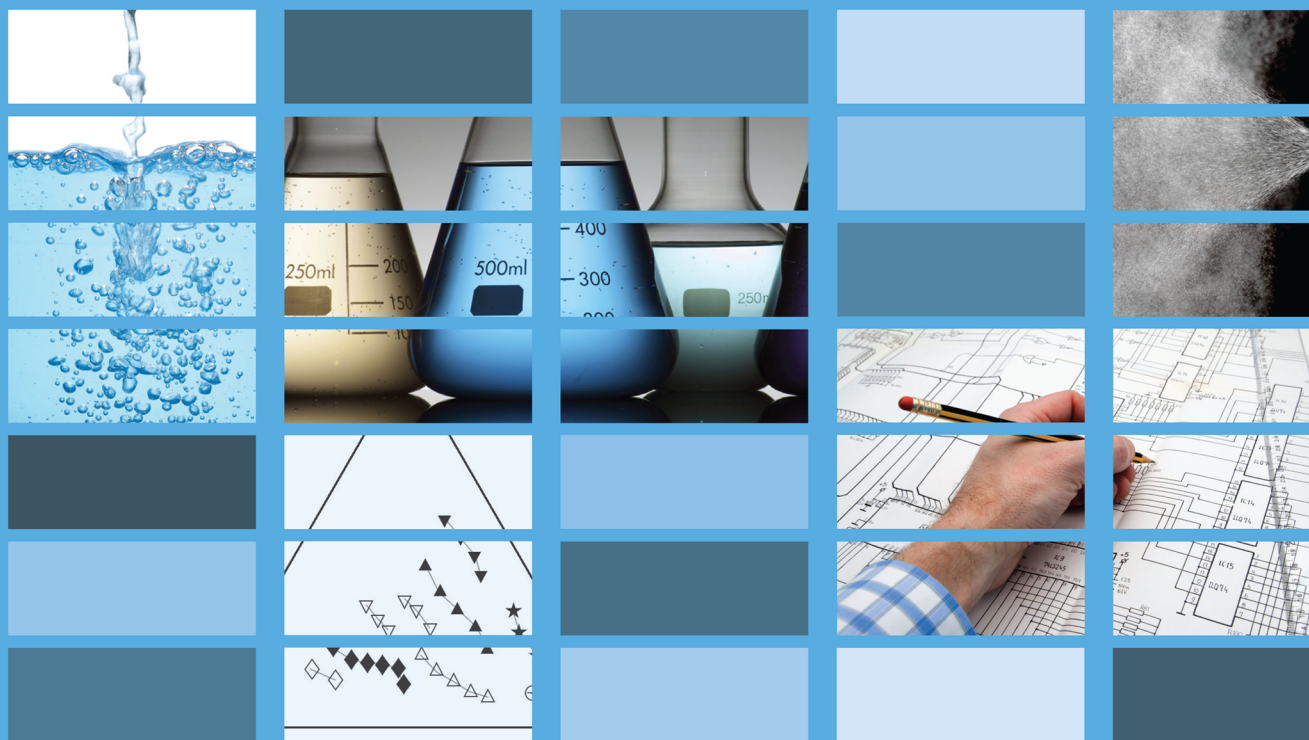
Edited by Barbara Kanegsberg
Edward Kanegsberg

CRC Press
Taylor & Francis Group

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CRITICAL CLEANING

Cleaning Agents and Systems

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Edited by Barbara Kanegsberg
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Cover design by David Kanegsberg.

To a beautiful, safe, productive world for the next generation

Noa Raeli Kanegsberg

To our most valuable collaborative efforts

Deborah Joan Kanegsberg and David Jule Kanegsberg

And to the memory and positive influence of

Israel Feinsilber

Jule Kanegsberg

Murray Steigman

Dr. Jacob J. Berman

Contents

Preface to the Second Edition

Why a Second Edition?

In the last few years, challenges to the manufacturing community have increased and so have performance expectations. With the ever-decreasing size of components, these expectations are becoming more difficult to meet. The second edition of the *Handbook for Critical Cleaning* hopes to help you meet these expectations and produce high-quality products in a cost-effective manner. Although cleaning is a process and not a chemical, increased awareness of the consequences of chemical use to workers, to the general public, and to the environment has prompted more stringent regulatory measures worldwide. Environmental and worker safety regulations are imperative to maintaining a decent quality of life on this planet and, perhaps, to our very survival. However, the goal of manufacturing is not to jump through regulatory hoops, but to produce efficient products. Compromising on the efficacy of cleaning and thereby producing a suboptimal product can affect public safety and can compromise on the quality of life. Manufacturers face the challenge of doing it all.

What Is Critical Cleaning?

Identify, then qualify/validate and monitor the critical cleaning steps. The terms "critical cleaning" and "precision cleaning" are often used interchangeably. However, we prefer the former term. Precision cleaning suggests cleaning in a highly restricted clean room, where each individual component is perhaps cleaned separately by a highly trained technician, where there are perhaps wet benches with automated product handling, and where there may be a multichamber-automated spray system that feeds directly into the clean room. This is a limited view of the important cleaning step. Perhaps the best way to define a critical cleaning step is to consider the negative consequences that arise if that step is not performed or is performed inadequately. Based on our experience, the important cleaning step, the *critical cleaning step*, may occur in a machine shop or in a job shop (e.g., a coating facility) in what appears, at first glance, like an automotive repair facility. If the soil (matter out of place) is not adequately removed at that step, subsequent processing and cleaning steps may not resolve the problem but may actually exacerbate contamination by inadvertent chemical reaction of the soil, drying of the soil, or by embedding the soil on the surface of the product. Contamination happens long before the product enters the clean room. A clean room can only minimize recontamination, and even the most sophisticated clean room or controlled environment cannot correct a contaminated product (Kanegsberg and Kanegsberg, 2010).

Lean Cleaning and Supply Chains

Economic pressures have led to the implementation of such concepts as lean cleaning and six-sigma; thus, we have to clean smarter. In fact, it is imperative that we clean smarter. Cleaning must be value added. Assess your own processes and understand the role that cleaning plays in those processes. Sometimes the value added is only appreciated by factoring in the costs of not cleaning or under-cleaning at a particular step. Critical cleaning is not just about *what* is done or *how* it is done. It is also about *when* it is done. This becomes even more important when we realize that most products are not built from scratch within one facility. There usually is a complex supply chain of autonomous or semiautonomous facilities, which may sometimes be separate divisions or departments of the same company. Regardless of whether the supply chain involves inter- or intracompany processes, it is crucial that communication take place and that process understanding and process integration occur. The most critical cleaning step may be one that needs to take place at a supplier, before the part reaches your facility.

Critical Cleaning and Surfaces

Cleaning is removing undesired materials from surfaces without changing the surface in an unacceptable manner. As products get smaller, the surface becomes a greater percentage of the product. When products are at the nanoscale, it can be said that the product *is* the surface.

New and Useful

Cleaning Is a Process

The economic and regulatory hurdles involved in introducing new cleaning agents have increased considerably (see "A balancing act" in book 2). Therefore, chemicals that have been developed for markets other than cleaning but have been adapted for the cleaning sector and complex blends have become increasingly prevalent. Therefore, the newer cleaning products are covered extensively in the second edition. Cleaning equipment has also evolved during the past decade, and meshing the appropriate cleaning agent with the right equipment requires a working understanding of chemistry, physics, and engineering. We have added discussion of ultrasonic techniques and monitoring. Partially spurred by regulatory pressures, an increased use of so-called nonchemical approaches is included.

Process Implementation

All of the knowledge in the world about cleaning agents, cleaning equipment, and process flow is of no use if you do not improve the cleaning process. We provide guidance to actually do something: to select, validate, implement, and monitor the cleaning process. We also cover new approaches to definitive, lean, analytical testing and provide discussions related to clean rooms, including construction and working in a clean room.

Applications

The application portion of the *Handbook for Critical Cleaning* has been expanded to include critical cleaning processes for high-value products such as for medical devices, pharmaceutical, food processing, aerospace, and military. Electronics cleaning, which had been considered to be "solved" a decade ago, has resurfaced as a critical issue due to such developments as miniaturization, increased component

density, and replacement of lead solders with lead-free, higher temperature solders. Conservation of fine art may not immediately be thought of along with manufacturing, but this involves critical cleaning and the requirements are in some ways similar. Two art conservators outline the thought processes and trial-and-error determinations to match cleaning agents to the soil when cleaning or restoring paintings.

Safety/Environmental Considerations

Safety and environmental considerations are not only global issues but are also important concerns at the national and local levels, and they do not always coordinate or mesh well. You cannot ignore them, and you should not ignore them. We have not attempted to outline all regulations. Dealing with such a moving target would be frustrating and futile, and most engineers would develop glazed eyeballs. Instead, we have attempted to discuss a few topics that are important to the critical cleaning community and to provide strategies for working constructively with the regulatory world. Some of this guidance comes from members of the regulatory community.

Resource conservation is becoming an important topic in the twenty-first century. Efforts to minimize or recycle water, chemicals, and energy will increasingly become a factor in keeping process costs competitive. Green cleaning, which considers both safety and environmental impact, is discussed throughout the two books. The definition of green is not set in stone; it will continue to evolve.

Web-Based Material

Some of the authors have submitted non-print media (color illustrations, animations, film clips, etc.) to augment their chapters. These can be accessed via the "Downloads & Updates" tab on the web pages for these books at CRCPress.com.

The Lady in the Saffron Sari

Barbara Kanegsberg

"You must run, you must flee," implored the earnest gentleman as he ran toward us.

Puzzled and slightly alarmed, our daughter Deborah and I peered down a corridor of immense, multicolored marble slabs while balancing a finished wood cabinet door, a celadon green tile, and some decorative hardware. It was a brilliant, Southern California morning. The silhouette of the plaster Disneyland Matterhorn broke through a cloudless blue sky. The only obvious danger was the trauma of remodeling the kitchen.

"Why do we need to run?" I asked.

"You must hide, my wife must not see you," he replied.

"Why can't your wife see us?" our daughter asked.

"Because, you see, I told her, first we will select the marble, then the cabinets, then the tile, then the door pulls. You are coordinating. If she sees you, she will want to coordinate."

At that very moment, an elegant woman wearing a luminous, saffron-yellow sari came gliding across the marble yard.

"You see, dear," she said, putting her arm around the gentleman and steering him purposefully toward the exit, "they are coordinating. Let's go, we must coordinate too."

Coordinate, Extrapolate, Optimize

The lady in the saffron sari had the right idea. You, too, must coordinate. Achieving a high-quality manufactured product in a cost-competitive manner requires coordination of critical cleaning and contamination control within your company and perhaps coordination with the efforts of a complex supply chain. If you are in charge of selecting cleaning equipment, please read over the chapters on cleaning agents and coordinate the two efforts (and vice versa). Coordinating cleaning efforts with regulatory requirements, including safety, environmental, and validation requirements, is also time well spent. Whether you are a job shop, an initial fabricator, a final assembler, or you have a repair facility, understanding the importance of critical cleaning is a must to achieve a cost-competitive advantage.

It is reasonably safe to say that your manufacturing situation is unique. We suggest that you consider, blend, and extrapolate from the information and advice provided in both books, even perusing those chapters that seem outside of your field. We often combine the approaches of what, at first glance, seem to be unrelated fields. As you read the chapters, think about how approaches might apply to your application and where cleaning is really necessary. Always clean critically.

Acknowledgments

Reference

Kanegsberg, B. and Kanegsberg, E. Contamination detection basics, *Controlled Environments Magazine*, June 2010.

Ed Kanegsberg
Barbara Kanegsberg

Preface to the First Edition

Adapted from: What is critical cleaning?, First Edition, *Handbook for Critical Cleaning*.

Critical cleaning is required for the physical manifestation of technology.

We are in the information age, an age of thought, ideas, communication. However, this technology is based on physical objects, parts, or components. Many of these objects require precision cleaning or critical cleaning because they are either intrinsically valuable, or they become valuable in the overall system or process in which they are used. Some parts or components require critical cleaning not because of the inherent value of the part itself but instead due to their place in the overall system. For example, inadequate cleaning of a small inexpensive gasket can potentially lead to catastrophic failure in an aerospace system.

Nearly all companies which manufacture or fabricate high-value physical objects (components, parts, assemblies) perform critical cleaning at one or more stages. These range from the giants of the semiconductor, aerospace, and biomedical world to a host of small to medium to large companies producing a dizzying array of components.

Soil

The concepts of contamination, cleaning, and efficacy of cleaning are open to debate and are intertwined with the overall manufacturing process and with the ultimate end-use of the assembled product.

Contamination or soil can be thought of as matter out of place (Petrulio and Kanegsberg, 1998). During manufacture, parts or components inevitably become contaminated. Contamination can come from the environment (dust, smog, skin particles, bacteria), from materials used as part of fabrication (oils, fluxes, polishing compounds), as a by-product of manufacturing, and as from residue of cleaning agent ostensibly meant to clean the component.

Cleaning

Cleaning processes are performed because some sort of soil must be removed. In a general sense, we can consider cleaning to be the removal of sufficient amounts of soil to allow adequate performance of the product, to obtain acceptable visual appearance as required, and to achieve the desired surface properties. You may notice that surface properties are included because most cleaning operations probably result in at least a subtle modification of the surface. If a change in the cleaning process removes additional soil and if as a result the surface acquires some undesirable characteristic (e.g., oxidation), then the cleaning process is not acceptable. Therefore, surface preparation and surface quality can be an inherent part of cleaning.

Identifying the Cleaning Operation

Cleaning processes and the need for cleaning would seem to be trivial to identify. If you had a child who appeared in the doorway covered with mud, you would do a visual assessment of the need for cleaning, perform site-directed immersion or spray cleaning in an aqueous/saponifier mixture with hand-drying. However, people perform critical cleaning operations without knowing it. This lack of understanding can detrimental to process control and product improvement.

Recognizing a cleaning step when it occurs is probably one of the major challenges in the components manufacturing community. Cleaning is often enmeshed as a step in the overall process rather than being recognized as a concept in itself. It may be considered as something that occurs before or after another process, but not as a process to be optimized on its own (Dorothy Rosa, personal communication). A cleaning process often not called a cleaning process. For example, optics deblocking (removing pitches and waxes), defluxing, degreasing, photoresist stripping and edge bead removal in wafer fabrication, and surface preparation prior to adhesion, coating, or heat treatment can all be thought of in terms of soil removal (cleaning). Sometimes the cleaning process is identified only by the name of the engineer who first introduced it.

The sociological and psychological bases for this aversion to discussing cleaning are no doubt fascinating, but are beyond the scope of this book. The important thing is for you to recognize a cleaning process when you see it.

There are several reasons. One obvious reason is process control. A second is trouble-shooting or failure analysis. If the product fails and you need to fix the process, it is crucial to identify not only where soil might be introduced but also what steps are currently being taken in soil removal. If the chemical being used comes under regulatory scrutiny, identifying cleaning is even more important. If a supplier provides the component and a problem arises, it is important to be able to recognize where the cleaning steps occur. Finally, identifying the cleaning steps allows you to apply technologies developed in other industries to your own process.

Critical Cleaning

Defining critical cleaning or precision cleaning is a matter of ongoing debate among chemists, engineers, production managers, and those in the regulatory community. Certainly the perceived value or end-use of the product is a factor as are the consequences of remaining soil. The level of allowable soil remaining after cleaning is a consideration. Precision cleaning has been defined as the removal of soil from objects that already appear to be clean in the first place (Carole LeBlanc, personal communication). In some instances, however, high levels of adherent soil are involved in the processing of critical devices. Precision cleaning was once euphemistically said to be YOUR cleaning process for YOUR critical application, whereas everyone else's process could be considered as general cleaning (Kanegsberg, 1993). In one sense, there is some truth that the manufacturer is often the one best able to understand process criticality. At the same time, recognizing general cleaning and critical cleaning as parts of other operations can lead to overall industrial process improvement.

Why Should You Be Concerned about Critical Cleaning?

Critical cleaning issues are becoming increasingly important. Competitive pressure is increasing. Higher demands are being made of industry. A clean component produced efficiently and in an environmentally preferred manner (or at least in an environmentally acceptable manner) is a given in today's economy.

Performance, Reliability

Products are becoming smaller, with tighter tolerances and higher performance standards. Some products, such as implantable biomedical devices, are expected to perform for decades without a breakdown. Small amounts of soil and very tiny particles can irreparably damage the product.

To successfully remove the soils, you have to understand the various cleaning chemistries and cleaning equipment, and how they are combined and meshed with the overall build process.

Costs

Pressure to keep costs down increases constantly. The costs of the effective processes have tended to increase. Choosing the best option for the application can keep costs down.

Safety and Environmental Regulatory Requirements

The manufacturing community needs a wide selection of chemicals and processes to achieve better contamination control at lower costs. However, our understanding of health and the environment has led to restrictions on chemicals and processes. The manufacturer needs an understanding of atmospheric science and of the approaches used by regulatory agencies to foresee future trends.

Overview of This Book

Philosophy

In setting out to put together this comprehensive book on critical cleaning, I sought inputs from the experts in the field. Frequently these are people associated with vendors of cleaning equipment and/ or cleaning agents. Naturally, each person's viewpoint is somewhat colored by their own portion of the market. However, on the whole, I was impressed with the scope and fairness of the material submitted. An attempt has been made to minimize use of brand names. In some cases, there are several contributors in a similar area. In general, my philosophy has been to include all but the most blatant material; by having a large number of contributors, a wide range of products and viewpoints are presented; the reader is expected to be intelligent enough to weigh the advantages and/or disadvantages of each approach for his or her own application.

Conclusions

While each application is very site specific, contamination control problems cut across industry lines. At the same time, each industry still tends to work in a separate little world. It is hoped that this book will provide a synthesis of cleaning approaches.

A diverse assortment of components and assemblies require critical or precision cleaning. Some examples include

Accelerometers
Automotive parts
Biomedical/surgical/dental devices (e.g., pacemakers)
Bearings
Computer hardware (metal, plastic, other composites—the insides of your computer and printer)
Consumer hardware (telephones)
Digital cameras
Disk drives

Electronics components
Flat panel displays
Gaskets
Gyroscopes
Motion picture film
Optics
Space exploration hardware
Wafers/semiconductors/microelectronics
Weapons, defense systems (missiles)

Acknowledgments

References

Carole LeBlanc, Toxics Use Reduction Institute, Lowell, MA, personal communication.

Dorothy Rosa, *A²C² Magazine*, personal communication.

Kanegsberg, B. Options in the high-precision cleaning industry: Overview of Contamination Control Working Group XIII, in *International CFC & Halon Alternatives Conference*, Washington, DC, October 1993.

Petrulio, R. and Kanegsberg, B. Back to basics: The care and feeding of a vapor degreaser with new solvents, in presentation and proceedings, *Nepcon West '98*, Anaheim, CA, 1998.

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About the Second Edition

Philosophy

We want to help you clean critically, productively, and profitably; our goal was thus to make the second edition of the *Handbook for Critical Cleaning* even more comprehensive than the first edition. Contributors are experts in their field. We have included the viewpoints of manufacturers of parts/components of those who supply cleaning chemistries and cleaning systems, of people in regulatory agencies, and even of other consultants. We have minimized the use of brand names, but have included enough information to be unambiguous. Our philosophy is to include a range of viewpoints, some differing from our own. We urge you to make the optimal decision for your application.

Organization

Chapters in the Second Edition

The second edition of the *Handbook for Critical Cleaning* is substantially new. While we have reprinted a few classic chapters from the first edition, most chapters are new or have been substantially updated. We suggest that readers peruse not only the chapters related to their line of work and applications, but also look at what might at first glance appear to be unrelated applications. By providing a synthesis of cleaning approaches, we hope to help you make better decisions about your own cleaning processes.

We strive to achieve the impossible (or highly improbable)—a perfect balance of topics. After the publication of the first edition, we received comments that we did not devote enough space to aqueous processes, an approximately equal number of comments that we did not devote enough space to discussions on solvent processes, and assorted comments about a lack of attention to other advanced cleaning processes. We thank everyone for their comments; you are probably correct. Therefore, if you have a different viewpoint or unique cleaning application, let us know. This is how we keep learning and improving.

This series is divided into two books with five parts:

- Book 1: *Handbook for Critical Cleaning: Cleaning Agents and Systems*
  - Part I: Cleaning Agents
  - Part II: Cleaning Systems
- Book 2: *Handbook for Critical Cleaning: Applications, Processes, and Controls*
  - Part I: Process Implementation and Control
  - Part II: Applications
  - Part III: Safety and Regulations

Following is a capsule summary of each of the book chapters.

Book 1: *Handbook for Critical Cleaning: Cleaning Agents and Systems*

Part I: Cleaning Agents

An overview of cleaning agents is presented by the editor, Barbara Kanegsberg. In this expanded overview, Barbara attempts to capture the diversity of cleaning chemistry options and to put those options in perspective.

The part begins with a discussion on aqueous cleaning agents (see Chapter 1, Kanegsberg). Water is the most common cleaning agent. Michael Beeks and David Keller of Brulin & Company, a producer of aqueous cleaning equipment, expand and update their chapter from the first edition and give a comprehensive review of aqueous cleaning essentials (Chapter 2). Much of the information is also applicable to nonaqueous solvent cleaning.

Many of today's chemicals, both aqueous based and solvents, are blends. JoAnn Quitmeyer of Kyzen Corporation presents a new chapter that is a comprehensive review of cleaning agent chemistries, including single components and blends (Chapter 3).

John Burke of the Oakland Museum of Art, California, updates his particularly informative discourse on solubility and the techniques used to classify solvents (Chapter 4). It becomes clear from this chapter as to why certain solvents are applicable to removing certain types of soil.

John Owens of 3M updates his chapter on the hydrofluoroethers (HFEs), a class of solvents that have been introduced as replacements for the ozone-layer depleting chemicals (ODCs) (Chapter 5).

Joan Bartelt of DuPont updates the chapter by Abid Merchant (retired fom DuPont) that discusses the hydrofluorocarbons (HFCs), another class of ODC replacements (Chapter 6).

John Dingess and Richard Morford of EnviroTech International Inc. update the chapter by Ron Shubkin (retired from Albermarle Corporation and Poly Systems U.S.A. Inc.) on normal-propyl bromide (NPB), a substitute for the aggressive ODC solvent, 1-1-1-trichloroethane (Chapter 7).

Stephen P. Risotto, formerly of the Halogenated Solvents Industry Association (HSIA) and now with the American Chemistry Council, updates his contribution on the chlorinated solvents, a group of traditional solvents that are seeing a resurgence of use in certain applications (Chapter 8).

Ross Gustafson of Suncor Energy discusses critical cleaning applications of the bio-based D-limonene (Chapter 9).

Dan Skelly of Riverside Chemicals reviews benzotrifluorides, a group of VOC-exempt compounds (Chapter 10).

Part II: Cleaning Systems

This part reflects the wide range of process choices. The importance of drying is emphasized. Advanced and so-called nonchemical systems, such as CO_2 cleaning, steam cleaning, and plasma cleaning, are also covered. In these systems, the cleaning agent and the cleaning equipment are inseparable.

The part begins with an overview of cleaning systems contributed by the editors (Chapter 11). As with the overview for cleaning agents, this reviews processes that are treated in this book by other authors as well as those for which there are no additional chapters.

There are six chapters dealing with ultrasonics and the closely related megasonics technologies. The technology is widely used, and the diverse insights of the authors will be helpful to select equipment. John Fuchs, retired from Blackstone—Ney Ultrasonics, and Sami Awad of Ultrasonics Apps., LLC each give an overview of ultrasonics (Chapters 12 and 13). Sami Awad then teams up with K.R. Gopi, from Crest Ultrasonics Corp., to provide a new chapter on multiple frequency ultrasonics (Chapter 14). Mark Beck of Product Systems Inc. covers the basic technologies of megasonics (Chapter 15). The theory of cavitation has been absent from most discussions of critical cleaning geared to the manufacturing community. Further, the important yet elusive topic of ultrasonics metrics has seen much progress. Along these lines, we are pleased to present two new chapters. In the first chapter, Mark Hodnett of the National Physical Laboratories (U.K.) provides graphics covering theory and discusses a new technique

for ultrasonics metrics along with case studies (Chapter 16). In the second chapter, Lawrence Azar of PPB Megasonics covers the principles and theoretical/mathematical basis of cavitation and discusses ultrasonics metrics (Chapter 17).

Edward Lamm of Branson Ultrasonics Corp. contributes a useful chapter, on optimizing the equipment design, covering solvent, aqueous, and semiaqueous cleaning equipment as well as rinsing, drying, automation, and other ancillary equipment (Chapter 18).

Ron Baldwin of Branson Ultrasonics Corp. contributes an important new chapter on equipment design for aqueous cleaning to help you during scale-up from laboratory cleaning to production cleaning (Chapter 19).

Dan Skelly of Riverside Chemicals contributes a chapter on equipment for cold cleaning, that is, where cleaning agents (notably solvents) are used below their boiling point (Chapter 20).

Richard Petrulio of B/E Aerospace provides a revised, expanded, and very readable chapter on the design of flushing systems (Chapter 21). This is one example where a company was able to design equipment for its own cleaning application. The chapter also provides very good guidance for the process of developing and testing a cleaning process.

Joe McChesney of Parts Cleaning Technologies updates and revises techniques for minimizing waste streams in solvent vapor degreasers, including methods for calculating the size or capacity of the required equipment (Chapter 22). Some recent case studies for the minimization of emissions have also been added.

Arthur Gillman of Unique Equipment Corporation contributes retrofitting vapor degreasers to allow the use of different cleaning chemicals or to meet newer emission control standards (Chapter 23). This option can obviate the need for new equipment.

John Durkee of precisioncleaning.com and Dr. Don Gray of the University of Rhode Island update their chapter on contained airless and airtight solvent systems, one approach for remaining in compliance with air regulations while using emissive chemicals (Chapter 24).

Wayne Mouser of Crest Ultrasonics Corp. contributes a new chapter on vapor phase organic solvent cleaning, a classic critical cleaning technique (Chapter 25).

In some cases, the cleaning agent and the cleaning equipment are inseparable. In particular, this is true for what are called "nonchemical" cleaning approaches. Several examples are provided in the next five chapters.

Ed Kanegsberg of BFK Solutions provides a new chapter, an overview to nonchemical cleaning, that addresses aspects covered in more detail by four of the authors and also reviews additional approaches, such as laser, UV/ozone, and fluidized dry bath cleaning (Chapter 26).

Jawn Swan of Crystal Mark, Inc. contributes a new chapter on micro-abrasive blasting, a technique with applications ranging from electronics and medical devices to architectural restoration (Chapter 27).

Robert Sherman of Applied Surface Technologies authors a new chapter on solid carbon dioxide cleaning, with applications for removing particles and small levels of soils from such critical surfaces as semiconductor wafers and precision optics (Chapter 28).

William Nelson of the U.S. EPA updates his chapter on supercritical and liquid CO_2 cleaning (Chapter 29).

William Moffat of Yield Environmental Systems (YES) teams with Kenneth Sautter, also of YES, to update the chapter on another approach to removing organics, plasma cleaning (Chapter 30).

Max Friedheim of PDQ Precision Inc. teams with his process engineer, Jose Gonzalez, to update and expand the chapter on the use of steam vapor cleaning for critical cleaning applications; additional case studies are included (Chapter 31).

John Russo of Separation Technologists has completely revised his chapter on selecting the best waste water treatment for aqueous operations (Chapter 32). This comprehensive chapter discusses pretreatment, posttreatment, and water recycling techniques.

Cleaning with liquids frequently means that drying is required. The final three chapters in Part II deal with this sometimes neglected process.

Barbara Kanegsberg of BFK Solutions provides an overview to drying (Chapter 33). Daniel VanderPyl of Sonic Air Systems updates his chapter on physical methods of drying (Chapter 34). Robert Polhamus of RLP Associates along with Phil Dale of Layton Technologies, Ltd. update their chapter on chemical displacement drying techniques (Chapter 35).

Book 2: *Handbook for Critical Cleaning: Applications, Processes, and Controls*

Part I: Process Implementation and Control

Part I integrates the topics of process selection and maintenance, contamination control, analytical techniques, and materials compatibility.

Barbara and Ed Kanegsberg lead off the part with a revised, expanded discussion of "How to Work with Vendors?" that applies to print, electronic, telephone, and face-to-face communication of information (Chapter 1). Barbara Kanegsberg continues with a new chapter, "The Balancing Act," discussing the technical, economic, political, and regulatory trade-offs and conflicts involved in developing and maintaining a process (Chapter 2).

Art Gillman of Unique Equipment Corporation contributes a new chapter, drawing on his many decades of experience as well as the experiences of his colleagues to present "Blunders, disasters, horror stories, and mistakes you can avoid," a compilation of cleaning lore that should be read and absorbed by all readers (Chapter 3).

Mike Callahan of Jacobs Engineering expands his chapter about optimizing and maintaining the process (Chapter 4). A number of topics such as fixturing, process monitoring, and process improvements are included.

Part I contains four new chapters related to clean room design, operation, and behavior. Controlling the cleaning environment improves the success of the cleaning process by minimizing product contamination. Scott Mackler of Cleanroom Consulting provides a comprehensive chapter on "Basis of design for life sciences cleanroom facilities" (Chapter 5). Kevina O'Donoghue of Specialised Sterile Environments brings a view from "across the pond" in Ireland with her chapter on "Validating and monitoring the cleanroom" (Chapter 6). Jan Eudy of Cintas Corporation provides a chapter on "Cleanroom management and gowning" (Chapter 7). Howard Siegerman of Siegerman & Assoc. and Karen Bonnell of Production Economics coauthor a chapter on the "Principles of wiping and cleaning validation" (Chapter 8). Ed Kanegsberg of BFK Solutions provides an overview of issues related to detection and measurement of contamination (Chapter 9). Finally, Ben Schiefelbein of RJ Lee Group provides a new, insightful chapter on the philosophy of and choices for analytical analysis with "Practical aspects of analyzing surfaces" (Chapter 10). Many of the techniques should be considered whether or not you operate in a clean room.

The next four chapters in this part address knowing when to clean, when the part is clean enough, and materials compatibility.

Mantosh Chawla of Photo Emission Tech. (PET), Inc. updates his chapter on the important topic of "How clean is clean? Measuring surface cleanliness and defining acceptable levels of cleanliness" (Chapter 11).

Two chapters are a must for those involved in process validation for implantable medical devices. Kierstan Andrascik of QVET Consulting brings her experience with analysis of medical devices in a new chapter on "Cleaning validations using extraction techniques" (Chapter 12). David Albert of NAMSA has expanded his chapter on "Testing methods for verifying medical device cleanliness" (Chapter 13).

Eric Eichinger of Boeing North America has expanded his chapter on the critical issue of materials compatibility both for metals and nonmetals (Chapter 14).

Part II: Applications

While each manufacturing situation may be thought of as unique, there are commonalities, and it can be helpful to explore common contamination problems in specific industrial sectors and to see how manufacturers in similar situations tackle cleaning problems. Therefore, the number of specific applications presented in this part has been expanded in the second edition.

Barbara Kanegsberg of BFK Solutions, with a contribution by Bev Christian of Research in Motion, provides "Clean critically: An overview of cleaning applications" (Chapter 15). Specific examples and case studies drawn from aerospace, electronics, and biomedicine are given.

A number of comprehensive new chapters are devoted to applications within the life sciences. John Broad of NAMSA and David Smith of Tissue Banks International provide a chapter on "Cleaning validation of reusable medical devices" (Chapter 16). Paul Lopolito of Steris Corporation provides insight into "Critical cleaning for pharmaceutical applications" (Chapter 17). Hein Timmerman of Diversey, Inc. in Belgium provides a chapter on "Cleaning in food processing" (Chapter 18).

Three new chapters reflect renewed importance of cleaning in electronic assembly applications. Mike Bixenman of Kyzen Corporation provides a comprehensive chapter on "Electronic assembly cleaning process considerations" (Chapter 19). Harald Wack of ZESTRON contributes a chapter on "Surfactant-free aqueous chemistries" (Chapter 20) and Helmut Schweigart, also of ZESTRON, writes about "Contamination-induced failure of electronic assemblies" (Chapter 21).

Ahmed Busnaina of Northeastern University treats the case of particle removal in his expanded chapter (Chapter 22). This is an effective treatment of surface physics presented in a readable and understandable manner.

Shawn Sahbari of Applied Chemical Laboratories, Mahmood Toofan of Semiconductor Analytical Services, and John Chu discuss the challenges faced in semiconducting wafer fabrication for aluminum interconnects (Chapter 23). In a new companion chapter, Shawn Sahbari and Mahmood Toofan discuss microelectronic cleaning with "Copper interconnect and particle cleaning" (Chapter 24).

The world of fine art is the subject of a new chapter, "The cleaning of paintings," by Chris Stavroudis, a paintings conservator in private practice, and Richard Wolbers of the University of Delaware (Chapter 25). Cleaning these valuable, critical surfaces involves careful formulation of cleaning chemistries as well as considerations involved in conserving surface qualities and attributes. If you are in manufacturing, peruse the chapter for ideas and approaches; there are more commonalities with the world of fine art than might be apparent on the surface.

Jason Marshall of Massachusetts Toxic Use Reduction Institute (TURI) provides a new "Road map for cleaning product selection for pollution prevention," outlining decisions that can be made to clean with less impact on workers and the environment (Chapter 26).

Bill Breault, Jay Soma, and Christine Fouts of Petroferm contribute a new focused case study on removing wax from aerospace build and assembly operations (Chapter 27). The approaches can be extrapolated to other operations.

Wayne Ziegler of the Army Research Laboratory and Tom Torres of the Naval Facilities Engineering Service Center (NFESC) team to provide a new chapter, "Implementation of environmentally preferable cleaning processes for military applications," that describes the efforts of the military Joint Services Solvent Substitution Working Group to implement processes across all military agencies with less use of hazardous or environmental degrading cleaning products while ensuring uncompromised performance (Chapter 28).

Part III: Safety and Regulations

Because cleaning almost always involves using materials or processes with environmental or safety "baggage," sucessfully navigating regulations and working with regulators has become part of the overall picture. This final part provides tools and approaches to achieving successful critical cleaning processes in a highly regulated world.

Barbara Kanegsberg begins with an expanded, frank overview of safety and environmental issues (Chapter 29).

Jim Unmack of Unmack Corporation contributes an updated and greatly expanded chapter that outlines health and safety aspects associated with cleaning processes (Chapter 30). Recognizing that manufacturing is a global issue, he provides insight on European as well as U.S. requirements.

Mohan Balagopalan of southern California's South Coast Air Quality Management District (SCAQMD) expands his thoughtful and frank discussion on working with regulators—from a regulator's viewpoint (Chapter 31).

Steve Andersen, recently retired from the U.S. EPA, teams with Margaret Sheppard of the U.S. EPA Significant New Alternatives Program (SNAP) to update and expand the discussion of how industry and government can work together, with a discussion on how lessons learned from the ODC phaseout can drive continuous environmental improvement (Chapter 32).

The book closes with an expansion of the chapter by Don Wuebbles of the University of Illinois-Urbana (Chapter 33). His chapter reviews "Screening techniques for environmental impact of cleaning agents."

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Editors

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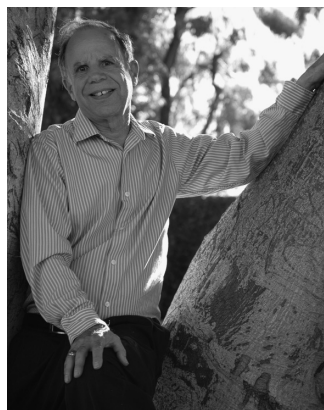
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I

Cleaning Agents

1

Cleaning Agents: Overview

Barbara Kanegsberg
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Introduction—More than Molecules

Cleaning is a process, not simply a chemistry, so it is important to look at the cleaning agent and at the entire cleaning process, including the specific equipment selected. Having said this, matching the appropriate cleaning agent to the job at hand can be a traumatic experience, even to those with some background in chemistry. This chapter provides an overview of cleaning agents and highlights a few additional cleaning agents not discussed in other chapters; it is by no means exhaustive.

Cleaning agents are generally divided into aqueous and solvent. When most people involved in cleaning refer to the term solvent, they actually mean organic solvent. Organic solvents are not those processed from, say, free-range, herbicide-free lemons. Instead, organic refers to materials that have the element carbon in them. However, when you think about it, both organic- and aqueous-based cleaning agents are solvents. If you dissolve sugar in tea, the water is acting as the solvent; the sugar is the solute. Because many oils are carbon based, organic solvents have been classically used for very heavy

degreasing jobs. However, other mechanisms such as saponification (as described in Chapter 2, Beeks and Keller) have been successfully used to lift heavy grease off of parts. Certainly, water-based cleaning is widely used; most of us have successfully removed oils and greases from dishes using semiautomated aqueous cleaning, not a vapor degreaser.

While a segment of the cleaning industry has traditionally been carried out by aqueous cleaning, until the mid-1990s, most cleaning was conducted using classic chlorinated solvents or with ozone layer depleting compounds (ODCs). In fact, many products were designed specifically around the solvency properties of chlorofluorocarbon-113 (CFC-113) and 1,1,1-trichloroethane (TCA). The loss of ODCs and increasing regulatory constraints on classic solvents (notably chlorinated solvents) has lead to upheaval in the manufacturing world, and, because there are no true drop-in substitutes for ozone depleters, the market has fragmented (Kanegsberg 1996). This fragmentation has continued for a number of reasons, including lack of understanding as to how to use the new methods, dissatisfaction with selected new approaches, high cleaning costs, development of new solvent and aqueous blends, increasingly stringent and ever-changing regulatory conditions, differences in regulations in various geographical locations, increasingly stringent cleaning and performance requirements, new product design including micro and nanoscale designs, and the use of new process fluids including metalworking fluids.

To make matters even more complex, the line between cleaning agent and cleaning equipment or cleaning is often blurred. Sometimes the cleaning agent is generated in use, for example, CO_2 (solid, liquid, and supercritical) and plasma. Solid or abrasive media are, in a sense, both the cleaning agent and the cleaning process; these topics are discussed later in Chapter 26 (E. Kanegsberg), and Chapters 27, 28, and 29 (Swan, Sherman, Nelson, respectively).

No one product or class of products is likely to satisfy all cleaning requirements. The cleaning agent must be matched to the soil, the substrate (the component or part to be cleaned), the cleaning requirements, drying requirements, and other performance and environmental constraints. Inorganic soils are often referred to as hydrophilic; they dissolve effectively in water. Organic-based soils, often referred to as hydrophobic, tend to dissolve more effectively in organic solvents. The choice of cleaning agent should ideally be based on technical considerations. Unfortunately, chemists, engineers, production people, and those involved in regulatory agencies may themselves become hydrophilic or hydrophobic (Kanegsberg 1996). While we all have cleaning agent prejudices, irrationally ruling out one class of cleaning agents can result in inadequate cleaning and can be economically and ecologically detrimental.

Another reason to keep an open mind and to try to understand a range of approaches to cleaning is that the line between aqueous and organic cleaning tends to blur, so even if you and your firm are unalterably devoted to organic solvents, it will be helpful to learn about aqueous cleaning (and vice versa). Some inert organic cleaners are blended with small amounts of surfactants to improve removal of soils. Many aqueous cleaners contain significant amounts of organic additives. Some may be basically blends of water-soluble organic compounds. In fact, certain similar organic solvent blends may be classified as semi-aqueous or co-solvent only in that very small formulation differences allow for rinsing in water (for semi-aqueous) or another solvent (for co-solvent). Therefore, this overview emphasizes a number of specific organic compounds, not simply because they can be used for solvent cleaning per se but also because they are used in cleaning agent blends, including aqueous blends. We have not discussed ionic liquids; they may eventually have widespread adoption in cleaning applications.

An Introduction to CAS Numbers

In this chapter and in various places in *Handbook for Critical Cleaning*, periodic allusion is made to the Chemical Abstracts Service (CAS) number for a particular cleaning chemical. The CAS number or CAS Registry Number® is a registered trademark. While CAS numbers do not have chemical significance, they are valuable tools for everyone involved in critical/precision cleaning and manufacturing because they are internationally recognized, unique chemical identifiers of elements, inorganic

compounds, and organic compounds. This means that even two optical isomers would each have a unique CAS number.

Because one chemical may have multiple names, in my experience, a CAS number is helpful in many aspects of precision cleaning, including process control, failure analysis, and safety/environmental regulatory compliance. For example, an engineer may refer to the cleaning agent as a nickname. "Trich" can refer to trichloroethylene or it may mean that, despite the phaseout of ozone-depleting chemicals, 1,1,1-TCA is being used. Freon® is a trade name, and it can refer to a number of chemicals.

We often find that it is difficult to identify the cleaning chemistry based on labeling information on drums, aerosol containers, and even material safety data sheets (MSDSs). Suppose you find that a cleaning process uses "FabuloKleen." You want to know the following: What is in the product? What are the technical/performance/compatibility characteristics? Are there regulatory issues? Someone hands you a bottle. You grab a magnifying glass, peer at the label, and find half a dozen chemicals, displayed in all of their incomprehensible, polysyllabic glory. Someone locates the MSDS; you find larger print, but the same problem. But wait! Next to each listed chemical, there is a CAS number. With that number and access to the Internet, it is typically possible to identify the chemicals in short order. This may set your mind at ease, or you may find a chemical that is overly reactive for your purposes or one that is under regulatory distress.

The CAS numbers provided in this and other chapters are believed to be from reliable sources. We consulted MSDS and Technical Data Sheets from established companies. In practice, we have encountered some inaccuracies, even in MSDSs, so it is best to cross-reference several sources. Additional clarification about CAS Registry numbers, including authoritative, definitive information (including issues such as intellectual property or Environmental Protection Agency [EPA] registration) is available online (CAS Registry 2010).

Please also be aware that the South Coast Air Quality Management District (SCAQMD), a regulatory agency in Southern California, has a CAS program; in this case, CAS is an acronym for Clean Air Solvent. The distinction should be apparent contextually.

Aqueous Cleaning Agents

Simple Additives

Water removes some soils. With appropriate cleaning action and constant rinsing to remove soils, water alone can clean. However, additives improve performance.

Some blends are relatively simple and are blended in-house. Such blends can be particularly desirable where residue is an issue either for the product or for disposal of the spent cleaning agent. Small amounts of peroxide (0.5%) have been added to water to clean and remove bacteria. Dilute hypochlorite (bleach) is often used to prevent biological contamination. Ammonia is often used for simple cleaning. Alcohol and acetone are sometimes added to boost cleaning power and promote rapid drying. Where low-flash-point solvents are used, flammability must be considered in process development, even with aqueous cleaning agents. Sodium bicarbonate may be added. Acid washing and acid etching with Piranha, chromic acid, and other strong acids can be thought of as selective cleaning. While the solutions are simple, process control, process monitoring, employee safety, potential flammability, and environmental regulatory issues must all be considered.

Commercial Blends of Aqueous Cleaning Agents

Commercially available aqueous cleaning agents contain additive blends, often consisting of a dizzying array of organic and inorganic compounds. Some additive packages are totally inorganic; most are a mixture. While a few companies disclose the additive package, more typically, for competition-sensitive issues and other factors, the exact formulation is a closely held secret. A few examples of additives are provided in Table 1.1 (Cala 1996). Well-designed aqueous formulations are complex, sophisticated, and

TABLE 1.1 A Few Additives Used in Aqueous Formulations

Additive	Function	Description with Examples
Surfactants	Wettability Soil displacement/dispersion Solubilization	Single molecule with hydrophilic and hydrophobic portions May have long-chain organic portion (many carbons in a row) For example, alcohol ethoxylates
Defoamers	Control excessive foam Allow use in high-pressure spray applications, etc.	Poorly soluble in bath at operating temperature Impart slight "oil-like" quality Usually nonionic surfactants For example, nonionic block copolymers
Solvents, assorted	Decrease surface tension Adjust pH Improve solubility range	Typically soluble in water May be VOCs For example, butyl cellosolve, pyrrolidone, morpholine, glycol ethers, alcohols
Corrosion inhibitors, passivating	Prevent corrosion of metals	React with metal surface to reduce reactivity Typically oxidizing agents For example, chromates, nitrates, permanganates, chlorates Some reducing agents, e.g., Na sulfite
Corrosion inhibitors, non-passivating	Prevent corrosion of metals	Adsorption, formation of protective films For example, silicates (most common), pyrophosphates, carbonates, amines, gelatin, tannic acid, thiourea
Builders	Promote efficacy of cleaning by surfactants Sequester water hardness Maintain pH (acidity, alkalinity) Decrease metal, lead content of waste stream	Typically salts Chelating agents, for example, sodium tripolyphosphate; sodium hexametaphosphate, sodium citrate Precipitating builders (e.g., carbonates)
Hydrotropes	Promote solubility of organics in presence of high levels of inorganic salts	Important with inorganic surfactant packages For example, toluene sulfonates, short chain alcohols, benzoate salts
Oxidizers	Corrosion inhibitors Adsorption, dissolution in soils, oxygen release Better soil removal	For example, hydrogen peroxide

Source: Adapted from Cala, F.R. and Winston A.E., *Handbook of Aqueous Cleaning Technology for Electronic Assemblies*, Isle of Mann: Electrochemical Publications, 1996.

are specifically designed to remove certain soils. Also, be aware that even though aqueous cleaning agents are used in dilute form, they are not formulated from organic carrot juice. As with other cleaning agents, aqueous cleaning agents must be used with understanding and respect.

For general metals cleaning, aqueous formulations with relatively broad range of acceptability for substrate and soil have been found. However, for most high precision applications the aqueous cleaning agent must be specifically matched to the soil, the expected soil loading, the substrate, and the expected end use of the product. For example, in some applications, phosphate or silicate residue is not acceptable. In addition, in cleaning certain metals, notably aluminum, careful selection of the aqueous cleaning agent and process is required.

Water-Soluble Organics

Some cleaning agents, nominally referred to as aqueous cleaning agents, are primarily or significantly high in organic solvent blends including long-chain nonlinear alcohols or D-limonene. They can be rinsed with water or, in some cases, with either water or solvents. Providing both solvent and aqueous

cleaning in the same process has advantages. However, recovery of the waste stream and carryover can become a problem.

Specific Blends

We will see more and more cleaning agent blends. As the number of manufacturing process fluids (e.g., metalworking fluids) proliferate, blends become important to fine-tune the performance aspects of the cleaning agents. Further, with the increasing proliferation of epoxies, potting compounds, elastomers, and composites, materials compatibility requirements must be met. Further, for a variety of reasons, including economic and regulatory constraints, the marketplace favors introduction of complex blends. There is a huge investment in developing individual molecules for cleaning. Individual molecules are readily identified by regulatory agencies and are therefore more likely to be restricted. Cleaning agent formulation combines science and art. This is true for aqueous, semi-aqueous, water-soluble organic, and organic solvent blends. Formulation is a bit like cooking. Even though the ingredients must be carefully defined both quantitatively and qualitatively, formulators have developed a style based on their education and experience. As you read the specific chapters dealing with formulated cleaning agents, you will develop an understanding of the basics and principles of formulation as well as the rationale and formulation style of the authors and of their companies. The goal is not to turn you into the next Julia Child of cleaning chemistries but rather to allow you to make rationale informed decisions as opposed to selecting cleaning agents based on Internet hyperbole.

Solvents and Solvent-Based Cleaning Agents

As in aqueous cleaning, there are mystery blends. However, it is often easier to identify the components of solvent-based cleaning agents. With the proliferation of new organic solvents, a number of by-products and natural products have been or are now used in cleaning processes. Cleaning agents based on orange, pine, cantaloupe, and grapes have been developed—an entire fruit basket of possibilities. Some solvents have been discussed in detail; others are alluded to in discussions or cleaning equipment or of specific cleaning agents.

A few additional solvents and solvent categories are worth noting. In general, one must consider that while many of these solvents have been used for years, long-term inhalation toxicity may not be available. In addition, blends and azeotropes of both new and well-established solvents may have their own solvency, compatibility, or toxicity properties. This holds true for organic and water-based cleaning agents. The best advice remains to test the solvent or blend in the application under consideration and to be conservative—minimize employee exposure and minimize loss of cleaning agent to the environment. In addition, compounds with higher boiling points and fairly complex blends with certain additives may leave undesirable residue, so rinsing is often required.

General Desirable Attributes of a Precision Cleaning Solvent

The following section is an excerpt from *Handbook for Critical Cleaning*, First Edition (Agapovich, 2000).

> For purposes of definition in this section, a solvent is defined as a cleaning agent which readily evaporates after use, when cleaning a component. No follow-up cleaning is required after the use of this class of material. These solvents will evaporate even after cold-cleaning. This will generally mean that the solvent has a vapor pressure of greater than 25 torr at ambient temperature. Another better quantifier of volatility is the evaporation rate compared to *n*-butyl acetate. *n*-Butyl acetate is set at unity. (ether and carbon tetrachloride are also used as reference materials) The majority of solvents discussed in this chapter all have an evaporation rate > *n*-butyl acetate or 1.

Another parameter related to volatility is the heat of vaporization, the heat required when a solvent transforms to the vapor phase from the liquid phase. When possible, it is best to choose solvents that have a low heat of vaporization as these materials will evaporate without absorbing heat (the part cools). Solvents with high heats of vaporization cool a part as more heat is absorbed from the environment. Often water condenses on a device that is cleaned, if the environment is humid. This is not desirable in precision cleaning.

Volatility and ease of vaporization has drawbacks. These include issues of containment, flammability, toxicity, and local regulations on emissions and cost. These issues will be discussed later in the chapter. Cleaners such as any aqueous based, terpenes and hydrocarbons in the combustible range (flash point >100°F) do not fall under the definition of a solvent and will not be discussed in this chapter.

Critical precision cleaning areas that use solvents under this definition include but are not limited to medical devices, directional devices (gyroscopes, accelerometers and including components within), computer components (disc drives), precision ball bearings, oxygen transport systems and circuit boards.

In addition to the need for volatility discussed previously, a precision cleaning solvent must meet other critical requirements. Obviously, the contaminant requiring removal must have a finite solubility in the cleaning solvent. This definition varies as factors such as time, temperature and agitation can be altered. Generally speaking, increasing the temperature of a solvent will improve cleaning effectiveness, as will increasing the exposure time. As an example, 3M defines "soluble" when a material dissolves in another in the range of 5 to 25 grams per 100 grams of solvent at room temperature (3M 1991). In another article, solubility has been defined as 50 grams per 100 ml of solvent (Agapovich 1997). There are many other range of definitions. The solubility and cleaning effectiveness required will vary depending on how contaminated the part is and also the users final requirements.

Other solubility parameters include a Kauri Butanol (KB) number. The KB numbers for CFC-113 and 1,1,1-trichloroethane are 31 and 124, respectively. Generally speaking, the highly chlorinated compounds have the higher reported KB values. The KB number reflects the ability of a solvent to dissolve heavy hydrocarbon greases. Specifically, it is a measure of ability to dissolve a solution of butanol and kauri resin. ASTM D 1133–90 describes the standard test method for determining the KB value of hydrocarbon solvents. This procedure has been extended to evaluate ODC replacements discussed in this chapter. It is not applicable to oxygen containing solvents.

However, the author [Agapovich] believes that as a first approximation, that the "like dissolves like" concept is very useful. This means that polar solvents dissolve polar contamination and nonpolar solvents dissolve non-polar contaminants. Hydrocarbon solvents will dissolve hydrocarbon oils and fluorocarbon based solvents dissolve fluorocarbon oils and greases. To clean solder flux residues from printed circuit boards, polar oxygen containing solvents like alcohols or chlorinated solvents are required.

In precision cleaning, it is beneficial to have a solvent with a low viscosity and low surface tension. This property will allow solvents to enter very narrow gaps in a complicated device, to clean a contaminant. Particle removal is often a critical part of precision cleaning operations. A solvent with a low viscosity and low surface tension also facilitates particle removal. A high density solvent provides additional momentum to remove particles from surfaces.

Another critical requirement is chemical stability during use and also a solvent having a long or infinite shelf life. This was been a problem with the use 1,1,1-trichloroethane without stabilizers. Some azeotropes and mixtures discussed later require stabilizers.

Of even more importance is compatibility with the component one is cleaning. There cannot be a chemical reaction, physical change such as irreversible swelling or extraction of the materials of construction of the component being cleaned. CFC-113 and 1,1,1-trichloroethane were compatible with most materials. ODC alternative solvent manufacturers are very cognizant of the concerns

of customers about solvent compatibility. Extensive solvent/materials compatibility tests are performed on a wide range of materials when a new solvent is introduced to the public. If one still has a question of the compatibility of material and solvent, it is best to have the solvent user perform the compatibility test in ones particular application.

Another critical solvent property is the non-volatile residue (NVR). It is critical when a solvent evaporates from a surface after cleaning, no residue is left behind. Solvent manufacturers typically have NVR specifications in the range of 1–10 parts per million (ppm) for precision cleaning. Very often the reported NVR of a given batch of solvent is well under the company set specification. The issue of NVR is also important when expensive solvents such as the PFCs, HFEs and HFCs are reclaimed and recycled. Any recycling process (such as distillation) must produce a product with the NVR meeting the original manufacturer (OEM) specifications.

Recycling is desirable for cost savings when using expensive solvents. The halogenated containing solvents (PFCs, HFCs and HCFCs) are particularly expensive. Recycling of used solvents is possible when solvents are used in cleaning and subsequently contaminated with particles or high boiling oils and greases. A simple strip or low theoretical plate distillation can be performed to purify the reclaimed solvent, to obtain NVR levels equal to or better than the OEM specifications.

Summary of Physical Properties of Primarily Unblended Organic Solvents

Table 1.2—consolidated, adapted, and where appropriate modified from the first edition (Agapovich 2000)—provides a comparison of some key physical characteristics of organic solvents. While a few are simple blends of two molecules, they can be thought of as simple cleaning agents. Almost all of them have relatively low boiling points and have a surface tension, density, and viscosity that are favorable for good wetting. This is important for cleaning components with miniature and microstructures.

We have not listed allowable inhalation levels or environmental regulatory information. Aside from the fact that such information does not represent physical characteristics, the safety and regulatory picture is a moving target that is geographically specific, nationally, regionally, and locally. The allowable inhalation level can vary by orders of magnitude, depending on the location. Many of aggressive cleaning solvents, and even some nonaggressive ones, have environmental and safety-related regulatory baggage. Very few chemicals have been banned; even highly restricted ones can be used safely and responsibly with the correct process equipment.

Old Reliable, Assorted Organic Solvents

Examples of classic organic solvents include toluene, hexane, heptane, benzene, and xylene. Flammability, worker exposure, air toxics, and company liability issues reduced the use of these solvents when ODCs were available. They have remained popular for specialized uses or as blends, particularly for specific, high-value applications. With decrease in availability of ODCs and an increase in low-flash-point and well-contained cleaning systems, these solvents have enjoyed a resurgence in popularity. They have a wide solvency range, but they are particularly "oil-like." If they are to be used, appropriate environmental and safety controls must be employed. Some specific organic solvents and categories of solvents are highlighted because they have found utility in critical cleaning applications.

Hydrocarbons (Mineral Spirits)

Hydrocarbon blends (mineral spirits or Stoddard solvent or kerosene) consisting of a petroleum cut of hydrocarbons with a range of molecular weights have been used in cleaning applications for many years. They are a mixture of molecules with closely related properties. Given the high boiling point and the potential for contaminants in some formulations, care must be taken in use and removal, and lot-to-lot variability may impact process control. Mineral spirits are not exempt as volatile organic

TABLE 1.2 Physical Properties of Solvents

Category	Solvent	CAS Number	Boiling Point (°C)	Vapor Pressure (Torr) at 20°C	Flash Point (TCC)°C (°F)	Density (g/cc) 20°C	Viscosity (cP) 20°C	Surface Tension (dyne/cm) 20°C
Hydrocarbon	*n*-Hexane	110-54-3	69	124	−26 (−15)	0.66	0.31	18 (25°C)
	n-Heptane	142-82-5	98	36	−4 (25)	0.68	0.41	20.3
	Isooctane	540-84-1	99	41	−12 (10)	0.69	0.50	18.8
	Cyclohexane	110-82-7	81	78	−27 (−17)	0.78	1	25
Ketone	Acetone	67-64-1	56	185	−17 (0)	0.79	0.36	23.3
	MEK	78-93-3	80	74	−1 (30)	0.80	0.43	24 (25°C)
Alcohol	Methyl	67-56-1	65	97	12 (54)	0.79[a]	0.55	22.6
	Ethyl (200 proof)	64-17-5	78	45	14 (58)	0.79[a]	1.1	22 (25°C)
	Isopropyl	67-63-0	82	32	12 (53)	0.78[a]	2.4	21.8 (15°C)
Chlorinated	Methylene chloride	75-9-2	40	350	None	1.33	0.44	28.1
	Trichloroethylene	79-01-6	87	47[b]	None	1.46	0.57	29.5
	Tetra-chloroethylene (perchloroethylene)	127-18-4	121	18[b]	None	1.62	Nl	Nl
	Trans-1,2-dichloroethylene	107-60-2	48	324[b]	6 (43)	1.26	Nl	Nl
Brominated	*n*-Propyl bromide	106-94-5	71	111	None	1.35	0.49[a] cS	26
Siloxane	Hexamethyl-disiloxane (OS-10)	107-46-0	100	42	−3 (27)	0.76[a]	0.65[a] cP	15.2
Benzotrifluoride	Para-chloro-benzotrifluoride (PCTBF)	98-56-6	139	7.9	43 (109)	1.34[a]	0.79[a] cP	25
HFC/HFE	HFE-7100	163702-08-7	61	202	None	1.52[a]	0.61[a]	13.6
	Methyl nonafluoroisobutyl ether, methyl nonafluorobutyl ether	163702-07-6						
	HFE-7200	163702-06-5	78	109	None	1.43[a]	0.61[a]	13.6
	Ethyl nonafluoroisobutyl ether, ethyl nonafluorobutyl ether	163702-05-4						
	HFC-XF 2,3-dihydroperfluoro-pentane	138495-42-8	55	226	None	1.58[a]	0.67[a]	14.1

HCFC Class II ODC	AK-225 (HCFC-255ca/cb)	422-56-0ca, 507-55-1cb	54	283	None	1.55[a]	0.59[a]	16.2 (25°C)
ODCs, phased out	CFC-113, 1,1,2-trichloro-1,2,2-trifluoroethane, Freon® 113	76-13-1	48	334	None	1.56[a]	0.68[a]	17.3 (25°C)
	1,1,1-TCA	71-56-6	74	121	None	1.32[a]	0.8[a]	25 (25°C)
	HCFC 141b, Dichlorofluoroethane	1717-00-6	32	572[b]	None	1.24[a]	0.43[a]	19.3
Perfluorinated	PF-5060, Perfluoro compounds, primarily with six carbons	86508-42-1	56	232	None	1.68[a]	0.4[a]	12.0
	PF-5070, Perfluoro compounds, primarily with seven carbons	86508-42-1	80	79	None	1.73[a]	0.6[a]	13.0
	PF-5052 Perfluoro compounds, primarily with five carbons	86508-42-1	50	274	None	1.70[a]	0.4[a]	13.0

Source: Adapted and expanded from Agapovich, J.W., Review of solvents for precession cleaning, in *Handbook for Critical Cleaning*, 1st edn., Boca Raton, FL, 2000.

Note: Nl, not listed in literature reviewed; TCC, tag closed cup.

[a] At 25°C.

[b] mmHg at 25°C.

compounds (VOCs). Some mineral spirit blends work effectively because they contain other chemicals that may show aggressive solvency but may also have safety and/or environmental regulatory restrictions. These additives are sometimes apparent from the MSDS, but not always. It is possible to obtain very pure mineral spirit blends with a narrow, defined range of hydrocarbon chain lengths. Such well-defined hydrocarbon blends are better suited to high-precision applications, both for cold cleaning and, in the appropriately designed system, even for vapor phase cleaning. The military has incorporated some of these well-defined mineral spirits into cleaning specifications.

Chlorinated Solvents

Methylene chloride, perchloroethylene (tetrachloroethylene), and trichloroethylene are used in precision cleaning applications (refer to Chapter 8, Risotto). The solvents are effective; they are also subject to many environmental and worker safety regulations. They can be used with appropriate safeguards. They tend to be good wetting agents, meaning that they are useful in removing soil that is trapped in tightly spaced components. The Hansen solubility parameters (refer to Chapter 4, Burke) are such that they are useful in removing a wide range of soils. However, soil blends that contain large amounts of inorganic, polar contaminants (such as salts) are generally more effectively used in aqueous cleaning.

Trans-1,2-Dichloroethylene

Trans-1,2-dichloroethylene (156-60-5) is a daughter compound of these chlorinated solvents, and it has many physical and solvency properties that are at least somewhat similar to the chlorinated solvents (refer Table 1.2). In the United States, *trans* has been adopted in industrial and precision cleaning applications, and it is increasingly used as a blending agent. Some desirable characteristics include aggressive solvency, rapid evaporation, high density, an odor that is similar to other chlorinated solvent, and reasonable solubility in a range of organic solvents; it can be used in aerosol formulations (Shaw 2010). *Trans* could also be used neat as a chlorinated liquid/vapor degreasing solvent with the proviso that it be used in an appropriately designed system for low-flash-point solvents. It should also be noted that the level of *trans* needed to provide appreciable solvency to an hydrofluorocarbon (HFC) or hydrofluoroether (HFE) azeotrope also contributes a significant level of VOCs. Therefore, while the base material may be noted as VOC exempt, the blend may or may not be a good candidate for cleaning in your location.

   Trans-1,2-dichloroethylene is said to have a relatively favorable worker safety profile, particular as compared with other chlorinated solvents and the *cis* isomer of *trans*. The notable safety and environmental constraints are that *trans* is a VOC and that it has a low flash point. The inhalation limit is 200 ppm (U.S. Department of Labor, Occupational Safety and Health Administration n.d.). As this book goes to press, the U.S. EPA appears to be at the initial stages of a health risk assessment of *trans*-1,2-dichloroethylene, and my understanding is that there is external peer review; one might anticipate that results will be posted in late 2010. The status and progress can be assessed online (U.S. EPA 2010).

Perfluorinated Compounds

Perfluorinated compounds (PFCs) contain fluorine and carbon, but no chlorine or bromine. They are exceedingly mild, inert cleaners that can be used for removal of fluorinated lubricants and as rinsing and drying agents. PFCs are very effective for particulate removal. They are not ODCs. They are still sold alone and in various formulations. However, because of the global warming potential associated with a long atmospheric lifetime, often ranging in the thousands of years, industry has been under what might be termed strong regulatory "encouragement" to find substitutes. HFCs and HFEs can and has replaced PFCs in many, if not most, applications.

TABLE 1.3 Some Characteristics of HFC-365 mfc and HFC-245 fa

Characteristic	HFC-365 mfc	HFC-245 fa
Structure	$CF_3CH_2CF_2CH_3$	$CF_3CH_2CF_2H$
Molecular weight	148	134
Boiling point (°C)	40.2	15
Flashpoint (°C)	Below −27	None
UEL/LEL (% by volume)	3.8–13.3	None
ODP	Zero	Zero
Atmospheric lifetime	10.8 years	Low to moderate
VOC status	Exempt	Exempt

Hydrofluorocarbons and Hydrofluoroethers

Some HFCs and HFEs with significant use in cleaning processes are discussed in Chapter 5 (HFEs) (Owens) and Chapter 6 (HFCs) (Bartelt and Merchant). Other HFCs and HFEs are used as part of cleaning products. Some of them have low boiling points but are useful as blending agents to suppress flammability, moderate aggressive solvency, and lower the VOC content. They are attractive for blending in aerosols and for other single-use applications as opposed to process baths (Knopeck 2000). Both HFC-365 mfc (Solvay, Solkane® 365 mfc) and HFC-245 fa (Honeywell) are very mild solvents. Both have been accepted under the EPA SNAP program as substitutes for ozone depleters; both are indicated as having relatively favorable worker exposure profiles. They were originally developed as foam blowing agents (Zipfel 2000). It should be noted that HFC 365 has a very low flash point. In nonflammable blends, and even in azeotropes, there is the potential for flammable mixtures to develop in-use. Therefore, you as the end user should work with your advisors and with responsible cleaning agent suppliers to carefully evaluate your own production situation. It is interesting the HFC 365 is blended with *trans*-1,2-dichloroethylene; the product literature indicates that commercially available blends of these two flammable solvents as well as a blend containing ethanol do not have a flashpoint as tested by DIN/EN/ISO 13736 (Solvay Fluor GmbH 2009). HFC-365 mfc has a significantly higher boiling point than HFC-245 fa. The differences may not seem significant, but remember that as a rule of thumb chemical processes double in rate with every 10°C increase. For both materials, some plastics compatibility studies have been conducted. Because synergistic behavior can occur, you would be well-advised to confirm the compatibility of any proposed blend to the specific mix of materials and in the application at hand (time of exposure, temperature, force of cleaning action). With a 15°C boiling point, many end users will find that HFC-245 fa would not be suitable for use in classic, unmodified vapor degreasers; flushing systems or airless/airtight systems might be useful. Some properties of HFC-365 mfc and HFC-245 fa are summarized in Table 1.3. Additional products are reportedly under development, and detailed information is not available as the book goes to press. Based on early indications and on the current global regulatory environment, while we might be pleasantly surprised, one would predict that these will be relatively mild solvents.

Oxygenated Solvents

Examples of oxygenated solvents include the short-chained alcohols (methyl alcohol, ethyl alcohol, isopropyl alcohol [IPA]), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and acetone. Compared with, say, hexane or heptane, the addition of oxygen makes these compounds more polar, that is, more like water. Relative to hydrocarbon blends, they are more suited to polar or inorganic soils. It should be noted that oxygenated solvents cannot systematically be used as drop-in replacements for

chlorinated solvents; they have different physical, flammability, and solvency properties. Despite the low flash point, some oxygenated compounds, such as IPA, can be used in appropriately designed vapor degreasing systems.

Alcohols and Ketones

IPA is widely used in critical applications, including aerospace and medical device cleaning. Despite its widespread use, IPA is not a universal solvent. Because of the use in hospital environments, some people feel that it connotes cleaning. It evaporates rapidly, and it typically does not leave a residue. It should be noted that where a residue is found, particularly in benchtop cleaning, one culprit can be plasticizers. Residue can come from using the wrong plastic container or from a well-loved plastic bottle that may have lurked on the benchtop for years (even decades). Another culprit is the shipping/ storage container. A third is the purity of the IPA. Purchase high-quality IPA. For exacting applications, it may need to be stored in glass. Finally, for benchtop use, select the correct dispensing containers. If you use plastic dispensers, please do not allow you or your assemblers to become devoted to a single plastic dispensing bottle. Change those dispensing containers often. Please also remember that IPA has a low flash point (12°C). This means that filling an ultrasonic tank with IPA is not acceptable; it presents a potential fire hazard. This means that you have to evaluate all processes involving IPA as well as those near IPA uses.

Long chain alcohols such as tetrahydrofurfuryl alcohol (THFA) are used alone and in blends. The longer the carbon chain, the more they become fat-like (able to dissolve oil). However, the alcohol portion confers some water-like qualities. Often, these alcohols can be part of aqueous, semi-aqueous (rinse with water), or co-solvent (rinse with solvent) blends. Alcohols of varying chain length have been used in blends, particularly aerosol blends, to confer appropriate solvency properties.

Acetone is a ketone; there is a double-bonded oxygen in the molecule. Acetone has an exceedingly low flash point (−17°C), so whatever (Pourreau 2006) cautions are used with IPA need to go up by orders of magnitude with acetone. Acetone has very different solvency properties than hydrocarbons, halogenated solvents, or alcohols (refer to Chapter 4, Burke). Because it evaporates very rapidly, it has been used for decades and decades as a final quick rinse and drying agent. After being delisted as a VOC, there has been increased interest in acetone. Acetone has been appropriately adopted for some processes, wishfully or inappropriately for others. The extremely rapid evaporation rate, incompatibility with some plastics, and low flash point remain issues. With, and only with, appropriately designed equipment, acetone can be used in cleaning systems. The exposure times tend to be longer than with benchtop cleaning, heat may be applied, and the impact of water dissolved in the acetone must be considered. For example, in a heated acetone system, a visible white "bloom" on magnesium was observed; the problem was observed after brief benchtop cleaning (Kanegsberg 2009). There has been increased use of acetone in aerosol applications, because it is a relatively low-cost alternative to other VOC-exempt compounds such as HFCs and HFEs. It also replaces hydrochlorofluorocarbon (HCFC)-141b, an ozone-depleting chemical. Of course, the use of acetone-based aerosols near sources of ignition is not advisable. In addition, acetone can react with some plastics even after brief exposure.

N-methyl pyrrolidone (*N*-methyl-2-pyrrolidone, NMP) is a high boiling (295°C), high flash point (91°C, 196°F) ketone, which is used alone and in blends. Because it is water-soluble, it can be blended for removal of both rosin and organic acid flux, and it is used in photoresist systems. Other pyrrolidones are being developed, notably *n*-octyl pyrrolidone (NOP) and *n*-hydroxy ethyl pyrrolidone (HEP). Used alone and in blends, they may serve to extend the range of cleaning in degreasing. For example, NOP has a longer carbon chain and is therefore more oil-like, so it could be used in formulations for degreasing, paint stripping, and de-inking of paper. HEP shows promise in photoresist removal (Waldrop 2000). Dimethyl sulfoxide (DMSO) has also been developed in some photoresist applications as well as in other processes requiring a fairly aggressive solvent.

Esters

Various monobasic and dibasic esters and notably lactate esters are used alone and in blends in semi-aqueous and co-solvent applications. They have proven particularly effective in the removal of pitches, waxes, and other difficult, mixed soils.

Most esters have a fairly strong or distinctive odor. They are high boiling and must be rinsed in high-precision applications. Esters may also be used in coatings formulations. *t*-Butyl acetate (TBAC) and dimethyl carbonate (DMC) have relatively low tropospheric reactivity and may therefore be particularly useful where VOCs are an issue. Methyl soyate, a biobased cleaning agent, has been developed as a cleaning agent alone, in blends, and in sequential cleaning processes. While methyl soyate is not exempt as a VOC at the Federal level, there has been acceptance of some methyl soyate products as clean air solvents in SCAQMD (see discussion of biobased materials in this chapter).

Esters hydrolyze in the presence of water; they break down to form an acid and an alcohol. Therefore, when any ester is used in a process bath for an extended period of time and perhaps in the presence of heat, it is important to consider the extent to which water can be dissolved in the ester, to consider how rapidly it hydrolyzes, to consider the potential impact of hydrolysis products on efficacy of cleaning, and to determine any worker safety, flammability, and/or environmental impacts. There could be four potential cleaning agents in the cleaning tank: the ester, the water, the acid, and the alcohol.

t-Butyl Acetate—Regulatory Complexity

However, the situation with TBAC illustrates issues associated with the complexity of environmental regulations, as discussed in "The Cleaning Agent Balancing Act (*Handbook for Critical Cleaning: Applications, Processes, and Controls,* Chapter 2)". TBAC has shown promise of utility in aerospace and other precision cleaning applications, including military and aerospace (Foreman 1999), for brake cleaners, and as a component of coatings and inks (Pourreau 2006). In the precision cleaning of electronics assemblies, TBAC has been found to provide a good complement to acetone. TBAC has a higher boiling point. Unlike acetone, it does not dissolve nitrile gloves, and in one test evaluation, the assemblers found the odor to be acceptable (Elias n.d.).

At the Federal level, while TBAC was eventually accepted by the EPA as having negligible reactivity relative to ethane and therefore is VOC exempt, acceptance by the EPA and at the State level took much longer than would have been expected. At the State level, the California Air Resources Board (CARB) was concerned with the potential toxicity of TBAC, both in and of itself and because it can break down to *t*-butyl alcohol (California EPA Air Resources Board 2006). Because TBAC is an ester, it can break down to an acid and an alcohol. The wording of the EPA exemption for TBAC is unique among those compounds that are listed as VOC exempt (U.S. EPA 2009; definitions of VOC and ROG 2009). While TBAC is not a VOC and is therefore exempt from limitations on use or emissions, it is treated like a VOC. That is, recordkeeping and reporting for TBAC is like that for VOCs; you have to keep records of use and report emissions to the State along with other VOCs. One might expect this to discourage the use of the chemical as a cleaning agent or process fluid, and it might be expected to result in confusion. In fact, the EPA indicated that SCAQMD did not fully comply with the EPA definition of TBAC as a VOC (U.S. EPA 2009). (Also see Chapter 29, B. Kanegsberg, in *Handbook for Critical Cleaning: Applications, Processes, and Controls.*)

Dimethyl Carbonate

In the United States, DMC (carbonic acid dimethyl ester, CAS Number 616-38-6) is a potentially attractive cleaning agent in part because it has been determined to have negligible reactivity and is therefore VOC exempt at the Federal level (U.S. EPA 2009). Not all states have approved the VOC-exempt status. DMC has a very low flash point and a fairly high boiling point. DMC is fairly soluble in water and therefore may be subject to breakdown by hydrolysis. Some important physical and chemical properties are summarized in Table 1.4.

TABLE 1.4 Physical and Solvency Properties of DMC

Property	Level
Boiling point (°C)	90
Freezing point (°C)	2–4
Vapor pressure (torr, 20°C)	42 (55 at 25°C)
Flash point °C (°F) closed cup	(63°F)
Density (g/cc) (20°C)	1.07
Viscosity (cP 20°C)	0.625
Surface tension (dyne/cm 20°C)	3.19×10^{-2} N/m
Hansen solubility parameter dispersion	15.5
Hansen polar	3.9
Hansen hydrogen bonding	9.7
Solubility in water (g/100 g water)	13.9

We have not evaluated DMC. A status summary has been provided by one supplier (Smith 2010):

DMC is a moderately evaporating solvent with an evaporation rate of 3.22 (BuAc = 1.0), which puts DMC right between methyl ethyl ketone (MEK, (4.03) and toluene (2.0). The solubility profile is similar to a number of common glycol ethers such as cellosolve acetate, propylene glycol monobutyl ether (PNB) and propylene glycol monoethyl ether acetate (PE acetate). DMC remarkably freezes approximately 36°F, although mixtures with other solvents can depress the freezing point. The extent to which DMC will be used in the cleaning industry will probably be dependent on what co-solvents can used with DMC to overcome the low flashpoint and high freezing point. Azeotropes may be developed as DMC is further researched for cleaning applications. The odor profile may be characterized as an alcohol or light ester odor. DMC has toxicological properties that favor industrial, automotive, or outdoor use, but it would not be recommended for indoor consumer or institutional use. DMC has a similar toxicological profile to methanol, its primary metabolite. The industrial exposure level recommended by a U.S. supplier for an 8-hour day by inhalation is 100 ppm (based on hydrolysis to methanol). California's CARB (Air Resources Board) does not immediately plan to exempt DMC for most cleaning or consumer applications. CARB needs to obtain typical formulations and determine what solvents DMC would replace in key applications. CARB can then do a health and safety assessment.

Biobased Cleaning Agents

Biobased (biologically based) products are industrial or commercial products (not for food products) that are composed of plant- or animal-based materials. One advantage of biobased products is that they are a renewable resource. Plant-derived biobased cleaning agents have been commercialized. Some are derived from one source, others are blends of biobased products; still others may have additives such as surfactants. Biobased materials can also be used as blending agents. Biobased products may be water- or solvent based. Many are used in inks and/or coatings; the extent of development as cleaning agents by different suppliers is variable.

Most have very high boiling points. Therefore, for critical/precision cleaning applications where residue is an issue, they may require rinsing and drying. Both water-rinseable and solvent-rinseable formulations are available. Some physical properties of biobased solvents are summarized in Table 1.5. We have found some variability in the numbers reported for boiling point and flashpoint; factors in this variability may include methodology, differences in chemical composition, and perhaps the presence of other chemicals.

TABLE 1.5 Some Physical Properties of Biobased Solvents

	Methyl Soyate[a]	Ethyl Lactate	D-Limonene
Specific gravity	0.88	0.83	0.84
Vapor pressure (mm Hg)	<1.0	1.7	1.4
Boiling point °C (°F)	216 (421)	154 (309)	178 (310)
Flash point °C (°F)	>100 (>212, approx. 360)	59 (139)	46 (115)
Kauri-butanol number	58	NA	67

[a] United Soy Board (2010).

Like all chemicals, biobased products should be managed with appropriate diligence, caution, and respect. The term "biobased" is often erroneously assumed to be synonymous with safe. Centuries ago, the de' Medici's were infamous for creatively dispatching their enemies through the use of poisons. I suspect that, rather than consulting with the formulator of a large chemical conglomerate, de' Medici's drifted serenely through the palace garden with the resident compounder and harvested a local, sustainable, renewable resource. The dose makes the poison. Understand what you are using and how you are using it. After all, biobased cleaning agents are extracted from living things and are therefore used in a concentrated form. They may be used where heat and mists are generated; some may oxidize and become ignition sources. They should be disposed of appropriately. When people use any cleaning agent, from any source, including biobased products, it is important to understand potential environmental and worker safety issues. It is also important to understand the potential for any residue, including residue from a biobased product, to interact with a living host. So, for those involved in medical device applications, evaluate all cleaning agents, including biobased cleaning agents, used within your company and by your supply chain. In conclusion, many biobased cleaning agents have very desirable properties. Use them with understanding and intelligence.

Soy-Derived Cleaning Agents

Methyl soyate (CAS Registry Number 67784-80-9) is a soy-derived product that was developed as a biofuel and can be used for cleaning applications, and may prove to be a renewable resource alternative to hydrocarbon blends in general metal cleaning; it could also be used in blends or sequential solvent processes for critical applications (Wildes 2002). Methyl soyate is used alone and in co-solvent blends. It is produced by the esterification of soybean oil. Heated soy oil and methanol react in the presence of a catalyst to produce methyl ester and glycerin. The general reaction is indicated below. The ester and glycerin are separated, and the ester is purified using a water-wash process and filtration. Catalyst

$$C_3H_5(O_2CR)_3 + 3MeOH \xrightarrow{\text{catalyst}} 3MeO_2CR + C_3H_5(OH)_3$$

Triglyceride   Methyl alcohol   Methylsoyate ester   Glycerin (Soy-derived)
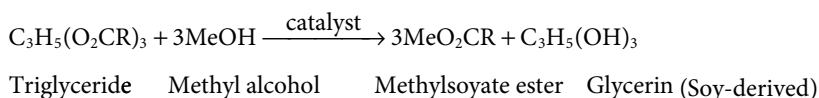
Neither OSHA nor ACGIH have established guidance for inhalation exposure to methyl soyate. Per a recent MSDS (AG Environmental Products, L.L.C. 2009), there is no OSHA PEL or ACGIH TLV. The manufacturer has indicated that exposure via inhalation is unlikely because of its low vapor pressure. However, exposure to aerosolized methyl soyate is possible and has not been well studied. While acute (very short-term) toxicity studies have been performed (United Soybean Board 2010), we have found no indication that long-term inhalation studies have been performed. It does have a high flashpoint, but care should be taken with heated baths to avoid potential problems with breakdown or oxidation products.

In terms of reactivity relative to ethane, methyl soyate is not VOC exempt according to the U.S. EPA, but it can be used in certain areas under certain state implementation plans. While the VOC content

is under 50 g/L (as estimated by EPA Method 24; ASTM D3960), for many cleaning applications, the VOC-exempt status is the one that matters. More pertinent to cleaning, for certain products, methyl soyate meets the requirements of the SCAQMD "Clean Air Solvents" (CAS) program; this program is not to be confused with the CAS system for uniquely identifying chemicals. Some products meet the CAS requirement because a technicality of the specific gas chromatography/mass spectrometry technique (SCAQMD 2004) results in some components not being picked up on the column and therefore not detected. Because the SCAQMD method has been accepted by the EPA as part of the SIP, to the best of my understanding and interpretation of the regulations, SCAQMD CAS solvents are treated as non-VOCs, either in SCAQMD or where SCAQMD regulations may have been cloned or adapted and where they may have been accepted by the Federal EPA (see Chapter 29, B. Kanegsberg, in *Handbook for Critical Cleaning: Applications, Processes, and Controls*). Where cleaning performance and/or regulatory characteristics are desirable, such a solvent could be rinsed with another lower-boiling, low-residue VOC-exempt solvent. The bottom line is that methyl soyate provides a possible option, even in areas of poor air quality.

Ethyl Lactate

Ethyl lactate (CAS Number 97-64-3), an ester produced from the fermentation of corn-derived feedstock, has also been considered for use as a cleaning agent along and in combination with methyl soyate (Henneberry 2000). It is produced from lactic acid, which is derived through the fermentation of cornstarch. It has been used periodically in cleaning for several decades.

D-Limonene and Alpha Pinene Blends

D-Limonene (citrus-derived) and alpha pinene (pine tree-derived) cleaning agents have been developed. Both have noticeable odors; both can leave appreciable residue, depending on the application, and must be rinsed completely. Both are VOCs. In practice, D-limonene-based cleaners have found more utility in critical cleaning applications (refer to Chapter 9, Gustafson). As with many esters, long-term inhalation exposure studies have not been completed.

Parachlorobenzotrifluoride

Parachlorobenzotrifluoride (PCBTF, CAS number 98-45-6) is a fairly aggressive solvent that has been used in cleaning agents, alone and in blends, as well as in coatings. It was commercialized and marketed in the United States by Occidental Chemical during the 1990s. PCBTF is VOC exempt. After fairly extensive testing, PCBTF processes have been developed for military and aerospace applications. Shortly before the first edition of *Handbook for Critical Cleaning* went to press, the manufacturer of the product exited the market. However, PCBTF from imported sources continues to be available and used. For additional information, refer to Chapter 10 (Skelly).

Volatile Methyl Siloxanes

The following is an excerpt from Cull and Swanson (2000)

A new class of fluid chemistry has been introduced to the precision- and industrial cleaning markets, based on linear and cyclic volatile methylsiloxane (VMS). The use of a silicone based cleaner may seem "counter-intuitive" to some people, since the low surface tension of silicone contamination has historically made it very difficult to remove. However, as a cleaning solvent the low surface tension becomes a definite asset, since it helps wet out and undercut soils. Drag-out is also reduced, because of the liquid's low viscosity. One of the keys to success with what appears at first to be an unlikely technology is the ability to manufacture VMS that dries with ultra-low non-volatile residue (NVR) so that it will evaporate completely, leaving behind a clean surface.

While VMS materials are new as cleaning solvents, they have been commercially available since the 1950s, primarily used as the building blocks for higher molecular weight, nonvolatile

silicone fluids and polymers. In addition, VMS fluids are widely used in the personal care industry, including many antiperspirant, hair care and skin care products. The majority of the personal care applications employ VMS materials with a *cyclic* structure, designated "cyclomethicones" by the Cosmetic Toiletry and Fragrance Association. In contrast, industrial- and precision cleaning fluids are made primarily with *linear* VMS fluids, which have a faster rate of evaporation and higher recommended exposure levels, but higher cost than the cyclics.

They are compatible with a variety of surfaces, and can be used on metals, glass, polycarbonate, acrylic and other plastics. With their low Kauri butanol (Kb) value, pure VMS fluids are not very aggressive cleaners, however, making them primarily effective on nonpolar contaminates like silicones, oils and light greases. Patented azeotropes have been developed that improve cleaning effectiveness on more difficult soils like rosin solder flux.

Linear, branched, and cyclic siloxanes are used in cleaning applications. Examples of linear and cyclic siloxanes are indicated in Figures 1.1 and 1.2. Volatile methyl siloxanes (VMS) are used in a variety of applications. Some physical properties are summarized in Table 1.6. As expected, on the basis of "like dissolves like," they can be used to remove silicone-based coatings. A patented blend has been used in electronics applications. They have been blended with parachlorobenzotrifluoride. In our experience, the siloxanes have greater solvency than might be expected based on the Kb value. Examples of unexpected solubility are illustrated in Chapter 7 (Dingess, Morford, and Shubkin). A recent NAVAIR study indicates that cyclic siloxanes may be useful as a replacement for mineral spirits in some military applications (Arafat 2009).
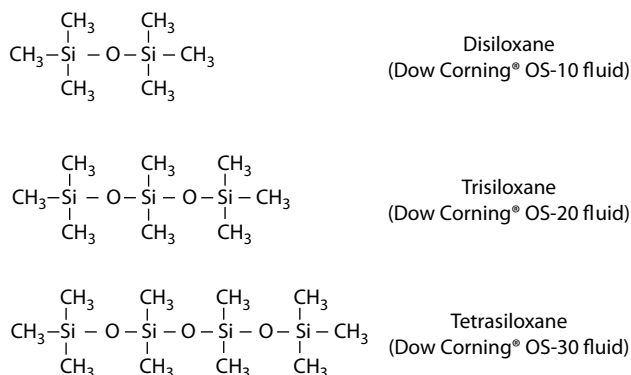
FIGURE 1.1 Chemical structure of linear VMS.
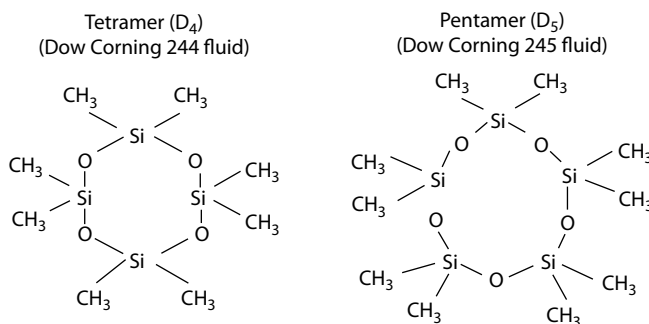
FIGURE 1.2 Cyclic VMS structure.

TABLE 1.6   Properties of Representative Methylsiloxanes

	Cyclotetra Siloxane	Cyclopenta Siloxane	Di-Siloxane	Tri-Siloxane	Tetra-Siloxane
Other names	Octamethyl-cyclotetra-siloxane, D4[a]	Decamethyl-cyclopenta-siloxane D5[a]	Hexa-methyldi-siloxane[b]	Octa-methyltri-siloxane[b]	Deca-methyl-tetra-siloxane[b]
CAS number	556-67-2	541-02-6	107-46-0	107-51-7	141-62-8
Flash point, closed cup (°C)	55	76	−3	34	57
Freezing point (°C)			−68	−82	−68
Boiling point (°C)	172	205	100	152	194
Evaporation rate (ASTM D 1901)	0.2		3.8	0.7	0.15
Viscosity, cSt at 25°C	2.5	4.2	0.65	1.0	1.5
Specific gravity at 25°C	0.953	0.956	0.76	0.82	0.85
Surface tension, dynes/cm at 25°C	17.8	18.0	15.2	16.5	17.3
Heat of vaporization, cal/g at 25°C	42	39	46 Estimated	44 Estimated	36 Estimated
Kauri-butanol value	14.5		16.6	15.1	13.4
VOC content, weight %	0	0	0	0	0

Source: Adapted from Cull, R.A. and Swanson, S.P., Volatile methylsiloxanes: Unexpected new solvent technology, in B. Kanegsberg and E. Kanegsberg (eds.), *Handbook for Critical Cleaning*, 1st edn., CRC Press, Boca Raton, FL, 2000.
   Dow Corning® designations OS-10, OS-20, OS-30.
   [a] Cyclic siloxanes.
   [b] Linear siloxanes.

VMS may be repackaged, blended, or sold under a commercial name. Therefore, it may not be readily apparent that the repackaged material is or contains a VMS. Determining where you have a VMS provides another illustration of the value of the CAS number. For example, in the NAVAIR study, three products were tested as a replacement for mineral spirits. Based on the MSDS, QSOL™ 300 is over 97% decamethylcyclopentasiloxane CAS number 541-02-6. Similarly, product literature indicates that Cyclo 147 F is primarily 541-01-6 (with another cyclic siloxane, CAS number 556-67-2). SB32 (apparently available through a VMS producer) is over 90% CAS number 541-02-6, with up to 5% mixed cyclosiloxanes (CAS number 69430-24-6).

Some of the VMS, particularly the cyclic VMS, have come under regulatory scrutiny, in part because they are marketed as alternatives for dry cleaning. Data have been provided by Dow Corning to the EPA (U.S. EPA 2009). While information received can be publicly accessed through EPA docket EPA-HQ-OPPT-2009-0180 and can be accessed online, the information is not presented in a form that is readily comprehensible to or digestible by me. Further, the EPA has not evaluated the data, and the timeframe for evaluating the data is not clear. Environment Canada has studied siloxanes extensively and has issued a summary report indicating that D4 and D5 do not pose a threat to human health; this appears to be based on the levels in personal care products. There is a proposal, not a regulation, that the levels of D4 and D5 in products be regulated to protect aquatic organisms (Environment Canada 2010).

Solvent Blends: Azeotropes, Co-Solvents

Aqueous additives are used for such purposes as improving wettability, solubilization and removal of soils, compensating for water quality, and forestalling corrosion. Solvents are blended for a number of reasons. Blends can blur the lines of demarcation among various categories of cleaning agents.

Stabilization

Water and acidity are the enemies of many halogenated solvents. Stabilizer packages are added to many chlorinated solvents (including TCA) and to *n*-propyl bromide (*n*PB) to prevent acid formation, breakdown, and reactivity with metals. Effective stabilization is important in degreasing (liquid/vapor cleaning). Stabilization becomes even more challenging in airtight and airless systems because the solvent is reused without replenishment over a much longer period than in traditional open-top degreasers. Stabilizers may be added to other solvents to prevent oxidation.

Extending the Solvency Range or Moderating the Solvency

Solvent blends can provide custom, fine-tuned cleaning options. Sometimes, blends provide surprises.

Azeotropes are strongly preferred over blends for vapor degreasing applications. An azeotrope is a constant-boiling mixture of two or more compounds. An extreme example of a non-azeotrope blend would be sugar in water. On heating, the water is boiled away, and the sugar remains. By contrast, IPA and cyclohexane form a constant boiling azeotrope. This means that the vapors contain both components in a constant proportion that does not change over the life of the blend. The cyclohexane/IPA azeotrope can be very useful in removing a range of ionic and nonionic soils from complex parts. Of course, it must be used in cleaning systems that are designed for low-flash-point solvents. Azeotropes have to be managed with care. Even azeotropes can vary in composition if they are used at a temperature not in the azeotropic range.

Blends that are not azeotropes will lose various components to evaporation at different rates. This means that the relative concentrations in the liquid and remaining blend will vary with time. Cleaning capability, compatibility, and flash point can all change. Blends that are not true azeotropes should be viewed cautiously, particularly in vapor degreasing applications.

In addition, azeotropes have been known to behave synergistically (non-additively) in terms of performance and compatibility. These properties are not necessarily predicted by solvency parameters. In other words, while two solvents may each show acceptable materials compatibility with a given component, the blend could produce component deformation. Therefore, even if you think you understand the solvency and compatibility issues of each component in an azeotrope, it is prudent to test the mixture.

Solvent blends are also used to modify or extend the solvency range in cold cleaning applications. An aggressive solvent can be toned down and a mild solvent made more aggressive. For example, HFE has been blended with *n*PB to tone down the aggressiveness of *n*PB. VMS may be blended with an alcohol or PCBTF to boost solvency.

Co-Solvents; Sequential Solvents, Bi-Solvent Process

The terminology of co-solvents is a bit confusing. Co-solvents have been thought of as two chemicals used in the same tank or used sequentially. Co-solvents are not necessarily miscible, so the cleaning process bath may require ongoing mixing or agitation. In one sense, any blended solvent could be thought of as a co-solvent system. Co-solvents can be blends that are primarily aqueous or primarily solvent. Supercritical or liquid CO_2 cleaning can also be accomplished with co-solvents; sometimes these are used in the same tank and at other times they are used sequentially. A patent for a process involving sequential solvents, termed a bi-solvent process, has also been described for cleaning precision components without VOCs (Mouser 2009).

Surfactants

Surfactants are used in solvent blends to provide some qualities similar to aqueous cleaners, to change emulsifying qualities and to allow the solvent to be readily rinsed in water (as in co-solvent processes). Some blended cleaning agents are offered as similar formulations, with or without the surfactant.

Emulsions: Macroemulsions, Structured Solvents, and Microemulsions

Oil and water do not mix, except in emulsions when they may coexist in a transient or relatively permanent form. An oil and vinegar salad dressing is typically a transient macroemulsion. Mayonnaise is a more permanent emulsion. Emulsifying qualities are used in aqueous blends, solvent blends, or both. In aqueous formulations, organic chemicals may be part of the mix only under certain conditions such as temperature. For example, the separation of the organic phase in an aqueous cleaner at the operating temperature may serve to defoam the blend, allowing for spray applications.

In the same way, immiscible organic chemicals may be used as emulsions, transient or permanent. Transient macroemulsions can be used to transfer the soil from one chemical to the other; the part is then rinsed in more of the chemical with very low solubility for the soil in question. Macroemulsions are typically cloudy. Sometimes one of the phases is aqueous; in other processes both are solvent.

Microemulsions, structured solvents, liquid crystals, or continuous phase emulsions have been introduced as cleaning agents. Structured solvents are stable mixtures of organic solvent, water, and coupling agents. The continuous phase may be solvent or water. They appear clear and may be primarily water or primarily solvent. Structured solvents can be made to separate during the application process. Such products are useful for mixed soils where both solvent and water-like characteristics are desirable (Shick 1996). Microemulsions are seen in consumer household products and in some single-use formulations for benchtop cleaning.

Mystery Mixes

Industry depends on mystery mixes. Blended solvents, particularly the high boiling blends involving hydrocarbons, esters, and nonlinear alcohols, greatly extend the specificity of cleaning that can be obtained. However, blended solvents can be particularly difficult for you, the components manufacturer, to evaluate. As with aqueous cleaning agents, many manufacturers consider the formulations to be highly proprietary and competition sensitive.

Many of the comments regarding mystery mixes apply to both aqueous and non-aqueous-based formulations. Improved performance and the desire on the part of formulators to maintain control of superior formulations have been in part responsible for the proliferation of mystery mixes. One additional observation is that a complex mixture where each chemical is used at a very low level could have the benefit to the cleaning agent producer of keeping the blend below the regulatory radar screen. Some areas of concern in using complex, mystery mixes include unexpected compatibility issues, regulatory constraints on one or more component, and unscheduled formulation changes. In such cases, it may be desirable to set up confidentiality agreements so that you understand the ingredients in detail. At the very least, particularly where the product is used in a process requiring high levels of validation and testing, it is prudent to obtain an agreement with the vendor that the product will not be changed.

In addition, supposed improvements in formulations can have unintended consequences. This author has observed many instances where a blended product was improved in such a manner as to adversely impact the process.

Ozone-Depleting Chemicals

CFC-113 and 1,1,1-Trichloroethane

CFC-113 and 1,1,1-TCA set the standards for cleaning for decades. CFC-113 has low to moderate solvency; TCA is an aggressive solvent. Both can be used for liquid/vapor phase degreasing. Both have high ozone depletion potentials; in the United States, they have been phased out of production. It is still possible to obtain recycled material, but at a high cost.

HCFC 141b

HCFC 141b (CAS no. 1717-00-6) has been phased out of production. Given the flashpoint-inerting properties, it has been widely used in aerosol cleaning agents, particularly where cleaning was needed near sources of ignition. While HCFC 141b is still available, we do not suggest using HCFC 141b blends; given worldwide distribution channels, we suggest that manufacturers be aware of what they are purchasing and that they test alternative cleaning agents.

Substitutes for HCFC 141b aerosols tend to be costly and/or to have other safety and/or environmental issues. Many manufacturers have switched to flammable blends for aerosol applications. Workers should be made aware of the chemical and flammability issues associated with such products.

HCFC 225

HCFC 225 is a versatile cleaning agent. The chemical was developed and marketed by Asahi Glass. It is typically sold as a mixture of two isomers, HCFC 225ca (3,3-dichloro-1,1,1,2,2-pentafluoropropane, CAS no. 422-56-0) and HCFC 225 cb (1,3-dichloro-1,1,2,2,3-pentafluoropropane, CAS no. 507-55-1). HCFC 225 has significant use in industrial cleaning, because of performance, overall environmental attributes, and worker exposure profile. HCFC 225 is the solvent with perhaps the closest properties to those of the late, lamented CFC-113 (Table 1.7).

One desirable attribute of HCFC 225 is that while it has some solvency for industrial soils, it can also be "fine-tuned" by blending to achieve the required solvency characteristics. Used neat, it is a mild to moderate solvent, much like CFC-113 (for those who recall manufacturing before the mid-1990s). HCFC 225 can also be blended with more aggressive organic solvents; stabilizers are also added. Examples of additives to increase solvency or performance include *trans*-1,2-dichloroethylene (*trans*), ethanol, and cyclohexane. Other blends include a proprietary surfactant, a proprietary fluorinated compound, and solvents at under 1%. Some but not all of the blends are azeotropes. Some blends are used as industrial process fluids as well as for critical cleaning.

TABLE 1.7 Comparative Attributes of HCFC-225 and CFC-113

	HCFC-225	CFC-113	CFC-113AES[a]
Boiling point (°C)	54	47.6	46.5
Freezing point (°C)	−131	−35	−41.8
Density (g/cm³)[b]	1.55	1.57	1.51[c]
Viscosity (cP)[b]	0.59	0.65	0.66
Surface tension (dyne/cm)[b]	16.2	17.3	18.5[c]
Latent heat of vaporization (cal/g,b.p.)	34.6	36.1	42.9
Relative evaporation rate (ether = 100)	90	123	120
Specific heat (cal/g,°C)[b]	0.24	0.229	0.272[c]
Solubility of water (wt%)[b]	0.031	0.109	0.25
Solubility in water (wt%)[b]	0.033	0.017	—
Flash point (°C)	None	None	None
KB value	31	31	39
ODP (CFC-11 = 1.0)	0.03	0.8	0.8
GWP (CO_2 = 1.0, 100 years)	370	5000	4800

Source: Adapted from Miki, T. et al., HCFC-225: Alternative precision and electronics cleaning technology, in *Handbook for Critical Cleaning*, 1st edn., CRC Press, Boca Raton, FL, 2000.

[a] Azeotrope of CFC-113 and ethanol.
[b] At 25°C.
[c] At 20°C.

The neat material and many of the blends do not have a flashpoint and have relatively favorable worker safety profiles. Asahi Glass Co. Ltd. has set an AEL (acceptable exposure level) of 100 ppm (8 h TWA) for the for the ca/cb mixture. The AELs for HCFC-225 ca and cb are 50 ppm and 400 ppm, respectively. Throughout the United States, HCFC 225 is exempt as a VOC, so it is favored for use in areas of poor air quality. Of course, the additives tend to be VOCs, and, since the blends may contain upward of 50% additive, it is important for manufacturers to evaluate blends in the context of allowable VOC emissions. It should be noted that a similar situation holds for many HFC and HFE blends.

HCFC 225 Phaseout

Unfortunately, because HCFC-225 depletes the stratospheric ozone layer, it is scheduled for global phaseout through the Montreal Protocol. In the United States, the Federal Clean Air Act calls for cessation of the use, sale, and production of HCFC-225 as of January 1, 2015 (EPA 2009). This might give pause to those using HCFC 225, particularly in the precision cleaning or critical cleaning of high value product.

This is an example of a situation where performance attributes must be balanced with the current and anticipated regulations. Cleaning protocols often require a substantial monetary and intellectual investment. With all of the pending regulations and discussions of regulations, in order to make informed, proactive decisions, it is important to understand exactly how manufacturers of critical components and products will be impacted.

It is helpful to clarify the meaning of "use" by the regulatory community (Kanegsberg 2010). Margaret Sheppard of the U.S. EPA's Stratospheric Protection Division explains that the EPA has interpreted the use ban to mean a ban on "use for manufacturing products." Sheppard explains that a solvent manufacturer or aerosol packager would no longer be able to use virgin material after December 31, 2014 to produce, for example, cleaning products. For more detailed information about EPA's interpretation of the regulations regarding HCFCs, the reader is welcome to peruse the 38-page document in the *Federal Register* (U.S. EPA 2009).

While users should be proactively looking at alternative processes, the door does not abruptly shut. The important point for those doing hard surface cleaning as part of manufacturing or repair is that end users could continue to use existing stocks of HCFC 225 that they have already purchased. Furthermore, the use of recycled HCFC 225 material is also allowed, either for end use or for use in the manufacturing of cleaning agents. This clarification should allow manufacturers to make informed, reasonable decisions about using HCFC 225 in current and impending projects. It also allows time to plan cleaning process changes.

Solvency and Physical Properties, Other Parameters

Kauri-Butanol Number

A number of solvency systems are described in Chapter 4 (Burke). In addition, other solvency systems are in use. One cloud-point test, the kauri-butanol (KB) number, is often alluded to. The KB number is determined by the volume of solvent required to produce a defined degree of turbidity when added to standard solutions of kauri resin in *n*-butyl alcohol. As a general rule, the higher the value, the stronger the solvent. The system was developed to indicate the relative solvent power of hydrocarbons, and it is not valid for oxygenated solvents. The KB number should be considered along with the boiling point, because, if the solvent can be heated to higher temperatures, more entropy is introduced into the system and better solvency occurs. Estimating solvency by mixing a cleaning agent with *t*-butyl alcohol and tree sap is a rather unsophisticated approach. However, the KB number remains widely used, and it is somewhat predictive of solvency (Kenyon 1995). Comparing the KB number with the Hansen system is somewhat analogous to comparing a black and white TV of the 1950s with a current, full-color, high-definition color broadcast. Table 1.8 lists the KB numbers and boiling points of several

TABLE 1.8 Kauri-Butanol (KB) Numbers and
Boiling Points of Representative Cleaning Agents

Cleaning Agent	KB Number	BP (°C)
CFC-113	32	48
1,1,1-TCA	124	74
HCFC 141b	56	32
Methylene chloride	136	40
Trichloroethylene	129	87
n-Propyl bromide	125	71
D-Limonene	68	150
PCBTF	64	139
HCFC-225	31	54
HFC 43-10	9	55
HFC 43-10 blend, including *trans*-1,2-dichloroethylene	30	37
HFE 569 sf 2	10	76
VMS OS-10	17	100

representative cleaning agents. You will notice that many cleaning agents with high KB numbers are no longer produced or are under severe regulatory distress.

Wetting Index

The wetting index has been used as a guideline to the ability of a cleaning agent to penetrate closely spaced components. The wetting index is directly proportional to the density and inversely proportional to the surface tension and viscosity. The higher the wetting index, the more readily can a cleaning agent penetrate closely spaced components. Dr. W.G. Kenyon has discussed the wetting index for many years. As he emphasizes, it is most useful as a teaching tool. In general, many of the vapor degreasing solvents have a high wetting index than do water or hydrocarbon blends. As with other indications, however, wetting index alone does not determine the efficacy of cleaning. While hydrophobic chemists could use the wetting index as evidence that aqueous cleaning "won't work," it is more constructive and realistic to explain that aqueous cleaning depends less on wetting and more on cleaning force. Of course, where residue is of concern on product with blind holes, when water is used as a rinsing agent, cleaning force, time, temperature, and fixturing must be carefully designed into the process. The wetting indices of a few common cleaning agents are provided in Table 1.9.

Other Physical Properties and Regulatory Issues

Other physical properties such as boiling point, flash point, and evaporation rate must be considered in choosing a solvent, and the solvent must be considered in the particular regulatory microclimate where the process is being carried out. Tables 1.10 and 1.11 list some physical properties and a few regulatory considerations of currently used, developmental, and phased-out, longed-for solvents.

Many solvents, including those that are VOC exempt, can be used in vapor phase cleaning applications. Those with low flash points, however, must be used in specially designed equipment. Such equipment has a high initial capital cost. Many solvents do not have a flash point but do have an upper explosion level (UEL) and a lower explosion level (LEL); this must be considered in specialized operations and in selecting and maintaining emission control equipment.

The boiling point must be high enough to allow efficient cleaning, but not so high as to damage materials of construction or slow the build cycle. A very high boiling point may preclude the use of the

TABLE 1.9 Examples of Wetting Index

Cleaning Agent	Density (g/cm³)	Surface Tension (dynes/cm)	Viscosity (cp)	Wetting Index
Generally desirable	High	Low	Low	High
CFC-113	1.48	27.4	0.70	121
TCA	1.32	25.9	0.79	65
IPA	0.785	21.7	2.4	15
nPB	1.33	25.9	0.49	105
HCFC-225	1.40	16.8	0.61	145
HFE 449 sl	1.52	14	0.6	181
Hydrocarbon blend	0.84	27	2.8	11
Water	0.997	72.8	1.00	14
Saponifier solution, 6% aqueous	0.998	29.7	1.08	31

TABLE 1.10 Physical Properties, VOC, ODC Status

Cleaning Agent, Comments	Boiling Point °C (°F)	Flash Point	UEL/LEL %	Evap. Rate (Ref. for Evap. Rate)
1,1,1-TCA, ODC, phased out	74 (165)	None	15/7.0	5 (buac = 1)
CFC-113 ODC, phased out	48 (118)	None (TOC)	NA	0.45 (buac = 1)
HCFC-141b, ODC, phased out	32 (90)	None	17.7/7.6	>1 (ether = 1)
Stoddard Solvent, typical (hydrocarbon blend) (VOC)	152 (305)	40.6 (106)	6.1/1/1	Hydrocarbon blend, VOC
n-Propyl bromide (VOC), worker exposure profile	71 (160)	None	8/3	4.5 (buac = 1)
Methylene chloride VOC exempt Hazardous air pollutant	40 (104)	NA	19/12	NA
Per-chloroethylene VOC exempt Hazardous air pollutant	121 (250)?	None (TCC)	none	2.1 (buac = 1)
HCFC 225 VOC exempt, ODC, impending phaseout	54 (130)	None	None	0.9 (ether = 1)
HFE 569 sf2 VOC exempt	76 (169)	None (TCC, TOC)	NA	
HFE 449s1 VOC exempt	61 (142)	None (TCC, TOC)	NA	
HFC 43–10mee VOC exempt	55 (131)	None (TOC)	NA	
Water	100 (212)	None	None	

Note: These data were obtained from various standard publicly available references, primarily MSDS from the Cornell University Program Design Construction Web site (http://msds.pdc.cornell.edu/ISSEARCH/MSDSsrch.htm), University of Vermont Web site, with some confirmation by Lange's *Handbook of Chemistry*, 13th edn. (McGraw-Hill, New York), and *Dangerous Properties of Industrial Materials*, 3rd edn. (N. Irving Sax, Reinhold Book Corp., New York). They should be used as guidelines only—the evaporation rate data in particular are prone to inconsistency among references). Boiling points rounded to nearest integer. Please confirm all information with current MSDS (buac = butyl acetate).

solvent in a standard vapor phase degreasing operation. The evaporation rate must be sufficiently rapid to allow rapid drying, but not so rapid that the solvent is immediately lost. These considerations are all relative to the operation in question.

Costs

Costs are relative. Cleaning is not a chemistry, it is a process. Costs are more than the price of the cleaning agent and the initial investment in capital equipment. The manufacturing community would

TABLE 1.11   Physical Properties, VOC, ODC Status of Low-Flash-Point Solvents

Cleaning Agent Comments	Boiling Point °C (°F)	Flash Point	UEL/LEL %	Evap. Rate (Ref. for Evap. Rate)
TBAC proposed VOC exempt	98 (208)	15 (59)	NA[a]/1.5	VOC exempt, with provisos
Para-chlorobenzo trifluoride VOC exempt	139 (282)	43 (109)	10.5/0.9	
Di-siloxane VMS VOC exempt	100 (212)	−3 (27)	18.6/1.25	Dow VMS OS-10
		TCC		3.8
Tri-siloxane VOC exempt	152 (306)	34 (94)	13.8/0.9	Dow VMS OS-20
		TCC		0.7
Cyclo-tetrasiloxane VOC exempt	205 (401)	76 (170)		Dow VMS OS-245
		TCC		Not calc.
Acetone VOC exempt	56 (134)	−20 (−4)	13/2.5	6

Note: These data were obtained from various standard publicly available references, primarily MSDS from the Cornell University Program Design Construction Web site (http://msds.pdc.cornell.edu/ISSEARCH/MSDSsrch.htm), University of Vermont Web site, with some confirmation by Lange's *Handbook of Chemistry*, 13th edn. (McGraw-Hill, New York), and *Dangerous Properties of Industrial Materials*, 3rd edn. (N. Irving Sax, Reinhold Book Corp., New York). They should be used as guidelines only—the evaporation rate data in particular are prone to inconsistency among references). Boiling points rounded to nearest integer. Please confirm all information with current MSDS (buac = butyl acetate).

   [a] Not available.

benefit from the availability of additional resources regarding cleaning costs. The efficiency of cleaning equipment and the impact on the manufacturing plant could be improved with better equipment insulation. In fact, environmental policy might benefit from a more holistic assessment of process impact. Extensive studies were performed a decade ago; the approaches hold true today (Kanegsberg 1999, 2000). Few solvents are inexpensive, particularly if total process costs are considered. To save money, invest in high-quality, well-designed cleaning processes, processes with excellent stewardship by your suppliers.

In terms of organic solvents, pound per pound, traditional solvents such as IPA, acetone, and the chlorinated solvents are relatively inexpensive. nPB and the VMS are moderately priced, and the engineered solvents (HCFC 225, HFEs, and HFCs) are the most costly.

Blended high boiling solvents can vary markedly in price. The costs may be perceived as high in applications where soil loading is a problem and frequent solvent change-out is required. With heavy soil loading, it may be more effective to perform initial cleaning in a relatively inexpensive product and then conduct subsequent steps in the more sophisticated cleaning agent.

Aqueous cleaning agents must be compared against each other in the intended application. Let us assume that two concentrates are under consideration and that one is twice as costly as the other. If the inexpensive cleaning concentrate must be used at a 1:4 dilution while the other provides equivalent performance at a 1:20 dilution, the picture changes (O'Neill 2000). Filtration markedly influences bath life and therefore modifies the overall cost of the cleaning agent.

How Not to Clean Critically with Household Products

This section was adapted from Kanegsberg (2007).

> For many manufacturers, setting up a cleaning process, even for critical product, involves a trip to the grocery store or home improvement center to purchase household detergent or liquid dish soap (Kanegsberg 2007). Or, it may involve a trip to the hardware store for containers of kerosene or some other "fix-it" blend. What's wrong with that? Especially if the process is working, why not let sleeping dogs lie?

Aqueous cleaning processes are most efficient when the appropriate chemistry for the soil and substrate (the part being cleaning) is selected. Solvents designed for the home maintenance or for hobbyists do not have to meet the exacting standards of industry; these include products based on organic chemicals such as mineral spirits or bio-based chemicals. In our experience, there have been too many instances of problems with build processes that could be traced directly to the use of consumer or household products Productivity decreases; costs increase. Sometimes, the problem chemistry was used during final assembly; in other cases, the problem occurred at a sub-vendor/supplier.

Household products are not optimized to critical and industrial cleaning. Many household products contain perfumes, colorants and lotions to make the product more pleasant to use. However, such additives can leave a thin, overall surface residue that interferes with subsequent processes like coating or deposition. Even with rinsing, additives can become trapped in the nooks and crannies of the product, leading to assembly problems, yield issues or unexpected, catastrophic product failure. Appropriate additives are added to industrial aqueous formulations; time should be invested in selecting products with additives most beneficial to your cleaning application.

Household cleaning products are sometimes selected on a "temporary" basis for prototype products because they are effective in a dip tank. However, they may not adapt well to an upgraded process. Even if you are using an immersion process bath, there can be problems with bath life in that dish soaps tend to hold soil in suspension. The high soil loading capacity of a consumer cleaning agent may lead to a false sense of security and mask bath degradation. The capacity for a degree of soil loading is necessary for practical cleaning processes. However, there can be too much of a good thing. Because consumer products typically hold soils in suspension, there can be problems related to soil overloading and redeposition. Even if a consumer product appears to be economical and the decision is made to use a dip-tank process bath, the costs of changing out the process bath, including labor time and costs to dispose of the spent cleaning agent.

In contrast, many industrial cleaning agents are designed as "oil-splitting" chemistries. That is, the chemistries are designed so that the oil pops up to the surface so that it can be removed leaving a clean process bath. Of course, if you currently clean in a simple immersion tank, when you switch to an oil-splitting chemistry, you may also need to modify the process so that you are not re-soiling product by dragging it through a layer of oil. The most efficient way to remove the oil involves a sparger or weir; this involves some investment in process equipment. If a high pressure spray, the appropriate defoamers must be present or unpleasant soapsuds will result. In addition some cleaning agents for critical applications are designed specifically for ultrasonics applications.

In choosing the cleaning for a given application, it is crucial to optimize relative to the material(s) being cleaned and the metalworking fluids and polishing compounds being used. Consumer cleaning agents are designed to remove typical consumer soils from typical household items. They are designed for cleaning dishes or perhaps for quickly wiping surfaces. Even if the product appears to remove soils effectively, it is important to evaluate the potential for substrate damage by testing the product with all of the materials of construction that will be exposed to the cleaning chemistry.

For critical cleaning, the cleaning agent must be well-defined and it must be consistent over time. For years, a dishwashing detergent was successfully used to clean critical aerospace subassemblies. Then, the word "improved" appeared on the label, a citrus scent was apparent and the cleaning process stopped working. In this actual "legend of aerospace," the contamination source was apparent. Sometimes, unannounced formulation changes are not so quickly identified; valuable time and product can be lost before a cause of the process failure is found. What if this happened to you? You might find another process; but if you had qualified the household cleaner with your customer such an emergency change might not be greeted kindly.

Try asking the supplier of a household, consumer cleaning agent for product support. We did, in the course of helping clients where household cleaners were enmeshed in in-house and supply chain

processes. We asked a number manufacturers of household cleaners used in industrial and critical cleaning applications and asked to speak with someone in the applications lab. For those products designed exclusively for household use, we were not put in contact with a chemist or product support specialist. After repeated conversations with company representatives who had not the foggiest notion about industrial and manufacturing processes, copious e-mail requests, an interminable amount of time spent on hold, and receipt of generous supplies of store coupons, some suppliers of household cleaning product either verbally or in a brief e-mail indicated that they declined to support the products for industrial assembly processes. There are a few "crossover" products. A few household cleaning agent manufacturers that also claim that their products can be used in industrial applications provide process and laboratory support. Occasionally, there is a genuine chemist to provide support. If you like a household product, they may be able to suggest a similar formulation that is better suited to industrial or critical cleaning applications. The above exercise is important for all cleaning chemistries, because the quality of support for products sold for critical and industrial applications varies.

Unfortunately, use of household products in critical cleaning applications is likely to be an ongoing problem for a number of reasons. The first is familiarity. If the dish soap removed last night's burnt-on dinner, it might seem reasonable to try it for burnt on lubricants. If it appears to work, assemblers continue to use it. There is the convenience factor. Particularly for small-scale processes, it may be easier to pick up a case of discount industrial cleaner at the "big box" store than to place an order with a distributor. Engineers may plan to worry about cleaning "later." Suddenly, it is time to validate or qualify the process; and the only tests have been run with non-industrial cleaners. We live in an age of advertising and most of us are probably responsive to publicity. Adverting appeals to our egos. In at least one instance, a cleaning agent was selected because it had the same name as the supervisor. We observed the power of the infomercial in the course of a comparison study of aqueous-based products for point of use or hand-wipe cleaning. One client was using a water-based spray cleaner that the operator had found on a late-night infomercial. We compared the product that supposedly worked with a number of other formulations and found it to perform at best marginally, even against the soils supplied by that client. The study was presented to the Joint Services Solvent Substitution Working Group (JS3WG) and is posted on their website (http://js3.ctc.com).

Other products have names that convey the concept of clean, or safe or ecologically-friendly. It is important to determine if the name is backed up by actual favorable safety or environmental attributes and if it performs acceptably in your application. In industrial applications there may be air and/or water regulations that impact use of the product. One individual commented that a consumer-oriented cleaning agent had grit to remove heavy soils from his fingernails, but left his hands soft. However, because industrial cleaning processes often involve heat, force and time, a consumer-oriented cleaning agent used in an industrial process cannot be considered immune to worker safety issues. Even if the product itself is biodegradable and kind to the earth, your process bath contains environmentally-unfriendly items like soils, polishing compounds and metal fines. In many cases, you cannot simply dispose of a process bath as if it were a dishpan. Finally, even if the dish soap does not damage your dishes and leaves your hands silky-smooth, even if it is totally organic and contains no hazardous ingredients, it may damage the product. You may not see the damage, but your customer could see an increase in defects.

A household product may be added when other parts of the build process change. All cleaning processes, particularly aqueous processes, have to be optimized to the total build process. If any factors change, for example a lubricant, the cleaning process may have to be modified. If the process is not working properly, and if the response from management is not rapid enough, it is very tempting to try a "patchwork" quick-fix from the local hardware store. If it seems to improve matters (at least visually), the product becomes an informal part of the process, but probably a poorly-controlled part of the process.

Do not let sleeping dogs lie, but wake them gently. Do *not* wait for a problem to arise. Review the written documentation. We have observed consumer products that are immortalized in aerospace documentation for critical assemblies—the documents often date back a generation or so. Next, and this is even more important, actually tour the fabrication areas. If you are a final assembler and use sub-vendor suppliers for part of the assembly and/or cleaning, contact them and perform a site visit there, too. If you find consumer-oriented cleaning products, flag those products, noting the brand, supplier, source and contact information. Then, contact the manufacturer or supplier and determine the level of technical support. If product support is not available, make plans to change the process. However, it is generally counterproductive to simply mandate immediate changes unless there is an urgent process or yield problem or a compliance issue. It is more effective to work with the technicians, the operators and the assemblers to determine why the consumer product was introduced. Rather than placing blame (which makes people avoid fixing the problem), this approach can provide invaluable information as to what is actually needed to achieve critical cleaning and contamination control. Only then should you evaluate cleaning agents designed for industrial and critical cleaning and find more supportive suppliers.

How to Choose a Cleaning Agent

One of the problems in developing a manufacturing process is the rather daunting list of considerations and provisos. To cope with the problem, there is the tendency to think linearly and to attempt to find the perfect cleaning agent. There is no perfect cleaning agent. However, we persist in our search for unattainable perfection.

All too often, when a cleaning process is being developed, a cleaning agent selection committee is established to screen out all undesirable applicants. The safety/environmental group is likely to rule out any environmentally challenged cleaning agent, even if it could be used in a non-emissive manner. Company management and sometimes the customer may submit a series of "don't" lists. Whole classes of cleaning agents may be ruled out as being unacceptable on general environmental principles. The materials and process chemists may insist that for any cleaning agent to be considered, it should be able to be in contact with all materials of construction at some elevated temperature for, let's say, 24 h. The purchasing department may insist that only one or two cleaning agents be selected - period. The manufacturing engineers may insist on an extremely rapid process time, instant drying, and aqueous cleaning. What is left? Sometimes nothing; sometimes a class of cleaning agents which is totally unsuited to the cleaning application at hand.

Perfection aside, for nearly every cleaning application, there are several workable solutions. Some of the considerations in cleaning agent selection are indicated in Table 1.12. The cleaning agent has to be considered in the context of the cleaning process and, indeed, in the context of the overall manufacturing process. The factors indicated in Table 1.12 are meant to provide a starting point. It usually becomes very apparent which factors are the most important in a given manufacturing situation.

It is more productive to proceed with a nonlinear approach that considers performance, costs, cleaning agent, cleaning equipment, suitability to the workforce, worker safety, and the local regulatory microclimate.

Cleaning is a process, not a chemical. The landscape of available cleaning agents and processes varies as advances in technology, requirements of build processes, and regulatory drivers change the perceived appeal of various options, because the assortment of products will inevitably change. To achieve ongoing, successful critical cleaning, our best advice is to develop an appreciation not just of the specific cleaning agents, but of the underlying, commonsense approaches to successful cleaning and contamination control.

TABLE 1.12 Overall Considerations in Choosing Cleaning Agents

Factor	Process Consideration
Cleaning properties	Cleaning requirements, your process (how clean is clean enough)
	Performance under actual process conditions
Cleaning performance	Solubility characteristics relative to soil of interest
	Wetting ability
	Boiling point
	Evaporation rate
	Soil loading capacity
	Ability to be filtered
	Ability to be redistilled
Materials compatibility	Compatibility under actual process conditions (temperature, time of exposure)
	Product deformation at cleaning, rinsing, drying temperatures
Residue	Nonvolatile residue (NVR) level
	Rinsing requirement
	Process time impact
Cycle time	Cleaning
	Rinsing
	Drying
	Product cool-down
	Component fixturing
	Loading and unloading equipment
	Product rework
Cleaning equipment	Suitability with current cleaning equipment
	Ability, costs of retrofit
	Costs of new cleaning equipment
	Auxiliary equipment required
	Maintenance, repair
	Automation, component handling
	Footprint (length, width, height)
	Equipment weight
	Component fixturing
Flash point	Choice of cleaning equipment
	Process control
	Control of proximal processes, activities
	Choice of auxiliary equipment
	Choice of emissions control
Toxicity	Acute
	Long term
	Anticipated exposure under process conditions (including sprays, mists)
	Employee monitoring
	Inhalation
	Skin adsorption
Worker acceptance	Method of application
	Drying speed
	Similarity to current process
	Automation
	Computer skills
	Perceived loss of control of process
	Odor
Cleaning agent management	Water preparation
	In-process filtration (water, organic, or aqueous cleaning agent)
	Waste water disposal
	On-board redistillation

TABLE 1.12 (continued)   Overall Considerations in Choosing Cleaning Agents

Factor	Process Consideration
Regulatory, air	Global, national, local (ODC, VOC, HAPs, GWP)
	Neighborhood concerns
	Environmental justice issues
	Production phase-out
	Usage bans
	Disposal of waste stream
Regulatory, water	Global, national, local
	Disposal of waste streams
Company, customer, product performance requirements	Contractual requirements, restrictions
	Company policy
	Testing, acceptance qualification required
	In-house safety, environmental policy
	Insurance company issues
Costs	Cleaning agent
	Cleaning agent preparation and disposal
	Costs as used (dilution)
	Capital equipment
	Disposables
	Sample handling
	Total process time
	Rework
	Insurance
	Regulatory permitting
	Process qualification
	Employee education, training
	Process monitoring
Supplier stewardship, cleaning equipment supplier	Responsive distribution, supplier
	Supportive technical staff
	Clear, understandable MSDS
	Provides required technical information
	Provides required regulatory information
	Supports process development

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Aqueous Cleaning Essentials

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Introduction

While aqueous cleaning is almost as old as man, industrial parts manufacturers and cleaners have long held the view that certain soils could only be cleaned adequately by non-aqueous methods. Starting in the 1970s, many environmental initiatives forced the industry to look at aqueous cleaning as an ecologically more responsible alternative to vapor degreasing and other solvent cleaning methods. As a result many, cleaning applications that were once strictly the province of non-aqueous cleaning methods are now being done quite successfully with aqueous processes. The following discussion serves as a brief primer on the many aspects and considerations needed to successfully understand the art of aqueous cleaning in the manufacturing environment.

Cleaning Overview

With few exceptions, there are certain principles treated generally here that apply to all types of cleaning.[4] Cleaning processes combine mechanical, thermal, and chemical energy sources to remove a soil from a substrate. The total energy needed is the sum of these energy sources over a given period. Within these parameters, the following general guidelines apply:

1. Cleaning efficacy and rate improve as temperature increases.
2. Agitation improves the rate and efficacy of soil removal. Agitation provides mechanical energy to physically remove soils and ensures that fresh cleaner will continuously contact the soil.
3. Cleaner solutions generally have a performance-versus-concentration curve. A minimum level of cleaner is generally necessary for effective cleaning. Cleaning improves with incremental increases in concentration up to some point after which further increases result in little or no further improvement in performance.
4. Removing soil requires a finite amount of time to apply the necessary energy to accomplish the task. There are four primary factors that govern the total energy that can be applied in a cleaning process: (1) cleaner concentration, (2) mechanical agitation, (3) temperature, and (4) time. The general expression for how these factors work together is

   $$\text{Cleaning energy} = \text{Cleaner concentration} \times \text{mechanical agitation} \times \text{temperature} \times \text{time}$$

   If one of the factors decreases, one or more of the others have to increase in order to maintain performance. Certain limitations may apply; for example, high cleaner concentration can lead to diminishing returns and increased costs. Cleaning performance response is not linear as a function of concentration and excessive cleaner concentration can create problems in the following rinse steps. Mechanical agitation is usually a fixed property that cannot be changed on most cleaning equipment. Temperature can be raised up to a point but too much temperature may damage the parts and cause excessive water consumption due to the increased evaporation rate. The ability to increase the time parameter is limited by the substrate's resistance to corrosion under the cleaning conditions and the required parts throughput rate for the system. For most cleaning applications, it is relatively easy to meet the necessary energy input to obtain the required cleanliness, but there are also some very challenging applications that are difficult or impossible to clean. In some cases, solvent cleaning is still the more appropriate cleaning method to use.
5. Rinsing is necessary to remove any cleaner or soil residue remaining on the parts after washing:
   a. Rinse type and quality is dependent on the cleanliness requirements of the application.
   b. Multiple small rinses are generally more efficient and cost effective than one large rinse.
   c. An agitated rinse is more effective than a still rinse.
   d. Final part cleanliness or conversely residue on the part is limited by rinse quality.
6. Soil must be prevented from redepositing on parts. The most obvious answer is to stop the soils from contacting the substrate after initial removal. Soil removal may be accomplished by using cleaners that include one or more of these methods:
   a. Emulsification
   b. Emulsification followed by demulsification
   c. Deflocculation
   d. Displacement
   e. Saponification
   f. Sequestration
   g. Wetting
   Additionally, redeposition can be controlled by
   a. Microfiltration
   b. Oil skimming and coalescing

    c. Using cleaning tanks of sufficient size to disperse the soil and slow the rate of increase of contamination concentration

7. The cleaning method or solution should not harm the item (substrate) being cleaned.
8. Precleaning to remove bulk soils may be an economical and common sense way to increase overall cleaner life.
9. Cleaning systems should be designed as a unit. That is, the cleaner and the cleaning equipment should be chosen to work together and address the particular cleaning application. Typical concerns that should be addressed include
   a. Cleaning temperature and its effect on the cleaner and the substrates. Some considerations include method of heating, insulation, and evaporation.
   b. Equipment design should include an evaluation of cleaner and part compatibility with regard to materials of construction, economy of operation, electrochemistry, OSHA and other regulatory guidelines, and ease of service.
   c. The suitability of the mechanical energy input must be addressed in terms of effectiveness of removing soil from the substrate, controlling foaming tendencies of the cleaner, avoiding mechanical damage to the parts, and avoiding degradation of the cleaner.

Aqueous cleaners can generally be categorized as being acidic, alkaline, or pH neutral. Alkaline cleaners are by far the most predominant of the three and are used in all commercial/industrial cleaning applications. Thus, this discussion will mainly cover alkaline cleaning but the principles will be applicable to all types of cleaners.

Agitation techniques represent the greatest variation in cleaning methods. The most important factor is that it costs money in equipment and/or labor to provide high levels of agitation. The equipment must be designed to meet the objective of providing adequate-to-superior agitation for soil removal at the lowest cost. The major limitations for providing adequate agitation are equipment costs, equipment size (i.e., how big of a "footprint" the equipment makes), excessive foam generation, excessive generation of mist/spray, toxic vapors, and the creation of flammable/combustible gases.

Now that we have taken a broad look at some cleaning principles, let us look a little more closely at each.

Cleaning Parameters

Temperature

The majority of industrial cleaning is carried out at 140°F–180°F. The effect of temperature depends on the type of soil being removed and the specific cleaner. The first consideration is what type of soil needs to be removed. Temperature is very important in speeding the removal of fats, greases, oils, and waxes. Increased temperature reduces the viscosity of oils and greases, making them more mobile and therefore easier to displace from the substrate. Fats and waxes are often solids at room temperature. It is critical to melt these fats and waxes in order to remove them by aqueous methods. If the melt range of the fat/wax is above the boiling point of the cleaner, aqueous cleaning will not be effective on these soils; solvents must be used instead.

There is a well-established principle that the rate of a chemical reaction is doubled for each 10°C (18°F) increase in temperature. If the cleaning process works by reaction between a fatty acid/oil and alkali, by a paint coating undergoing chemical decomposition, or by an acid chemically removing rust and scale, then this reaction rate relationship is applicable. It is possible to remove solid fats/waxes if they can chemically react with the cleaner without melting them first but the rate of removal is often too slow for manufacturing applications.

On the other hand, excessively high temperatures could "set" proteinaceous soils or may cause an undesirable reaction between the soil and the substrate, resulting in the soil becoming more difficult to remove. Just as increasing temperature will increase the rate of cleaning, it will increase the rate of

undesired reactions as well. Most corrosion inhibitors work by forming a loose barrier on the clean metal surface. Excessively high temperatures can disrupt this barrier and result in chemical attack, usually seen as discoloration and etching.

Agitation

As has been previously stated, agitation techniques represent the greatest variation in aqueous cleaning techniques. It is usually possible to find an aqueous cleaner to remove a soil from a substrate. One of the biggest problems users run into is inadequate cleaning performance due to inadequate or improper choice of agitation. The method of agitation should be matched to the size and shape of the part. For example, while spray washing may be very effective for cleaning large relatively flat parts, it is usually not suitable for parts with blind holes where direct impingement is problematic. Relatively flat objects and components that do not have hidden areas can be cleaned by immersion or spray wash. Parts that are very large or very small often cannot be cleaned effectively by spray wash. An exception on small parts is possible if specialty mounting racks can be built. Spray wash cleaning is also limited on the chemical side because the formula must not create excessive foam. Eliminating foam restricts the choices of raw materials a chemist can use in formulating a spray wash cleaner.

Parts that can be damaged from spray impingement should instead be cleaned by immersion. Virtually all parts can be cleaned by immersion. Ultrasonic cleaning is the most effective method of agitation for immersion cleaning. Ultrasonic cleaning is restricted by cost (comparatively expensive equipment) and size. (Ultrasonics are not as effective on tanks above approximately 1000 gal capacity.)

Spray under immersion, oscillating lifts, and turbulation are the next most effective methods of immersion agitation. Combining an oscillating lift with ultrasonics provides superior agitation and works well on removing highly viscous soils such as wheel bearing greases found in automotive repair applications.

Chamber-type cleaning units, commonly called "cellular" or "cell systems," allow the use of a combination of agitation techniques. In cell systems, parts are cleaned in a basket that resides in a chamber. The chamber is first subjected to spray washing until the basket is completely immersed. The chamber is then agitated ultrasonically and then drained. The parts are then rinsed using spray followed by ultrasonics agitation. Cell systems may even incorporate basket rotation in the wash and rinse cycles. The three agitation methods can sometimes create excessive foam if care is not taken in choosing a cleaner.

While air-sparging can be very effective at agitating an aqueous cleaner, there are several provisos:

1. The cleaner must be a low-to-non-foaming product. Air-sparging will cause foam to overflow the tank. Only cleaners designed for continuous spray washing should be used with this form of agitation.
2. The popping of the bubbles formed by air-sparging generates mist and spray that may create an exposure problem for workers. Aerosol mists generated from using air-sparging on alkaline derusters are very corrosive and must not be inhaled or get in the worker's eyes! Some approaches to addressing worker exposure to mists and sprays include covering the tank, installing aggressive exhaust ventilation to remove the mist and spray, or placing the tank within a cabinet to contain the mist/spray. However, it is usually impractical to put a cover on most immersion tanks due to the mechanics of opening and closing the cover during parts transfer in the cleaning cycle. Adding aggressive exhaust ventilation increases the cost of the cleaning system and may affect temperature stability in the work environment. Enclosing the system in a cabinet increases the cost of the cleaning system and will likely increase the "footprint."
3. Air-sparging can shorten the life of alkaline cleaners by neutralization with carbon dioxide (CO_2). Carbon dioxide is a weak acid. Acids and bases neutralize each other when combined. Even though CO_2 makes up only a fraction of a percent of the atmosphere (0.035% measured at Mona Loa Observatory, 1990, as reported in *Handbook of Chemistry and Physics*, 1996)[20], over time, the large volume of air passing through the tank results in exposure of the cleaner

to a significant amount of CO_2. The CO_2 neutralizes the alkaline builders, especially sodium or potassium hydroxide. The CO_2 reacts with free hydroxide ions (OH^-, the cause of alkaline pH) to form bicarbonate ions:

$$CO_2 + OH^- \rightarrow HCO_3^-$$
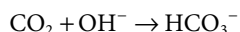
The bicarbonate then goes on to react with more hydroxide ions to form a carbonate ion and water:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
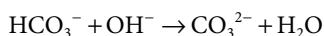
As the hydroxide ions (OH^-) are consumed, the pH of the cleaner decreases. Heavy-duty caustic cleaners are especially prone to this problem whereas mildly alkaline cleaners are much less sensitive. Acidic and pH-neutral cleaners are not affected by this problem.

General agitation from pump circulation can be adequate for noncritical cleaning applications, but it is not usually suitable for precision cleaning. Finally, soaking the substrate in a stagnant tank is unacceptable, even for noncritical cleaning applications.

Concentration

Concentration, also called use-dilution, can affect multiple attributes of the cleaning process. In many cases, minimum or maximum cleaner concentrations impact corrosion characteristics, chemical etching, or the deposition of protective barriers as well as cleaning efficacy. The required cleaner concentration depends on the type of agitation and temperature. As an example, in the absence of foaming problems, it may be possible to obtain similar cleaning performance from the same alkaline cleaner at 5%–10% by immersion, 3%–5% by spray, 1%–3% by steam cleaning or high-pressure hot spray, or 2%–4% in a high-pressure room temperature spray. For each of these applications, increasing the cleaner concentration provides better cleaning performance up to a certain point and then levels off. The leveling-off point is dependent on the specific chemistry used in the cleaner, the soil being removed, the agitation technique, and the temperature.

Time Required for Cleaning

It is important to emphasize that cleaning is not instantaneous; some time is required for the cleaner to perform its work on the soil. As with the leveling-off point, the cleaning time depends on the concentration of the cleaner, the specific chemistry used in the cleaner, the soil being removed, the agitation technique, and temperature. In a stagnant bath, cleaning may take between 5 min to over an hour to occur, if cleaning occurs at all.

In agitated systems, most immersion cleaning times do not exceed 10 min, although numerous exceptions can be found. Spray washes typically take no more than 5 min.

One general rule of thumb does exist for ultrasonic cleaning; if it takes more than 5 min to clean, either there is something deficient in the cleaner or the process itself is not suited for the application.

One notable exception to the 5 min rule for ultrasonics is the cleaning of used automobile cylinder heads and other major engine components. Many automobile repair facilities have adopted ultrasonic processes as an alternative to heavy-duty caustic or solvent cleaning tanks. Heavy-duty caustic tanks have fallen out of favor because they cannot be used on aluminum parts; nearly all major engine parts are now made of aluminum. Corrosion hazards and waste disposal considerations also have contributed to the decline of the caustic stripping tank. Solvents have been on the decline mainly due to environmental regulations that govern volatile organic content (VOCs), ozone-depleting substances (ODS), and hazardous air pollutants (HAPs). The few solvents (chlorinated solvents and cresylic acids) that are effective on baked-on soils also pose serious health risks. Ultrasonic cleaning with highly concentrated,

moderately alkaline cleaners has been found to be effective at removing most of the baked-on soils. The drawbacks include long processing times (often 15–45 min) and some cavitational erosion. Cavitational erosion occurs with softer metals (mainly aluminum) and typically appears as a "star- or Y-shaped" pattern on the surface.

It must be stressed that the time available for cleaning is very closely related to the economics of the cleaning operation. The increased cost in equipment, energy, and chemicals to reduce time must be weighed against the economic gains in increased production rates. Additionally, consideration must be given to effects on reject rates and customer satisfaction.

Rinsing

No matter what cleaning method has been employed, the surface of the freshly cleaned part contains some soil and cleaner residue. In some situations, the residue may present no problem, but in many others, the residue must be removed to yield acceptable parts.

The value of pressure sprays and mechanical action in rinsing is often neglected in general parts' cleaning applications. In our experience, direct spraying is far more effective in flushing away the loosened soil than just soaking the part in a stagnant immersion tank. Static or slow-moving rinses in which there is improper/inadequate flow usually results in parts that must be recleaned or discarded. The use of a short spray rinse followed by an agitated immersion rinse is very effective at reducing residue.

The number of rinses performed is an important factor affecting final parts' cleanliness; two rinse steps are more effective than one, three are better than two, etc. Multiple rinses can be of shorter individual duration and still be more effective than a single rinse due to the exponential dilution of contaminants as the parts proceed from one rinse to the next.

Another important consideration is the quality of water used in the rinse step. The quality of rinsing can only be as good as the quality of water used in the last rinse. Unsoftened water obtained from a municipal source or well contains varying levels of hard water ions, carbonates, phosphates, sulfates, and organic by-products from treatment processes. The water hardness can often be extremely high, leading to hard water deposits and soap scum residue. Softening the water to remove hard water ions (calcium, iron, magnesium, and manganese) will eliminate those hard water salts but may still leave other impurities and therefore may not be adequate. Using deionized, distilled, or reverse osmosis (RO) purity water gives the best rinsing performance. As expected, as the quality of water required for the application goes up, so does the cost. The level of water quality must meet the requirements of the application. The application requirements must be evaluated for each system.

It is possible to equip the multistage rinse with a set of deionizing resin beds and an activated carbon filter. Closing the rinsing loop by deionizing the overflow water can reduce water consumption, replacing only the water lost to evaporation. Users with significant wastewater disposal costs should consider a closed loop setup.[3,4]

Redeposition

The design of the tank and cleaner is an important factor in reducing/eliminating redeposition of soils. The tank must be of sufficient capacity to provide room for the soils to move away from the parts. The size is also important to moderate the rate at which soil loading increases; too small of a tank can result in the cleaner becoming saturated in a matter of hours or days. Bag filters can be used to remove gross particulate matter. The cleaner may incorporate phosphates, silicates, specialty surfactants, and synthetic polymers which remove and suspend soils in solution. The use of aqueous cleaners that can "split out" oils instead of emulsifying them in combination with an oil coalescer/skimmer slows down and possibly even prevents the soil from reaching a saturated condition in the cleaner. Oil splitting followed by physical removal results in longer bath life and minimizes soil redeposition. Self-emulsifying oils cannot be removed by oil skimmers/coalescers; they can only be removed by microfiltration.

A good rinse must always follow the cleaning step to prevent soil redeposition. Waxes typically require a hot rinse to prevent resolidification on the clean surface.

Protecting the Substrate

The cleaner must be compatible with the substrate. The cleaner must not discolor, etch, or otherwise damage the substrate, unless these side effects are desirable in a specific application. Thus, the cleaner must contain additives to protect the substrate from these effects. Good rinsing, careful drying, or use of inhibitors may be necessary to avoid tarnishing. Transfer time between cleaning and rinsing tanks should be minimized to avoid drying of cleaner residue on the substrate, especially with silicate-based cleaners. If silicates are allowed to dry on a part, the residue is very difficult to remove without resorting to use of acid fluoride cleaners or scraping/sanding. The dried silicate residue can turn from a corrosion inhibitor to a corrosion promoter on some metals if it is allowed to remain on the part for too long.

Controlling the Cleaning Line and Monitoring the Cleaner

It is necessary to determine when the cleaner is nearly exhausted so that fresh cleaner can be prepared or the old cleaner can be rejuvenated; this is not always easy. Measuring properties such as alkalinity, conductivity, and pH are useful in determining the state of the cleaner but it is not uncommon for tanks to fail even when the above-mentioned test results are within normal tolerance. The properties that should be measured are those that are critical to the specific process. For example, silicate-based aluminum cleaners should be monitored mainly for pH; silicate testing should also be done if affordable. Silicates protect aluminum from corrosion and they participate in soil anti-redeposition. The problem with silicates is that their solubility in water decreases as the pH drops in the cleaner. At some point, the silicate level will drop below the minimum level necessary to protect aluminum. When this happens, spotting or etching may occur.

Heavy-duty caustic cleaners are best monitored by active and total alkalinity titration or by conductivity. Acid cleaners are best monitored by total acidity titration or by conductivity.

Cleaners that undergo microfiltration to remove emulsified oils present the greatest difficulty in monitoring. The pH may need to be monitored if they contain silicates. Alkalinity titration is useful but it does not detect many of the surfactants that are stripped out by the microfiltration process. The emulsified oils may contain ingredients that severely impact the pH and skew the alkalinity titration. Monitoring the refractive index, how much the solution bends light, can help in tracking loss of cleaner due to stripping by the microfilter. Unfortunately, refractive index requires that the solution be relatively clear; cloudy solutions are difficult or even impossible to measure.

Some tanks are so difficult to maintain that the user must enlist the assistance of a chemical management firm or change some of the manufacturing processes that precede the cleaning step.

Improving Bath Life

Great strides have been made that allow some aqueous baths to last for several years with periodic replenishment. However, cooperation between chemical and equipment manufacturers as well as industrial end users is critical to achieving this result.

One way of improving bath life is to have two cleaning tanks in series. Most of the soil is removed in the first tank. The parts going into the second tank are relatively clean. After the first tank becomes heavily contaminated, it can be discarded and the cleaner in the second tank pumped over to the first tank. In this manner, the cleaners can be used for long periods. With careful management, it is possible to continue operating the first bath with very high contamination levels that would require replacing the bath if only one wash tank was employed.

The contamination of the second tank can be reduced by employing a short rinse after the first cleaning operation; the rinsing water either goes to sewer or back to the first tank. Besides better performance and economy, this procedure may be necessitated or modified by governmental regulation of effluent that prohibits or limits the discarding of cleaning baths.

The single biggest problem in obtaining long tank life is understanding that cleaning is part of the overall manufacturing process and must be evaluated as part of the whole. The design of the cleaning process must consider the soils and their effects not only on processing but also on disposal. The choice of cleaning equipment and cleaner should be made as a coordinated effort that takes into account soil removal from the part and from the bath. These choices must also take into consideration the ultimate costs of operation, including the costs of disposal. It is in this area that chemical and equipment manufacturers and their customers most often fail.

The best example of failure to design a process from beginning to end is using self-emulsifying oils in a machining step and then expecting long tank life from the aqueous cleaner. Self-emulsifying oils are easy to remove from the parts but usually cannot be removed from the cleaning tank by oil coalescers/skimmers. Self-emulsifying oils contain their own detergents that form very stable emulsions. The emulsions formed by self-emulsifying oils cannot be broken by the aqueous cleaner without destroying the cleaner at the same time. Thus, the emulsions build up in the tank and eventually lead to soil redeposition problems.

Microfiltration in the 0.1–0.5 μm pore size range can remove self-emulsified oils; the equipment is expensive; it is not a simple "turnkey" process; and some chemical add-back is needed to replenish cleaner that is removed in the filtration process.

While the microfilter will remove nearly all of the emulsion, typically >90% reduction per turnover, the cleaner must be designed to pass through the filter. Only immersion cleaners that are operating at temperatures significantly below their cloud points can be processed through a microfilter in an economical manner. The *cloud point* is the temperature at which the surfactants become insoluble and the cleaner turns from clear to cloudy/turbid. Most spray wash cleaners cannot be microfiltered because their surfactants purposely become partially insoluble in water to control the foam. When a spray wash cleaner reaches its cloud point, the surfactants form aggregates that are too big to pass through the filter. In microfiltration of spray wash cleaners, surfactant stripping rates of >90% per turnover are common. Therefore, the microfiltered spray wash cleaner is no longer able to clean and control foam. Generally, it is not cost-effective to use chemical additives to maintain a spray wash cleaner in a microfiltration operation.

Microfiltration has been successfully used with immersion cleaners; but there will still be some stripping of surfactants, typically 5%–30% per turnover on properly formulated cleaners. Monitoring and adjusting a microfiltered immersion tank can be difficult and may not be an economically viable option.

Similarly, ultrafiltration (pore sizes below 0.1 μm) is not recommended because the stripping rate of cleaner components becomes too aggressive regardless of the cloud point. It is not cost effective to offset additive losses through add-back packages.

The ideal manufacturing process uses straight oils (non-emulsifying) which can be split out of solution by the cleaner and then isolated through coalescing/skimming. Unfortunately, many machining processes require the use of self-emulsifying oils to extend tool life due to the excellent heat dissipating property of water. If the overall process cannot sacrifice the use of self-emulsifying lubricants and the soil loading rate of the cleaning tank is high, then tank life will be short (possibly only several hours to 1 week at most). Very short tank life increases overhead due to the increased down time for recharging the tank and increased disposal costs. Incorporation of a crude precleaning tank/spray wash to remove the bulk of self-emulsified oil residue will significantly extend the life of the main wash tank. Manufacturers should review their overall process and find ways to minimize the use of self-emulsifying oils when possible.

Another good example of failure in designing a process for long bath life is choosing to use hard water to charge and replenish the wash tank. Most aqueous cleaners are formulated with some hard water tolerance. However, over time, water must be added to the tank to replenish losses due to evaporation. The problem is that while the water evaporates off, the hard water ions remain in the tank. As more

hard water is added to the tank, the hard water ions will build up and eventually overwhelm the built-in tolerance of the cleaner. Once this occurs, problems such as soap scum formation and deposits on the parts and in the tank arise. The cleaning solution must be discarded when this occurs. If the problem is allowed to continue, scale formation will build up. Scale results in increased costs to heat the tank (the scale is an insulator) and eventual burnout of the electrical heating elements.

Water

For most aqueous cleaners, water comprises 80%–99% of the cleaning solution and is used in practically all rinsing steps. Although most people do not think of it in this way, water is actually a solvent in aqueous cleaners. A major key to understanding the efficacy of aqueous cleaners lies in the role played by water, its natural properties, and impurities.

Water has been vital to man and nature since the beginning of time. The basic cycle by which water evaporates, condenses, and flows along the surface of the earth governs all animal and plant life. Approximately 61.8% of the human body is water.[1] Almost 70% of the Earth's surface is covered with water, most of it in oceans with the balance found in lakes, rivers, the atmosphere, and absorbed into soil and rocks. Water is never absolutely pure in nature and its impurities are factors of concern in industrial applications. Man has contributed to impurities found in water sources. The disposal of spent cleaning solutions into surface waters has been one source of man-made impurities; but this is on the decline due to the rise of environmental protection regulations since the 1970s.

When an aqueous cleaner is used to remove contaminants from a surface, the water is basically the solvent in which the cleaning takes place. The importance of water's function cannot be overstated. As the solvent, water is able to dissolve and disperse the soils being removed. Additives such as acids, alkalis, chelants, and detergents significantly augment the cleaning process. These additives are not nearly as effective by themselves unless they are dissolved in a solvent, i.e., water. The combination of these additives with water yields the powerful, synergistic effects that we exploit today.

Physical Properties of Water

Pure water is colorless, odorless, and tasteless. Its chemical formula is H_2O, which shows that it is made from the two elements, hydrogen and oxygen, in a ratio of two to one, respectively. These two specific elements combined in that ratio yield physical properties unmatched by any other molecule. These properties are:

1. Very small size.
2. Not flammable or combustible.
3. Very high boiling point for its size.
4. The two elements that make it up are so different that they impart a high polarity to the molecule.
5. The high polarity of water accounts for the high boiling point. It also accounts for
   a. The high level of thermal energy that it can absorb per degree of temperature increase (heat capacity) and the level of thermal energy needed to get it to boil once it has reached the boiling point (heat of vaporization). The high heat of vaporization is what makes water so effective in steam boiler heat exchanging systems.
   b. The ability to dissolve numerous substances, especially minerals and other polar substances.
   c. The inability to dissolve nonpolar substances like fats, greases, and oils.

The very high boiling point gives aqueous cleaning processes the flexibility of a range of operating temperature options. The temperature of choice can be fine-tuned to the properties of the soil and substrate. This property also minimizes loss due to evaporation. However, water loss due to evaporation may become a concern, especially at temperatures above 150°F. The very high boiling point, 212°F, is beneficial in that most aqueous cleaning operations do not exceed 180°F so outright boiling is not

a problem. Many substrates cannot tolerate the extreme heat of boiling water without suffering from discoloration, etching, or mechanical deformation.

The high heat capacity of water makes it very effective in heating metal parts up to the cleaning temperature of the bath while having minimal impact on the bath temperature. Because metals have a low heat capacity, significantly less energy is expended in raising them to the bath temperature. In contrast, traditional organic solvents have low heat capacities like metals, so they are more prone to temperature fluctuations when used as heated immersion cleaners.

The high polarity of water can be viewed as a double-edged sword. The high polarity makes it possible for water to dissolve many inorganic compounds such as caustic soda, caustic potash, borates, carbonates, phosphates, and silicates. Water is also an effective solvent for many surfactants used in formulating aqueous cleaners. Unfortunately, this polarity also results in water being contaminated by numerous impurities both from the earth's crust and man-made pollution. Some of the impurities in the starting water are identical to cleaning ingredients, i.e., carbonates and phosphates. The key is which impurities are beneficial and which are detriments. Contaminant levels in water used to make aqueous cleaners are usually low, so we have to focus on which impurities are detrimental. The elimination/suppression of these impurities is essential to prevent problems, including reduced cleaner performance, longevity, corrosion, contaminated surfaces, and water spotting.

Chemical manufacturers and industrial users spend millions of dollars annually on water conditioning equipment to reduce or remove the impurities as part of preventive maintenance. Many users remain uninformed about their water quality needs. Undesirable consequences of the impact that poor water quality has on the cleaning process include increased cost of recleaning and rejects. See the section "Water Pretreatment" for more details on water purification methods.

An often forgotten property of water is its ability to dissolve oxygen gas. Oxygen gas dissolved in water can be corrosive and attack metals during immersion. High chrome and mild carbon steels as well as cast iron are exceptionally prone to rusting in these situations. When such parts are damp and left exposed to the air, flash rusting will occur. The boiler water treatment industry knows all too well how detrimental dissolved oxygen is in boiler systems. They have to treat boiler systems with what are known as "oxygen scavengers" to chemically remove the oxygen gas from water. Oxygen scavengers are not normally used in aqueous cleaning but corrosion inhibitors may have to be used to combat the corrosive effects of oxygen and other materials dissolved in water.

Impurities

If water were H_2O and nothing else or if all waters carried the same impurities, the use of water for industrial applications would be simple and straightforward. However, natural waters, even rain, snow, sleet, and hail, as well as all treated municipal supplies contain some impurities. The type and amount of contaminants in natural waters depend largely on the source. Well and spring waters are classified as ground waters whereas rivers and lakes are designated as surface waters. Ground water picks up impurities as it seeps through the rock strata, dissolving some part of almost everything it contacts. On the other hand, the natural filtering effect of rock and sand usually keeps the water free and clear of suspended matter. Surface waters often contain organic matter, such as leaf mold, and insoluble matter, such as sand and silt. Pollution from industrial waste and sewage is also frequently present. Stream velocity, amount of rainfall, and where this rain occurs on the watershed can rapidly change the character of surface water. All these forms of water contain inorganic salt impurities with the most common being in the following descending order: (1) bicarbonates, (2) sulfates, (3) chlorides, and (4) nitrates. Below is a list of the more common and troublesome water impurities and properties:

Turbidity: Turbid water is characterized by suspended insoluble matter, including coarse particles (sediment), that settles rapidly on standing. Amounts range from zero in most ground waters to over 6% or 60,000 parts per million (ppm) in surface sources such as muddy and turbulent rivers.

Hardness: The level of soluble calcium and magnesium salts is called "hardness" and is expressed as calcium carbonate equivalents in gpg (grains per gallon) or ppm (parts per million). 1 gpg = 17.1 ppm. Calcium salts are typically present at about twice the concentration of magnesium salts. Hardness ions are undesirable because they become less soluble and drop out of solution as the water is heated. Upon drying, they produce hard, stony water spots that can be difficult to remove.

Iron: The most common soluble form of iron in ground water is ferrous bicarbonate. Although some water is clear and colorless when drawn, upon exposure to air, ferrous bicarbonate can cause water to become cloudy and deposit yellowish or reddish-brown stains on everything it contacts. Iron can also shorten the life of a water softener by contaminating the ion exchange resin. Although the majority of iron-bearing waters have less than 5 ppm, as little as 0.3 ppm can cause trouble.

Manganese: Although rarer than iron in water, manganese occurs in similar forms. Manganese can form deposits in pipelines and tanks very rapidly at levels as low as 0.2 ppm. Manganese deposits are dark gray to black in color. The Delaware River area of the United States is well known for having elevated manganese content in the water.

Silica: Most natural waters contain silica at levels ranging from 1 ppm to over 100 ppm. Silica spotting can be very difficult to remove. The only way to remove silicate scale is mechanically (scraping and sanding) or by dissolving in acidic ammonium bifluoride or hydrofluoric acid solutions. Acidic fluoride cleaners are highly corrosive and poisonous and may pose acute worker safety hazards on inhalation or adsorption!

Mineral acidity: Surface waters contaminated with mine drainage or trade wastes may contain sulfuric acid plus ferrous, aluminum, and manganese sulfates. These contaminants are corrosive; and therefore, waters contaminated with mineral acidity are unfit to use without a pretreatment system.

Carbon dioxide: Free carbon dioxide is found in most natural water supplies. Surface waters tend to have the lowest levels of CO_2, although some rivers contain up to 50 ppm. In ground waters (wells), the concentration varies from zero to levels so high that carbon dioxide bubbles out when pressure is released (as in "sparkling" or seltzer water). Most well waters contain from 2 to 50 ppm. Carbon dioxide is also formed when bicarbonates are destroyed by acids, coagulants, or heating the water. The formation or absorption of carbon dioxide can reduce the pH of an alkaline cleaning solution, especially if air-sparging is used to agitate the cleaner. Carbon dioxide is corrosive and accelerates the corrosive properties of oxygen.

Oxygen: Oxygen is found in surface and aerated waters. Deep wells contain very little oxygen. The oxygen content of water is inversely proportional to the temperature, meaning that the hotter the water, the less oxygen is present. Note, however, that while water at elevated temperature contains less oxygen, the oxygen that remains is much more aggressive and corrosive. Oxygen is very corrosive to iron, zinc, brass, and other metals. Flash rusting of metals can be a problem when hot parts are rinsed in cold water that contains high amounts of dissolved oxygen.[2]

Water Pretreatment

General

The impurities that cause the most trouble in aqueous cleaning processes are the inorganic salts. Salts are ionic compounds. Ionic compounds are chemicals that have a positively charged species called a cation and a negatively charged species called an anion. It must be pointed out that the term "salt" has commonly meant sodium chloride, i.e., table salt. The chemical definition is "salts are ionic compounds that contain any negative ion except the hydroxide ion (OH^-) and any positive ion except the hydrogen ion." An ionic compound that contains the hydrogen ion (H^+) is called an acid and one that contains the

TABLE 2.1   Dissolved Impurities in Water

Ion Type	Impurity	Property
Cations	Ca^{2+}	Hardness
	Mg^{2+}	Hardness
	Fe^{2+} and Fe^{3+}	Iron stains
	Mn^{2+} and Mn^{4+}	Manganese stains and scales
	Na^+	Too much sodium in rinse water can cause spotting
	K^+	Too much potassium in rinse water can cause spotting
Anions	CO_3^{2-}	Alkalinity—carbonates form hard water deposits with calcium, magnesium, iron, and manganese
	HCO_3^-	Alkalinity—bicarbonates form hard water deposits with calcium, magnesium, iron, and manganese
	PO_4^{3-}	Alkalinity—orthophosphates form hard water deposits with calcium, magnesium, iron, and manganese
	SiO_4^{4-} and SiO_3^{2-}	Silicates can form the most tenacious of deposits, especially in the presence of calcium, magnesium, iron, and manganese
	SO_4^{2-}	Sulfates promote tenacious hard water deposits with calcium and manganese
	Cl^-	Chlorides promote corrosion on aluminum, iron, and steel. Excessive chlorides in rinse water can cause spotting
	NO_3^{2-}	Excessive nitrates in rinse water can cause spotting

hydroxide ion is a base. Specific examples of common ionic impurities that are encountered as impurities in water are given in Table 2.1.

It must be pointed out that silicates are usually discussed/represented as silicon dioxide (SiO_2), when they are actually present in the form of the ions listed on Table 2.1. There are more complex forms of phosphate and silicate ions and numerous other trace impurities that can be present in natural, untreated water, but the above examples represent the bulk of the impurities that the cleaning industry must be concerned with.

Principles of Water Softening

The most problematic impurities are the cations. The most economical method for removing cations is by passing the water through a cation exchange column, better known as a water softener. A standard water softener contains polystyrene beads that have been modified such that the surface of each bead has numerous negatively charged sites. Nature requires that charge must be balanced. The balance of charge is accomplished by pairing each negatively charged site with a sodium or potassium cation. As the impure water passes through the water softener, the hard water ions become attached to the resin beads and displace the sodium cations. The number of displaced sodium cations equals the charge of the hard water ions trapped in the softener. The hard water ions are bound more tightly to the resin because higher positively charged cations bind more strongly to negatively charged surfaces.

Basically, the water softener removes highly charged cations and replaces them with sufficient weaker charged sodium cations to maintain the balance of charge. Thus, sodium ion contamination increases but it does not cause nearly as much trouble as calcium, magnesium, iron, and manganese. There are only a finite number of resin beads in a water softener so there is a point where the softener becomes saturated with hard water cations.

At the saturation point, the softener must be recharged. This is accomplished by passing a saturated salt solution, usually sodium chloride, through the softener. The overwhelming quantity of sodium cations slowly displaces the calcium and magnesium ions; this returns the softener back to working order. Iron and manganese are more difficult to remove from a water softener. Iron and manganese can have

very high positive charges, +3 and +4, respectively, which make them bind so tightly to the resin beads that the mass action of the regenerating salt solution cannot knock them off. When a softener becomes saturated with iron, it is referred to as suffering from "iron poisoning." The iron and manganese cations can be washed out of the softener if their charge is lowered first. Reducing agents can be added to the salt recharging solution to lower the charge of the iron and manganese ions. Typical "reducing agents" are sodium sulfite, sodium hydrosulfite, and sodium thiosulfate.

Deionization

Basic water softening removes only the undesirable cations by replacing them with less problematic cations. It is also possible to replace anions by the same technique, only this time the charge on the surface of the resin bead is positive and the charge is balanced by pairing up with an anion. The chloride anion is the most economical choice for balancing charge in an anion exchanger. Unfortunately, excessive chloride content in water can lead to stress cracking of certain stainless steels and promote corrosion on aluminum, magnesium, and mild steels.

When industry has to be concerned with both cation and anion contaminants, it is easier to perform a process called "deionization" than to replace the undesirable cations with sodium and the anions with chloride. Deionization involves passing impure water through a series of cation and anion exchange resins where the cations are replaced by hydrogen ions (H^+, acid) and the anions are replaced by hydroxide ions (OH^-, base). The liberated acid and base then neutralize each other to form water:

$$H^+ + OH^- \rightarrow H_2O$$

When deionization is performed, theoretically an equal amount of acid and base is liberated. While the neutralization reaction should then result in pH neutral water, this is usually not the case. Deionized water typically is slightly acidic with a pH of 4.5–5.5. The mild acidity is caused by the carbonates initially present in the water. As the carbonates pass through the cation exchange column, carbonic acid is formed. The examples below will assume that the carbonates are passing through as sodium salts:

$$Na_2CO_3 + 2H^+ Resin^- \rightarrow H_2CO_3 + 2Na^+ Resin^-$$
$$NaHCO_3 + H^+ Resin^- \rightarrow H_2CO_3 + Na^+ Resin^-$$
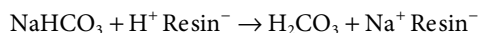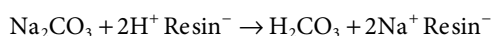
Carbonic acid is not stable in water so it self-destructs to form carbon dioxide, CO_2, and water:

$$H_2CO_3 \rightarrow CO_2 + H_2O$$
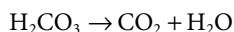
Carbon dioxide has some solubility in water; so unless the water is boiled to drive off the CO_2 after deionization, the reverse reaction occurs which liberates some acid. This causes the low pH:

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$
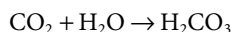
Both water softening and deionizing systems are very effective at removing impurities but they are not perfect. The exchange of ions is really an equilibrium process, so some impurities can work their way through a column before the resin becomes saturated. Imperfectly sealed control valves and excessively high flow rates can result in some impurities never coming in contact with the resin so that

exchange never occurs. In addition, ion exchange columns will not effectively remove nonionic impurities. The incorporation of carbon filters, nanofiltration (NF), or a RO unit will remove the nonionic impurities.

Reverse Osmosis

RO involves separating water from a solution of dissolved solids by forcing the water through a semipermeable membrane. As pressure is applied to the solution, water and other molecules with low molecular weights pass through micropores in the membrane. The membrane retains larger molecules, such as organic dyes, cleaners, oils, metal complexes, and other contaminants. RO membrane systems feature crossflow filtration to allow the concentrate stream to sweep away retained molecules and prevent the membrane surface from clogging or fouling.

In the past, RO applications for industrial operations were mostly limited to the final treatment of combined wastewater streams. Such applications typically involved discharging the permeate (the purified liquid) to a publicly owned treatment works (POTW) and returning the concentrate to the head of the wastewater treatment system. Because of the high flow rates associated with treating combined wastewater streams, large, costly RO units were required. More recent applications in cleaning involve installing RO units in specific process operations (such as a wash tank or for rinse water maintenance), allowing return of the concentrate to the process bath and reuse of the permeate as fresh rinse water.

RO systems have been successfully applied to a variety of industrial operations. By closing the loop, process contaminants are removed and fresh water is recycled. Furthermore, a waste stream is eliminated, one that would otherwise be discharged to the POTW or hauled away. An additional benefit is reducing the cost of waste treatment and disposal.

Reverse Osmosis Components

The essential components of an RO unit include a strainer, a pressure booster pump, a cartridge filter, and the RO membrane modules. The strainer protects the pump by removing large, suspended solids from the feed solution. The booster pump increases the pressure of the feed solution. Typical operating pressures range from 150 to 800 psi. Commercially available cartridge filters are used to remove particulates from the feed solution that would otherwise foul the RO membrane modules. Cartridge filter pore sizes are typically between 1 and 5 μm. The final RO membrane pore size is less than 0.001 μm and it removes impurities down to a molecular weight of about 200 Da.

Cleaning Chemistry[22]

Aqueous cleaners are acidic, neutral, or alkaline. Acid products, which have a pH of less than 6, are used for removal of inorganic scales and to pickle or passivate metallic surfaces. Neutral and alkaline cleaners have a pH range from 6 to above 13. These products are very effective on organic oils and greases.

Additional ingredients are frequently added to provide increased effectiveness on inorganic soils as well. For example, sodium gluconate and glucoheptonate additives turn highly caustic degreasers into alkaline rust removers due to the affinity of the gluconate/glucoheptonate for oxidized forms of iron.

When defined as the removal of soil or unwanted matter from a surface to which it clings, cleaning can be accomplished by one or more of the following methods:

Wetting: The cleaner penetrates and loosens the substrate–soil bond by lowering surface and interfacial tension through the use of surface active agents.

Emulsification: Once wetting occurs, the two mutually immiscible liquids are dispersed via emulsification. Oil droplets are coated with a thin film of surfactant which prevents them from recombining. The emulsion may float to the surface, hover in the solution, or sink to the bottom, depending on the size and density of the emulsion particulate versus the density of the cleaning solution.

Solubilization: Solubilization is the process by which the solubility of a substance is increased in a certain medium. The soil is dissolved in the cleaner bath.

Saponification: The reaction between an ester (can be animal- or vegetable derived as well as synthetic) and free alkali to form soap and an alcohol is *saponification*.

Insoluble ester + alkali = water-soluble soap + alcohol
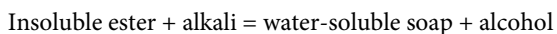
Deflocculation: The process of breaking particulate types of soils into very fine particles and dispersing them in the cleaning media is *deflocculation*. The soil is then maintained as a dispersion and is prevented from agglomerating. This process is similar to emulsification but does not operate on liquid/greasy types of soils.

Displacement: Soil is displaced by mechanical action. The movement of the workpiece or fluid enhances the speed and efficiency of soil removal. Agitation by scrubbing/rubbing is another variation of displacement.

Sequestration: Undesirable ions such as calcium, magnesium, or heavy metals are deactivated via sequestration, thus preventing them from reacting with materials that would form insoluble products (i.e., hard water soap scum).*

Water-based cleaners are generally divided into five major pH groups as follows:

    Caustic, pH > 13
    Highly alkaline, pH 10–13
    Mildly alkaline, pH 8–10
    Neutral, pH 6–8
    Acidic, pH 1–6

Acid Cleaners

Acid cleaners are generally not used for the removal of organic oily soils. These cleaners are used primarily for the removal of metal oxides and/or scales prior to other surface pretreatment steps or painting. Strongly acidic cleaners typically use dodecylbenzene sulfonic acid (DDBSA), hydrochloric acid, nitric acid, or sulfuric acid. Mildly acidic cleaners typically use citric acid, gluconic acid, glycolic or phosphoric acid. Acid cleaners usually contain some nonionic surfactants for degreasing and wetting purposes.

Systems using acid cleaners generally require constant maintenance because the aggressive chemistry attacks tank walls, pump components, and other system parts as well as the materials to be cleaned. Corrosion inhibitors can be used to reduce this attack. Acid cleaners often suffer from rapid soil loading, particularly metal ion loading. The metal ion loading leads to the need for frequent decanting and dumping of the cleaner solution. Spent acid cleaning solutions almost always are classified as hazardous waste. All of these disadvantages lead to relatively high operating costs compared to alkaline cleaners.

Alkaline and Neutral Cleaners

Ingredients frequently contained in alkaline cleaners include alkaline builders, water conditioners, surface active agents, corrosion inhibitors, fragrances and/or dyes, defoamers or foam stabilizers, and water. Occasionally, hydrocarbon solvents are also added to a formulation.

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* See Acknowledgment section.

Alkaline Builders

Alkaline builders are selected based on the pH, detergency, corrosion inhibition, and/or cost limitations required for a specific formulation. Environmental or process restrictions must also be considered. These builders may include one or more of the items listed in Table 2.2.

Neutral pH cleaners contain little or no alkalinity builder(s); or the alkalinity reserve is neutralized with an organic or mineral acid.

Water Conditioners

Sequestrants or chelators are frequently used to deactivate undesirable ions such as calcium, magnesium, or heavy metals. The sequestered ions or heavy metals are then no longer free to react with bath substances that would subsequently form undesirable compounds such as hard water soap scum. Some of the more commonly used sequestrants are as follows:

ATMP	Amino trimethylene phosphonic acid
EDTA	Ethylenediamine tetraacetic acid
HEEDTA	*N*-(hydroxyethyl)-ethylenediamine triacetic acid
IDS	Iminodisuccinic acid
NTA	Nitrilotriacetic acid
SHMP	Sodium hexametaphosphate
STPP	Sodium tripolyphosphate
TKPP and TSPP	Tetrapotassium and tetrasodium pyrophosphate, respectively
HEDP	1-Hydroxyethylidene-1,1-diphosphonic acid
Sodium gluconate	
Sodium glucoheptonate	
Low-molecular-weight polyacrylates and polyaspartic acids	

EDTA has maximum effectiveness in tying up calcium, magnesium, and heavy metal ions, thereby softening the water used to dilute the cleaner bath and preventing unwanted electrodeposition onto

TABLE 2.2 Alkaline Builders

Component	Advantages	Disadvantages
Caustic cleaners (pH > 13)		
Hydroxides	Alkalinity, cost-effective	Corrosive
High-alkaline cleaners (pH 10–13)		
Amines	Alkalinity, detergency, corrosion inhibition	More costly, can interfere in wastewater treatment
Carbonates	Detergency, soil anti-redeposition, cost-effective	Consumable
Hydroxides	Alkalinity, cost-effective	Corrosive
Phosphates	Detergency, sequestration, soil anti-redeposition, corrosion inhibition	Environmental restrictions
Silicates	Detergency, corrosion inhibition, soil anti-redeposition	Residues, restricted use
Low-alkaline cleaners (pH 8–10)		
Amines	Alkalinity, detergency, corrosion inhibition	More costly, can interfere in waste water treatment
Borates	Alkalinity, corrosion inhibition, soil anti-redeposition	Limited effect, environmental restrictions
Sulfates	Filler, carrier	Restricted use

Source: Quitmeyer, J., All mixed up: Qualities of aqeous degreasers, *Precision Cleaning*, September 1997.

other substrates. The use of EDTA has been strongly discouraged in the last decade due to its ability to tightly bind toxic heavy metals and because it is not biodegradable. Sodium gluconate and gluco-heptonate have maximum effectiveness in tying up calcium only at high pH but they will tightly bind some heavy metal ions at lower pH. Complex phosphates are cost effective but have come under environmental pressure since the late 1960s due to the problems they cause with eutrophication in lakes and streams. Low-molecular-weight polyacrylates have been growing in use as the result of increasing implementation of phosphate bans. Polyaspartic acids and iminodisuccinic acid have only been around for a few years so their impact is unknown at this time. Many of the water conditioning agents are also alkalinity builders.

Surface Active Agents

Surface active agents, also known as surfactants, are used to reduce the surface or interfacial tension of a water-based solution. The selection of the surfactant package used in cleaner formulations depends on the performance characteristics desired. Today, surface active ingredients frequently used in water-based cleaners are predominantly synthetic surfactants. However, there are still some cleaners that rely on naturally derived fatty acid soaps. Surfactants are classified into four basic types:

1. *Anionic*: negatively charged ions that migrate to the anode
2. *Cationic*: positively charged ions that migrate to the cathode
3. *Nonionic*: electronically neutral
4. *Amphoteric*: ions charged either negatively or positively, depending on the pH

Physical properties affected by surfactants include the cloud point, foaminess, detergency, emulsification, and wetting mechanisms used to facilitate the cleaning process. The nonionic surfactants are the primary work horses for grease and oil removal. They also play a key role in controlling the foam profile of the finished product through the cloud point effect. Anionic, cationic, and amphoteric surfactants are multifunctional; they affect foam profile, assist in grease and oil removal, can provide corrosion inhibition, help prevent redeposition of particulate soils, and can modify the cloud point of the nonionic surfactant. Nearly all cleaners use a combination of surfactants to obtain the specific properties desired.

Corrosion Inhibitors

Corrosion inhibitors are also included in some acid and alkaline cleaners, depending on the application involved. If a wide variety of substrates are involved, a combination of inhibitors may be used. These inhibitors are water soluble and therefore most are removed with a thorough rinse, if desired. Corrosion inhibitors frequently added to aqueous cleaner formulations include, but are not limited to, amines, benzoates, borates, carboxylates, molybdates, nitrites, silicates, thiadiazoles, triazoles, and urea. Phosphates and gluconates could also be added to this list, although their efficacy is more limited. The intended cleaner application dictates the type of inhibitor package selected. As the alloying of metals and composites becomes more complex, there is a greater need for sophisticated inhibitor packages that provide protection over a broad spectrum of substrates. The synergism of chemicals allows the formulator to obtain the inhibiting properties desired. Achieving the desired inhibiting properties may be limited only by the imagination of the formulator and the cost restrictions of the chemicals selected.

One very important rule about using silicate-based cleaners is that they should be rinsed off with heated water, preferably no less than 115°F. Silicates release themselves from metal surfaces at slower rates than most other cleaner ingredients. Rinsing with cool water can result in excessive residue remaining on the parts. This residue could interfere in a later manufacturing step such as alodining, anodizing, or plating. Poor rinse agitation can also lead to excessive silicate residue even if the water is heated.

Additional Ingredients

Aqueous cleaner formulations may also contain a broad spectrum of ingredients designed to affect the appearance, odor, or physical properties of the composition. These ingredients include dyes, fragrances,

thickeners, defoamers, foam stabilizers, or fillers for cost reduction. Again, the intended cleaner application will dictate the final composition of a formula.

Solvents

A variety of solvents have been blended with surfactants to make emulsions or semi-aqueous cleaners. Environmental regulations have identified nearly all solvents as volatile organic compounds (VOCs). Formulation chemists must be careful about which solvents they choose during product development in order to conform to environmental regulations while, where possible, avoiding making flammable/combustible products. The few VOC-exempt solvents find nearly zero use in aqueous cleaners due to problems with flammability, odor, and difficulty in emulsifying or cost.

For example, it is easy to make an aqueous cleaner with a flash point that is low enough to be categorized as "flammable" or "combustible" and they do exist in the market. It often takes as little as 1.0%(w/w) D-Limonene to drop the flash point below 140°F. The presence of isopropyl alcohol at around 2%–3% can yield a flash point below 100°F. The VOC-exempt solvents such as acetone, methyl acetate, and the linear methyl siloxanes all have flash point in the 50°F–60°F range. There are several surfactants that are purposely cut with ethanol or methanol to make them more pourable/pumpable for manufacturing purposes. Use too much of these surfactants and you will get a flash point as a result of too much alcohol being present. The cleaners may lose their flash points when diluted for final use applications but these days, environmental health and safety departments usually block purchasing of products with flash points when possible.

Simple aromatic solvent emulsions are great for cutting through greases and carbonized soils but they have very disagreeable odors. Glycol ethers have been added to stabilize formulations and to increase the grease cutting/ink removal efficiency of a composition. In addition, certain glycol ethers, including 2-butoxyethanol or "butyl cellosolve," have been identified as health hazards.

D-Limonene, orange oil, pine oil, and other terpene-based solvents have found widespread use in removing inks and polyurethanes that have not set up or cured. *N*-methyl-2-pyrrolidone (NMP) is a very polar solvent that can impart the ability to strip some paints in aqueous cleaners. The terpene solvents also have the added benefit of acting as fragrances in some applications. Drawbacks of terpene solvents are that they have low flash points that are very difficult to suppress in the final blend; and their cost is very volatile due to the occasional crop disasters that affect supply.

The recent drive to use as many raw materials derived from renewable resources has resulted in the increased use of solvents such as ethyl lactate, methyl soyate, and other methyl esters. Methyl soyate exhibits solvency that is similar to D-limonene, but it typically requires heating to achieve similar solvency.

Environmental Regulatory Effects on Cleaning Chemistry

Water has been used as a cleaner for centuries. The first water-soluble soaps were blends of lye and animal fat. The chemical reaction of this mixture is a process defined as saponification. The addition of heat made the soap work better at removing the oils and greases of the day which were also made from animal fat.

As industry advanced and metal processing became more sophisticated, various organic and inorganic salts were found to enhance detergency. The salts tie up metal ion impurities that could react with the soap to inhibit cleaning and deposit as soap scum. They also provide alkalinity and improve pH buffering capacity.

Today, traditional neutralized fatty acid soaps make up only a small portion of the surfactants used in industrial and consumer cleaning applications. The development of synthetic detergents as a substitute for soap starting in the 1920s and 1930s has completely changed the cleaning industry. Problems with some synthetic surfactants became obvious in the 1960s when foaming in rivers and wastewater

treatment plants indicated that the most popular detergent at that time, branched propylene tetramer-based alkyl benzene sulfonate, was not readily biodegradable. To correct the problem, manufacturers of aqueous cleaners in Europe and the United States voluntarily changed over to biodegradable linear alkyl benzene sulfonates by 1965. Other problems that became apparent over time were eutrophication of lakes and streams from excess phosphate pollution and possible endocrine disruption in amphibians and fish by alkylphenol ethoxylate surfactants (APEs).

By the mid-1970s, government regulations were starting to be felt at the job site. The EPA, California Air Resources Board (CARB), OHSA, and Material Safety Data Sheets (MSDS) became common terms within the industrial arena. Chemicals came under increasing scrutiny for worker safety.

During the following decades, environmental issues played an increasingly important role in chemical evaluation. The terms chlorofluorocarbons (CFCs), the Montreal Protocol, global warming potential (GWP), HAPs, ODS, SARA Reportables, and air quality boards became commonplace.

Bans on some APE surfactants and phosphates have been spreading rapidly. Finding replacements for APEs has been fairly easy but at an increased cost; phosphate replacement has not been as easy, especially in the automatic dish detergent market.[5]

Many new regulatory agencies/programs have appeared since the late 1980s. Organizations and programs such as Canada's Ecologo, the EPA's Design for the Environment (Dfe), Europe's Registration Evaluation Authorization and restriction of Chemicals (REACH), Green Seal, and individual State's own legislation have come together to form a massive body of laws and rules.

It can be very time consuming for the manufacturer of cleaners to determine how best to conform to the assortment of requirements and directives. Some inconsistencies have led to chemical cleaners being restricted from some markets. This results in increased costs due to the need to manufacture more than one type of cleaner to accomplish the same task; there is a decrease in the economy of scale. Because regulations are also changing at increasingly shorter intervals, the lifespan of a chemical cleaner/cleaning process is sometimes shortened.

Increased environmental restrictions have played a role in forcing manufacturers to move their factories from Canada, Europe, and the United States to Mexico, China, and Third World countries in order to avoid the cost increases of complying with the latest environmental regulations.

Ultimately, no cleaning process can completely escape the concerns of health, safety, and the environment. The chemical and manufacturing industries have learned to embrace the changes and have been successfully rising to the challenge of these new regulations.

Guidelines for Cleaning Common Substrates

All metals are sufficiently reactive in the presence of oxygen in the atmosphere that they form a metal oxide layer on the surface. The chemical behavior of the oxide layer plays a significant role in determining the type of aqueous cleaner that can be used in the cleaning process. Metals whose oxide layers readily dissolve in both acidic and alkaline cleaners are classified as amphoteric metals.

Several metals/alloys and their general cleaning chemistry needs are detailed below. Plastics and composites have been added due to the increased use of these as construction materials.

First, a bit of WARNING must be given concerning some of the chemistries required for these substrates. There will be applications where there is no alternative to using a heavy-duty caustic or strongly acidic cleaner. The operator must read the MSDS and product labels to determine the appropriate safety equipment required for each cleaner. Heavy-duty caustic cleaners are very dangerous if they get in your eyes or on your mucous membranes. Acidic cleaners are also dangerous to eyes and mucous membranes. Skin burns are also possible with either type of cleaner. Of particular concern are acids that contain hydrofluoric acid or ammonium bifluoride. Acidic fluorides are highly corrosive but they are also very poisonous. Acidic fluorides can be absorbed through the skin and the symptoms of poisoning do not appear immediately. Thus, extra care must be taken to protect the worker when using these cleaners.

Aluminum

This is the second most common metal used in manufacturing and it is strongly amphoteric. Acidic solutions below pH of ~5 will dissolve the metal oxide surface layer. Once the oxide layer has been removed, the base metal will dissolve in most acids. Phosphoric acid and diluted hydrofluoric acid solutions are the most common of the acid cleaners for general cleaning and brightening of weathered aluminum that do not cause excessive etching. Fresh/unweathered aluminum is not typically exposed to acid cleaners unless the surface requires an etching step or smut formation from a previous process must be removed. Smut removal is typically accomplished with strong nitric acid solutions that contain low levels of hydrofluoric acid. Neutral and mildly alkaline cleaners that are silicate free are safe on aluminum as long as the pH does not exceed ~8.7. Above this pH, the etching of the base metal will occur unless silicate or chromate corrosion inhibitors are present.

The use of chromate corrosion inhibitors has been largely discontinued due to environmental and worker safety concerns. Thus, currently, mild and strongly alkaline cleaners only use silicate corrosion inhibitors to prevent etching. Etching can be stopped up to about a pH of 12 with silicates. Between pH of 12 and 13, etching can still be suppressed if the cleaner contains massive amounts of silicates. At this high a pH, some discoloration of the base metal can be expected. Therefore, these cleaners typically are only used in applications like automatic and manual transmission overhaul where aesthetic appearances are not a big concern.

A fairly common problem with alkaline cleaning of wrought aluminum alloys (e.g., AL2024 and AL6061) is the formation of a fine black particulate smut that forms shortly after the cleaning process. This smut is not readily visible by the naked eye but is easily detected by the white glove test. The problem appears to be related to a combination of magnesium silicate inclusions and submicron particles absorbed at the surface. The smut formation can be stopped by first cleaning the metal with an acid solution (typically phosphoric acid) followed by an alkaline cleaner. The acid cleaner removes the magnesium occlusions and submicron particles from the surface which stops the smut from forming.[7]

Aluminum is sufficiently chemically reactive that temperature is a major consideration, especially with neutral and alkaline cleaners. Neutral and mildly alkaline cleaners that do not contain silicates should be limited to about 150°F due to the tendency of some alloys to discolor. While alkaline silicate-based cleaners have been safely used up to 180°F, it is still preferable to limit the temperature to 160°F. Alodined and anodized aluminum must be limited to a temperature of 145°F–150°F to prevent damage to the conversion coating.

It is possible to clean conversion-coated aluminum parts with silicate-based cleaners as long as the pH is not too high (does not exceed 11.5 at use-dilution) and the temperature limits are still obeyed. The key is that the manufacturer must test the cleaner on their specific parts. There are several types of alodined and anodized coatings and they do not all behave identically. Conversion coatings that incorporate dyes are the most difficult to clean successfully with silicate-based cleaners; blotchy color patterns from leaching of the dye are common.

Cobalt

This metal is not amphoteric. For this discussion, we are dealing only with cobalt-cemented carbide tools such as drills and saw blades. Cobalt containing alloys such as the Haynes series fall under the guidelines given for steel. Many tools use chromium carbide or tungsten carbide to increase hardness and wear resistance. The carbide material cannot be blended into the tool's base metal during casting or forging processes. The carbide material is "glued" to the metal substrate with cobalt metal in an electroplating process. The cobalt glue must not be attacked by cooling fluids and cutting oils during normal use nor must any attack occur when the tools are manufactured or undergo periodic maintenance. Not only will attack weaken the cement bonding leading to shorter tool life, this will allow cobalt metal to build up in the wash tank. Cobalt metal is a known sensitizing agent so keeping

cobalt leaching under control is important to the employee's health. Alkaline cleaners are very tricky to formulate for compatibility with cobalt. Typically, the cleaner must not contain any of the ethanol- and isopropanol-based amines commonly used in cleaners, coolants, and lubricants. The cleaner must also not contain citrates, EDTA, gluconates, phosphates, and sulfates.[8–10] One strange contradiction is that on the alkaline side, phosphates are unsafe but acid cleaners based on phosphoric acid cause no problems with cobalt.

Copper (Includes Brass and Bronze)

Copper and bronze are not amphoteric but brass is amphoteric. These metals are sensitive to tarnishing by combinations of elevated pH, moisture, and temperature. The upper pH limit on alkaline use-dilutions is typically about 11.5; cleaning at higher pHs can lead to significant darkening. Discoloration is a problem with neutral and alkaline cleaners when the temperature exceeds 130°F. Discoloration can be suppressed by using cleaners that contain thiadiazole or triazole corrosion inhibitors. These inhibitors can raise the maximum allowable cleaning temperature up to approximately 150°F. Silicate-based cleaners also suppress stock loss on copper alloys, but discoloration is still possible.

Cleaners that contain amines may be problematic with these alloys because the copper oxide and zinc oxide top layers (zinc is a component of brass) readily form water-soluble ammoniacal complexes. The leaching of copper and zinc may change the color of the base metal, typically making the metal lighter in color. Eventually, the dissolved metals content will increase to a level such that the spent tank will be classified as a hazardous waste. Cleaning stressed brass parts with cleaners that contain amines is not recommended because prolonged exposure can lead to stress cracking.

Care must be taken to not overheat the parts if a blown hot air process is used to accelerate drying of parts; excessively high temperatures will darken these alloys. Finding the right neutral or alkaline cleaner may require an exhaustive trial and error process if even the slightest amount of discoloration imparted by the cleaning process is unacceptable (e.g., decorative household fixtures). In some cases, it may be necessary to clean with solvents only.

Copper that does not suffer from significant discoloration can usually be brightened with a citric acid-based cleaner. The brightening of noticeably discolored copper alloys with acid cleaners can only be done if an oxidizer is present; these are more commonly referred to as bright dips. Oxidized copper exists in two states; a reddish-pink cuprous oxide and a black cupric oxide. Alkaline and pH-neutral cleaners that contain amines can only remove the black cupric oxide but are unable to remove reddish-pink cuprous oxide. Oxidizing acid cleaners such as sulfuric acid/hydrogen peroxide and nitric/hydrochloric acid are required to convert the cuprous oxide to a cupric oxide before it can be removed. Nitric acid/hydrochloric acid blends have fallen out of favor due to the generation of chlorine gas which is corrosive and poisonous. Alkaline cyanide cleaners also can remove cuprous oxide; these cleaners are still used in plating facilities.

Magnesium

While this metal is not amphoteric, it is the most chemically reactive metal commonly used in industry. Bare magnesium will slowly corrode in water and eventually dissolve if given enough time.

The trick to cleaning magnesium is to incorporate a chemical that forms a very water-insoluble by-product right on the surface, as soon as the etching starts. The most effective chemicals that do this in alkaline cleaners are sodium and potassium hydroxide. The pH must remain high at use-dilution for these hydroxides to be effective in preventing attack on magnesium. Experience has shown that the pH must stay above 11 to protect magnesium from corrosion.

Magnesium should always be segregated and cleaned with dedicated cleaners/equipment if at all possible. Magnesium is also very prone to discoloration at high pH. If discoloration is objectionable, highly alkaline/caustic cleaners containing high levels of silicate corrosion inhibitors can suppress this

problem. Acid cleaners that are safe on magnesium are hydrofluoric acid, ammonium bifluoride blended with other acids, and phosphoric/nitric acid blends. Magnesium forms an insoluble barrier of magnesium fluoride or magnesium phosphate as part of the corrosion inhibition process. Avoid all cleaners that contain chlorides as those will promote corrosion. It is possible to clean magnesium at milder pH. However, to prevent excessive stock loss/discoloration, this is usually only possible at temperatures below 130°F and for limited exposure periods.

Magnesium should be anodized at the end of the manufacturing process to suppress its tendency to corrode in the presence of moisture and dirt.

Plastics and Composites

These materials are not amphoteric. The properties of these substrates are so varied that no one rule is universally applicable, except "Don't clean at a temperature above the substrate's glassy transition point or decomposition point." Exceeding these points will irreversibly damage the substrate.

Materials like Kalrez®, polyethylene, polypropylene, and Teflon® are inert to nearly all chemical conditions that occur in aqueous cleaning. Other materials like the Lexan class of polycarbonates will suffer stress cracking in acidic and alkaline cleaners, especially chlorinated bleach formulas. Polyethylene terephthalate (PETE) will stress crack in the presence of alkaline cleaners. The author once ran into a polyetherimide plastic used as a housing for a medical diagnostic tool that had poor chemical resistance (it softened and cracked) to any ingredient used in water-based cleaning other than the water itself.

The take-home message is that the manufacturer must know what specific plastics and/or composites they are dealing with and provide that information to the cleaner manufacturer. The cleaner manufacturer may already know if their product is safe on the substrate. In some cases, the manufacturer can only find the right cleaner through trial-and-error testing.

Steel (Mild Carbon and Stainless)

These alloys are the most widely used in manufacturing and are not amphoteric. Steel alloys are quite chemically resistant to nearly all pH-neutral, alkaline, and heavy-duty caustic cleaners over a wide temperature range.

The presence of chlorides/halides in alkaline cleaners is undesirable because they promote rusting of mild steels and can cause stress cracking in some stainless steels. Certain high tensile strength steel applications require that the cleaner does not cause hydrogen embrittlement.

Rust and scale deposits can be removed by highly caustic cleaners loaded with sodium gluconate or glucoheptonate. Gluconate-based derusters are preferred over glucoheptonates due to the strong ammonia odor associated with the latter. Acid cleaners are also commonly used to remove rust and scale from mild steels. Mild steels are typically cleaned with inhibited hydrochloric or phosphoric acid cleaners whereas stainless steels use nitric acid spiked with a small amount of hydrofluoric acid.

Mild- and high-chrome-content steels are very prone to flash rusting, especially during transfer from the wash to the rinse tank, during rinsing, and during drying. The transfer time between the wash and rinse tank must be quick enough to minimize drying of the cleaner on the part, otherwise rusting will occur. It may be necessary to maintain a wet spray on the parts to protect them during the transfer. The rinse tank must be heated to reduce the amount of dissolved oxygen present in the water. Dissolved oxygen readily promotes rusting on mild and high chrome steels. A common cause of flash rusting is transferring a part from a heated wash tank to a cool rinse tank; the increased temperature of the metal combined with the higher oxygen content in the cool rinse causes rusting almost immediately. It may be necessary to add a corrosion inhibitor such as an amine or a nitrite to the rinse tank even when the water is heated. The drying step must be quick. Slow drying times promote rust on mild and high chrome-content steels.

Tin

This metal is weakly amphoteric. Tin is less sensitive to high pH than aluminum and zinc; but one must not clean with very high pH cleaners (>12 at use-dilution) such as alkaline derusters because heavy etching will occur. Silicate-based cleaners are excellent at suppressing discoloration and etching. Chromate inhibitors also are effective at stopping etching in alkaline cleaners; but they are rarely used due to the environmental health hazard they pose. While tin is not very reactive to diluted hydrochloric and sulfuric acids, heated and concentrated forms of these acids readily attack the metal. Neutral pH cleaners do not have any compatibility problems with tin.

Titanium

This metal is not amphoteric. Titanium is a fairly robust metal when it comes to aqueous cleaning applications. However, acid cleaners are generally not used except in pickling operations because the metal is readily attacked at low pH. There are specialized acid cleaners used on titanium-based turbine compressor components, but the exposure times are very short.

Alkaline, caustic, and neutral cleaners have very few restrictions due to the chemical inertness of titanium. Exceptions include cleaning critical components of turbine engines used in aircraft and power plants. Formulations used to clean turbine compressor components must have very low halide salt and sulfur content; they must not cause hydrogen embrittlement and their dried residue must not corrode the metal if the turbine is reassembled and operated without rinsing first. Alkaline derusters are commonly used in the overhaul of turbine compressor components.

Some compressor components are made of super alloy steels which can be cleaned at 180°F–200°F. However, titanium becomes too reactive in this range; so cleaning temperatures should be restricted to a maximum of 170°F.

Titanium should have its own separate cleaning tank when undergoing alkaline derusting; the presence of dissolved iron from cleaning cast iron and steel parts in the same tank significantly accelerates attack on titanium.

Medical applications such as titanium hip implants also have cleaner restrictions. The cleaners cannot contain ingredients that are animal derived and/or paraffin based. These medical restrictions are not based on corrosion problems with the base metal. Instead, they must be avoided to prevent the patient from getting infections and/or to avoid their body trying to reject the implant. In general, residue levels must be low, and the residue must not present toxicity issues for the recipient.

Zinc

This metal is amphoteric. Overall, it is very chemically reactive, almost as reactive as magnesium. Cleaning zinc is further complicated by the fact that it loves to form water-soluble complexes with amines. Amines usually do not cause problems with the physical appearance of the metal, but they will cause zinc to build up in the wash tank. This presents a disposal problem. High-pH cleaners (pH > 12 at use dilution) should be avoided because the surface begins to dissolve at an appreciable rate. Zinc is typically brightened in acid cleaners; but because zinc is readily soluble in all acids, the exposure time must be short, and brightening is typically done at room temperature. It is possible to clean at alkaline pH if the cleaner contains silicate corrosion inhibitors. However, the process may still result in discoloration of the metal.

Rinsing

Rinsing is often the most overlooked aspect of cleaning. While a process may employ the best cleaning equipment money can buy and an optimized cleaning solution, without adequate rinsing, the overall result is often unsatisfactory.

Rinsing is no more than a reduction in contamination by dilution. Adding mechanical or thermal energy will enhance rinsing. While it is important to use adequate water in rinsing, the key to economy is to use no more than is necessary to achieve acceptable parts.

Importance of Rinsing

Rinsing is a science by itself. Many factors enter into the design of a rinse system. Let us start with the end result in mind. Below is a partial list of considerations:

- Part cleanliness required
- Production levels required
- Type of contamination to be removed (amount and type of drag-in)
- Incoming water quality
- Treatment capabilities
- Number of rinse tanks, size, layout
- Water usage and disposal

Each of these concerns is discussed in further detail below.

Part Cleanliness Required

This consideration is the controlling factor in the whole process of rinsing. If the manufacturer is only concerned with gross contamination, then perhaps rinsing may not even be necessary. At the other extreme, if the slightest residue leads to failure, then the final rinse typically requires the use of deionized water. Obviously, final cleanliness requirements must be determined before other decisions can be made.

Production Levels and Drag-In

Production levels and drag-in will determine what measures are needed to meet the determined quality requirements. Drag-in depends on many factors, including part configuration, orientation, temperature, drain time, etc. Production levels and the shape of the parts determine the amount of drag-in per time.

Parts that are shaped like cups or bowls must be racked in a manner that allows them to drain completely as they are moved from the wash to the rinse tank. If complex parts are allowed to dragin large volumes of wash solution, the chemical costs of replacing lost cleaner will rise rapidly. The amount of water needed to maintain a quality rinse will also increase massively, leading to further increases in costs. Rinsing equations must deal with these factors to predict final rinse quality.

Incoming Water Quality

Incoming water quality can vary from naturally soft water with few contaminants to water that contains many hundreds of ppm hardness. Water hardness is generally measured either in ppm of equivalent calcium carbonate, $CaCO_3$, or in grains of hardness (*note*: 1 grain = 17.1 ppm). Values greater than 120 ppm are considered to be hard water, with values greater than 180 ppm considered to be very hard.

Hardness can have many deleterious effects in the cleaning process. Hard water can react with the surfactants (mainly anionic) to deactivate them. Consequences include increased corrosion on steel surfaces, and/or deposits on the cleaned surfaces. Impacts of these residues include paint adhesion problems, plating problems, and aesthetic problems, just to name a few. Fortunately, as we have already discussed, there are alternatives to using unsoftened water. Whether softened water, deionized, distilled, or RO water is chosen depends on the application.

Number of Rinse Tanks

One of the most common problems manufacturers face in properly setting up a cleaning line is that they are unable or unwilling to allocate enough funds and/or floorspace to incorporate an adequate rinsing step.

Generally speaking, one large rinse is less effective than multiple small rinses. A single rinse may be adequate for intermediate manufacturing steps. However, as a rinse in the final or critical cleaning process, this is seldom true. Increasing the number of rinses is usually necessary for sensitive manufacturing processes and final manufacturing steps. Unfortunately, multiple rinses lead to higher costs in equipment (i.e., number of tanks needed and the footprint taken up on the plant floor).

The increased equipment cost can be offset by counterflowing the water from the last rinse back into each previous rinse. Counterflowing significantly reduces water consumption; some of the overflow can be used as add-back into the cleaning tank to replace evaporated water. Studies have shown that a counterflowed, triple rinse has the optimum balance of reducing water consumption, obtaining clean parts, and recouping capital costs. Greater than three rinses tends to yield diminishing returns.

Rinse Tank Design and Placement

Rinse tank design and placement can greatly affect rinsing efficiency. Rather than being an afterthought, rinsing needs should be addressed early in the planning of the cleaning line. Considerations should include tank geometry and composition, degree of agitation, rinse flow, rinse temperature, and necessary final quality of the parts.

It should be noted that rinsing will only be effective when the water contacts the whole surface of the parts. Part orientation, loading, and rinse flow dynamics are important and often overlooked considerations.

There must be adequate agitation to sweep away the soil-loaded cleaner, especially with cleaners that contain free caustic and/or silicates. These chemicals are inherently slow at releasing from the parts surface. The rinsing needs are quite different for the manufacturer of circuit board components versus the rebuilder of lawn mower engines. In the first case, the choice might be a heated cascaded triple rinse with a deionized water source. In the second case, perhaps a quick dip in a warm tap water tank is sufficient.

Drag-In and Final Rinse Quality

Knowing and understanding the volume and composition of drag-in from the previous step is crucial to predicting rinsing needs. Quite simply, drag-in over a given time equals the quantity of residue that must be diluted to some lower specified level.

In a dynamic situation at equilibrium, the rate that the rinse water must be overflowed must equal the drag-in times the wash tank chemical concentration divided by rinse tank chemical concentration:

$$\text{Overflow} = \text{Drag-in} \times \left(\frac{\text{wash tank concentration}}{\text{rinse tank concentration}} \right)$$

If this equation is extended to multiple rinse tanks, the dragin is reduced in each successive tank. If the overflow for each rinse tank is cascaded to the previous tank, for all practical purposes, the equation takes the following form:

$$\text{Overflow} = \text{Drag-in} \times \left(\frac{\text{wash tank concentration}}{\text{rinse tank concentration}} \right)^{1/\text{number of rinse tanks}}$$

Cascading obviously reduces water use dramatically over a single rinse and over multiple rinses that are not cascaded while achieving the same final rinse quality.

The final rinse quality should be maintained just as carefully as the processing tanks. After all, the rinse is the last liquid the parts will see. It does not make sense to go to great lengths to clean the parts only to recontaminate them with a low-quality rinse.

Acceptable rinse quality depends on the requirements of the application. As such, the steps to measure rinse quality will vary. Generally speaking, cleaning performance needs to only be sufficient to eliminate subsequent problems.

While rinse quality is relative, some general guidelines may be helpful. Some sources would classify applications into general cleaning, critical, and very critical cleaning. While different standards may be proposed, one suggestion is to use conductivity as a guide and divide these applications as follows:

- General rinsing operations having a residual level of 1000 μS
- Critical rinsing with a residual of 500 μS
- Very critical at less than 50 μS

Most conversion coating and plating operations call for a high-quality final rinse of less than 50 μS as the minimum water quality. It can be seen that at these higher quality rinses, higher quality water must be used to achieve the desired cleanliness. These guidelines are suggested as a place to start when determining final rinse quality.

Disposal

Oftentimes, local regulations limit or prohibit the discharge of any process water to sewers. The most common properties that are commonly regulated on spent wash and rinse solutions are

- pH
- Dissolved heavy metals content
- Total solids
- Biological oxygen demand
- Chemical oxygen demand
- Emulsified oil content

Some geographical regions will also impose restrictions on phosphate and/or alkylphenol ethoxylate (APE) surfactant content. Spent wash and rinse solutions that cannot meet allowable discharge purity limits require on-site chemical treatment systems to purify them for discharge. Otherwise, they must be hauled away as hazardous waste. Either option is expensive.

The increasing world population is now beginning to put tremendous strain on nature's ability to supply us with sufficient potable water. For social and economic reasons, bath life and water conservation have become very important issues. The result is that overall planning and coordination includes a cradle-to-grave approach for setting up a cleaning line, including the rinse and chemical disposal factors. Closed-loop systems for water treatment are becoming economical long-term alternatives that can reduce costs and hazardous waste generation. At the very least, water use minimization is an important consideration.

A whole chapter could be easily devoted just to basic rinsing concepts. Certain basic principles can be summarized as follows:

- Multiple rinses are more efficient than single rinses, with the optimum balance being about three rinses.
- Water usage can be minimized by cascading the final rinse overflow into the previous rinse and that rinse into the one before.
- The final rinse quality is the determining factor in final residue on the part.
- Rinsing will not be effective if it does not reach the parts.

Conclusion

Aqueous cleaning is an increasingly important segment of the cleaning industry. This importance will probably increase with time and the development of improved cleaning systems. The emphasis must be on careful design of cleaning systems, because the interactions between parts, soils, equipment, cleaner, and water are much more complex than they appear on the surface.

Environmental, economic, and other business concerns demand that industry obtain acceptable parts with minimal impact on the environment and at the lowest possible costs. The challenge to the

cleaner manufacturer and the equipment manufacturer is to develop effective cleaners and equipment that meet those criteria and that are compatible with each other.

The newer generation of aqueous cleaners is designed to reject contaminants rather than emulsify soils. This feature allows the cleaner to be filtered routinely without significant adverse effect on the cleaner chemistry. Many of the newer formulations can be replenished with routine chemical additions of the cleaner concentrate, according to the maintenance procedures recommended by the chemical supplier.

The extension of cleaner bath life obtained with regular bath maintenance results in reduced chemical consumption, reduced waste generation, reduced waste liability, and reduced cleaning costs. Very often, the newer cleaning processes also yield cleaner parts as well.

Clearly, the future progress of aqueous cleaning will require close cooperation between the chemical and equipment industries. It is also apparent that water quality is a make or break issue in critical cleaning, especially as it applies to rinsing. This area is consistently the most neglected aspect of aqueous cleaning.

Aqueous cleaning is changing to meet the economic and environmental needs of the times. Its future is clear.

Acknowledgment

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3

Cleaning Agent Chemistry

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Introduction

Legislative changes have forced industry to reevaluate cleaning needs. Today "green technology" and waste minimization are driving forces in process optimization. Once process requirements have been defined, chemical choices must be made.

Cleaning agent chemical options include hydrocarbon solvents, semiaqueous or emulsion cleaners, or aqueous cleaning technologies. These cleaning agents may be single-component materials or they may be blends containing over 20 different chemical substances classified as solvents, surfactants, acids, alkalinity builders, inhibitors, stabilizers, viscosity modifiers, colorants, or fragrances.

Depending on the soils involved and the mechanical method of fluid application, the formulator may customize a composition to meet exact specifications required to meet production needs. An informed manufacturer can then optimize his or her cleaning process for maximum output and quality.

Cleaning Agent Base Solvents

A solvent is a liquid or gas that dissolves a solid, liquid, or gaseous solute, resulting in a solution. The most universal solvent is water, a natural resource covering over 70% of the Earth's surface. Other solvents, called organic solvents, are carbon-containing fluids. These aqueous or hydrocarbon solvents form the basis for cleaning agents.

Water is a compound containing two parts hydrogen (H) and one part oxygen (O), with the chemical formula H_2O. The term refers to the liquid state although the compound also exists in solid and gaseous states as ice and steam. Water is a tasteless, odorless, transparent polar solution. In the liquid state, it is miscible with many other polar substances forming a single homogenous solution. It is immiscible with aliphatic, aromatic, and halogenated hydrocarbons and some oxygenated solvents and it forms an azeotrope (a mixture that boils with a constant composition) with others. When combined with acids, alkalinity builders, or surfactants, aqueous-based cleaning agents are effective on a wide range of polar and nonpolar soils.

As a major solvating material, vast amounts of this natural resource are used as cleaning agents, especially in industrialized countries. Environmental awareness is making aqueous cleaning processes the preferred means of soil removal.

$$H-C\equiv C-H$$

FIGURE 3.1 Aliphatic hydrocarbon structure.

Organic solvents are compounds composed of the elements carbon (C) and hydrogen (H). These hydrocarbon solvents are further classified as aliphatic, aromatic, halogenated, or oxygenated materials.

Aliphatic hydrocarbon solvents are carbon atoms that are joined together in straight or branched chains, as shown in Figure 3.1, or in alicyclic rings by single, double, or triple bonds.

Alicyclic rings are closed chains. Alicyclic compounds may have double bonds. In contrast to a benzene ring, for example, they are not aromatic; so alicyclic compounds behave similarly to aliphatic compounds. They are classified as flammable or combustible depending on the flash point. The vapor pressure is an indication of how rapidly the solvent will evaporate. Water has a vapor pressure of approximately 17.5 mmHg at 20°C. As the vapor pressure increases, the faster the solvent will evaporate. Materials with a vapor pressure less than 17.5 will take longer to evaporate than water. Examples of aliphatic solvents are listed in Table 3.1.

The kauri-butanol (Kb) value[1] is a standardized measure of solvent power governed by ASTM D1133 giving a scaleless index; more precise, complex descriptions of solvency such as the Hansen solubility parameters are discussed in other chapters. As Kb value increases, the more solvent power the material has. The Kb of a solvent shows the maximum amount of hydrocarbon that can be added to a kauri resin solution without causing cloudiness. Strong solvents can be added in greater amounts so they have a higher value than weaker solvents. Unlike hydrocarbon solvents, aqueous cleaners are measured by their pH and the concentration of hydrogen ions in the solution. Since aliphatic hydrocarbons do not use water, they cannot have a pH; they instead are classified by Kb value.

This group of nonpolar solvents is most effective on nonpolar soils including mineral and vegetable oils and grease. All are hydrophobic; water solubility is negligible.

Aromatic hydrocarbon solvents are molecular structures where one or more planar sets of six carbon atoms (a benzene ring) are connected by delocalized electrons numbering the same as if they consisted of alternating single and double covalent bonds. Figure 3.2a and b shows the chemical structures of this type of hydrocarbon and Table 3.2 lists examples of these solvents often used in immersion and manual industrial cleaning operations.

Aromatic solvents are derived from petroleum and coal tar.[2] They have a low to moderate flash point and dry rapidly without leaving residues. These nonpolar hydrophobic solvents are effective at dissolving nonpolar soils including oils, grease, and some resins and rubbers.

TABLE 3.1 Aliphatic Hydrocarbon Solvents

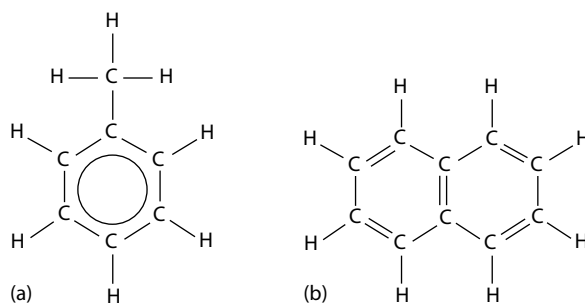| Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	Kauri-Butanol (Kb) Value
Mineral spirits	Mixture	21–54	770	2.0	33–37
Mineral seal oil	Mixture	52	847	<0.01	27.5
Kerosene	Mixture	65	810	0.4	34
Lacquer thinner	Mixture	7	758	38.0	46
Heptane	C_7H_{16}	<−6	696	45.0	29
VM&P naptha	Mixture	11.1	739	52.0	34
Hexane	C_6H_{14}	<−6	676	137.0	30
Turpentine	$C_{10}H_{16}$	34	862	13.4	64
Pine oil	$C_{10}H_{16}$	46	853	1.3	62
d-limonene	$C_{10}H_{16}$	43	841	<2.0	67

FIGURE 3.2 Aromatic HCs: (a) toluene and (b) naphthalene.

TABLE 3.2 Aromatic Hydrocarbon Solvents

Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	Kauri-Butanol (Kb) Value
Toluene	C_7H_8	7	872	22.0	105
Xylene	C_8H_{10}	27	868	5.1	98
Heavy aromatic naptha	Mixture	82	930	<10.0	112

Aliphatic and aromatic solvents are safe to use on virtually all metals, glass, and ceramics. With adequate ventilation, they can be used in immersion and manual cleaning applications and spent solutions can be reclaimed by distillation.

Halogenated solvents have one or more of the hydrogen atoms replaced with chlorine (Cl), fluorine (F), or bromine (Br). Many, but not all, of these solvents are self-extinguishing, have low surface tension for good penetration in tight spaces, and evaporate rapidly without leaving a residue. They are nonpolar and solubilize or swell nonpolar soils including oils, grease, flux, adhesive, and paint. They have worker exposure limits as defined by the Occupational Safety and Health Administration (OSHA) and some have ozone-depleting potential (ODP).

Examples of halogenated solvents are listed in Table 3.3. These solvents are typically used in vapor, immersion, or manual cleaning applications for the removal of nonpolar soils including oils, grease, resins, waxes, pitch, and tar; they are ineffective on inorganic and polar soils. A typical chemical structure is shown in Figure 3.3.

Halogenated cleaning agents are compatible with virtually all metals, glass, and ceramic substrates. They clean by solubilization or swelling and may be reclaimed by distillation. For many halogenated

TABLE 3.3 Halogenated Solvents

Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	Kauri-Butanol (Kb) Value
Trichloroethane	CH_3CCl_3	None	1340	100	124
Chloroform	$CHCl_3$	None	1484	159	115
Trichloroethylene	$ClCH=CCl_2$	None	1470	57.8	129
Perchloroethylene	C_2Cl_4	None	1620	18.2	92
Methylene chloride	CH_2Cl_2	None	1327	350.0	136
n-Propyl bromide	C_3H_7Br	None	1350	111.0	129
Decafluoropentane	$C_5H_2F_{10}$	None	Exempt	226.0	NA
Methyl nonafluoroether blend	Mixture	None	Exempt	202.0	NA

Note: NA, not available.

solvents, inhibitors are added at the point of manufacture to forestall the formation of acids (HCl, HBr); care must be taken to insure that redistillation leaves an adequate level of inhibitor to make sure corrosion and stability problems do not arise during reuse.

FIGURE 3.3　Halogenated HC.

Oxygenated solvents are a series of petroleum-derived oxidates composed of organic acids and esters. They contain oxygen (O) in addition to carbon and hydrogen as shown in Figure 3.4a and b. Examples listed in Tables 3.4 through 3.7 are polar solvents miscible with water; they have a broad range of flash points and all dry residue-free.

- Alcohols are a broad class of these hydroxyl ($^-$OH) containing organic solvents that occur naturally in plants or are made synthetically from petroleum derivatives. Being polar solvents, these fluids are effective in removing polar soils including finger prints, synthetic coolants, flux, and some inks.
- Depending on the chemical blend, alcohols may be used in immersion or manual processes when applied straight. When mixed with water, they may also be sprayed. Table 3.4 lists examples and comparative chemical data of these chemicals. These alcohols are flammable or combustible and must be used with adequate ventilation for optimum worker safety. All evaporate completely and dry residue-free. They are miscible with water and can be diluted further with water or water-rinsed depending on the process involved.
- Glycol ethers are a group of solvents based on alkyl ethers of ethylene glycol or derived from diethylene glycol. They have excellent solvency, chemical stability, and are compatible with water and many organic solvents. Examples are given in Table 3.5. Shown structurally in Figure 3.4c, these solvents have a characteristically sweet odor and taste. They are hygroscopic, compatible with virtually all metals, glass, and ceramics, and are effective on polar and many nonpolar soils. Used straight, they can be applied by immersion and manual methods. When diluted with water they can also be applied by spray-in-air processes.
- Glycols are classified as the "E-Series" of ethylene glycol based solvents or the "P-Series" based on propylene glycol.
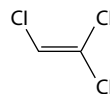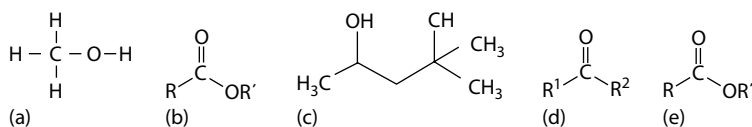
FIGURE 3.4　(a) Oxygenated solvent, alcohol; (b) oxygenated solvent, ester; (c) glycol ether; (d) ketones; and (e) esters.

TABLE 3.4　Alcohol Solvents

Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	Kauri-Butanol (Kb) Value	HAPs
Isopropanol	C_3H_8O	12	Exempt	44.00	50	No
Methanol	CH_4O	12	791	125.00	NA	Yes
Benzyl alcohol	C_7H_8O	93	1050	0.15	NA	No
Cyclohexanol	$C_6H_{12}O$	63	960	0.98	NA	No
Ethanol	C_2H_6O	13	789	60.00	NA	No
Butanol	$C_4H_{10}O$	37	810	5.00	NA	No
Phenol	C_6H_6O	79	1070	0.35	NA	Yes

Note: HAPs, hazardous air pollutants; NA, not available.

TABLE 3.5 Glycol Solvents

Series	Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	HAPs
E	Glycol ether EB	$C_6H_{14}O_2$	72	902	0.60	No
E	Glycol ether DB	$C_8H_{18}O_3$	106	955	0.06	No
E	Glycol ether DB acetate	$C_{10}H_{20}O_4$	116	980	0.01	No
P	Propylene glycol	$C_3H_8O_2$	99	1036	0.13	No
P	Glycol ether TPM	$C_{10}H_{22}O_4$	121	962	0.03	No
P	Glycol ether DPnB	$C_{10}H_{22}O_3$	100	912	0.02	No
P	Glycol ether DPnP	$C_9H_{20}O_3$	88	922	0.05	No

TABLE 3.6 Ketones

Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	HAPs
Acetone	C_3H_6O	−20	Exempt	400	No
Methyl ethyl ketone (MEK)	C_4H_8O	−9	810	78	Yes
Methyl isobutyl ketone (MIBK)	$C_6H_{12}O$	14	800	16	No

TABLE 3.7 Esters

Common Name	Chemical Formula	Flash Point, °C	VOC, g/L	Vapor Pressure, mmHg at 20°C	HAPs
Methyl acetate	$C_3H_6O_2$	−10	Exempt	170	No
Amyl acetate	$C_7H_{14}O_2$	23	876	5	No
n-Butyl acetate	$C_6H_{12}O_2$	26	882	15	No
n-Propyl acetate	$C_5H_{10}O_2$	14	900	23	No
Dibasic ester	$C_7H_{12}O_4$	100	1092	0.20	No

- Ketones are compounds that contain a carbonyl group (C=O) bonded to two other carbon atoms. They are derived by oxidation of secondary alcohols, have low flash points, and are fast evaporating with no residues. Typically used in immersion or manual cleaning applications, ketones are safe to use on virtually all metals, glass, and ceramics and are effective on a broad spectrum of soils including glues and adhesives, inks, resins, and waxes. These solvents tend to be hygroscopic and effectively solubilize polar and some nonpolar soils. A typical chemical structure is shown in Figure 3.4d and examples are listed in Table 3.6.
- Esters are organic compounds that are derived from acids by the exchange of the replaceable hydrogen atom with an organic radical, usually a reaction of an acid with an alcohol. Where an inorganic or organic acid where one hydroxyl group (−H) is replaced with an alkyl group (–O–), the preparation process is called a condensation reaction or esterification.

Many naturally occurring fats and oils are the fatty acid esters of glycerol. Typical esterified acids include carboxylic acids, phosphoric, sulfuric, nitric, and boric acids. The ester structure is shown in Figure 3.4e and typical examples are listed in Table 3.7.

Esters are multimetal safe and effective at removing reactive soils including inks, glues, and adhesives. They are typically not water soluble and have boiling points higher than similar molecular weight hydrocarbons. Most are VOC reportable and many have a characteristic fruity odor; the low-viscosity essential oils are frequently used as fragrances in cleaning agents.

Local municipalities govern the manner of disposal of spent cleaning solutions containing oxygenated solvents. Depending on the contaminants introduced into the wash bath, most wash bath solutions are disposed of as nonhazardous wastes by licensed waste haulers. Frequently rinse waters are permitted to be disposed of by local publically owned treatment works (POTWs).

Cleaning Agent Chemical Components

Cleaning agents contain typical building blocks; components are selected depending on the contaminants involved, the degree of cleanliness needed, and the market segment being served. In addition to the base solvent, chemical component categories include surfactants, pH modifiers, stabilizers, conditioners, inhibitors, viscosity modifiers, odorants, dyes, and surface sanitizers.

Surfactants

Surface-active agents, also called surfactants, are a family of organic compounds, both natural and synthetic, that are added to cleaning agents to reduce surface and interfacial tension to enhance cleaning efficiency, lubrication, wetting, solvency, and rinsing properties of a fluid.[3] As shown in Figure 3.5, surfactants reduce surface tension and enhance the wetting properties of a cleaning agent, allowing the agent to penetrate tight areas and undercut soils.

A surfactant or amphiphile is a linear molecule with a hydrophilic (water loving) head and a hydrophobic (water hating) tail, as shown in Figure 3.6. This characteristic enables them to be soluble in both polar and nonpolar solutions.

During the washing process, once an amphiphile stops functioning as a monomer, it starts functioning as a micelle. This point is called the critical micelle concentration (cmc). The hydrophobic tails form the core that encapsulates nonpolar substances while the hydrophilic heads form an outer shell that maintains contact with water or other polar substances. The average number of amphiphile molecules in a single micelle is described as the aggregate number (m). The (cmc) and (m) together characterize the micelle the amphiphile will form under a given set of conditions, spherical or planar, as shown in Figure 3.7.

Some generalizations made about micelles are the following:

1. As chain length increases, water solubility decreases.
2. Single micelle chain amphiphiles have a higher cmc than two carbon chain micelles.
3. Ionic solutions have greater solubility and higher cmc than nonionic solutions.
4. Ionic solutions have greater rejection forces between polar groups than nonionic solutions.

Water molecules dissociate into H^+ and OH^-, allowing the positive ions to equilibrate among protonatable groups (those groups of molecules capable of adding protons) and making them convenient ions for the creation of electrical potential differences. Hydrogen bonds are fairly strong so in air–water mixtures, molecules orient themselves with higher bonding potential in the center and lower bonding potential on the edges. To increase the entropy of the system, water minimizes its surface area, resulting in high surface tension.

Nonpolar molecules do not form hydrogen bonds. The bonding potential of neighboring water molecules is negligible. They do not attract each other; rather they are pushed together as they are mutually rejected from the water. This is called the hydrophobic effect.

Nonionic solutions form micelles with smaller surface areas per amphiphile. Increase in ionic strength decreases rejection forces between polar groups in an ionic solution while m increases.
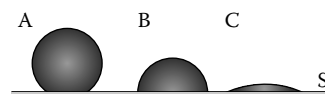

FIGURE 3.5 Wetting agent effect.

Hydrophilic (ionic) head
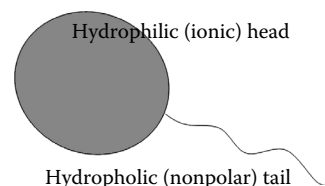
Hydropholic (nonpolar) tail
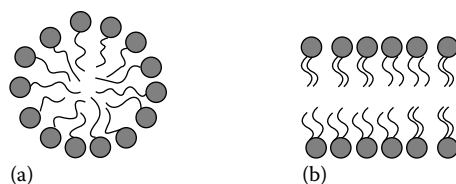
FIGURE 3.6 Amphiphile.

FIGURE 3.7 Spherical and planar micelle structures.

In addition to surface tension modification, surfactants may also be used as antistats, antifoaming agents, bacteriastats, corrosion inhibitors, detergents, dispersants, emulsifiers, foaming agents, or soaps.

There are four general classifications of synthetic surfactants: anionic, cationic, nonionic, and amphoteric.

Nonionic surfactants are materials that carry no electrical charge. Their water solubility is driven by the presence of polar functionalities capable of hydrogen bonding with water. Accounting for 45% of industrial production, nonionic surfactants offer formulation flexibility and include the following list of materials:

Glycerides	Glycol esters	Fatty amine ethoxylates
Block copolymers	Glycerol esters	Ethoxylated propoxylated copolymers
Alkanolamides	Polyglycosides	Alkylphenol ethoxylates
Amine oxides	Alcohol ethoxylates	Polyoxyethylene-based materials
Polyglycerides	Fatty acid ethoxylates	Polyglycerol polyol derivatives
Glucosides	Sucrose esters	Sorbitan esters (ethoxylates)

Materials can be selected based on foaming characteristics and cloud points to customize cleaning agent compositions as desired. Often a combination of materials is used.

Anionic surfactants are a group of materials that carry a negative charge on the active portion of the molecule. These surfactants make up approximately 50% of the world production and include the following list of materials:

Sulfate esters	Aliphatic sulfonates	Sulfated fatty acid condensation products
Fatty alcohol sulfates	Alkylaryl sulfonates	α Sulfocarboxylic acids/derivatives
Sulfated ethers	Carboxylate soaps	Alkyl glyceryl ether sulfonates
Sulfated fats and oils	Lignosulfonates	Miscellaneous sulfo esters and amides
Sulfonic acid salts	Phosphate esters	

As a general rule, anionic surfactants exhibit superior wetting and emulsifying properties while tending to be higher foaming materials.

Cationic surfactants are a group of materials carrying a positive charge on the active portion of the molecule. They include the following:

Imidazoline derivatives	Pyridines	Quaternary ammonium compounds
Betaines	Morpholines	

These materials have excellent antibacterial properties, provide corrosion protection, and are used as demulsifiers.
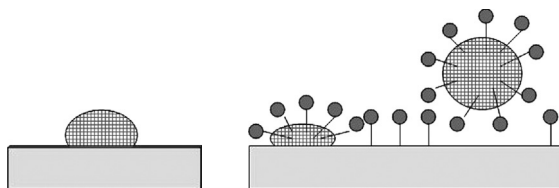
FIGURE 3.8   The cleaning process.

Amphoteric surfactants are a group of materials that can be either cationic or anionic depending on the solution pH. This group includes Zwitteronic types that possess permanent charges of each. Included are the following materials:

Imidazoline derivatives	Amine condensates	Quaternary ammonium compounds
Betaines	Sulfobetaines	Phosphatides

At low or acid pH, these materials function as cationic surfactants and at high alkaline pH, they are anionic. When formulated into cleaning agents, these surfactants function as bacteriastats and tend to be high foaming.

The formulator has many hundreds of surfactants to choose from to customize the wetting, emulsifying, and foaming characteristics most required to meet any cleaning need. Once the cleaning agent reaches the soil, it encapsulates and lifts the soil from the surface and dissolves or disperses it in the cleaning solution as shown in Figure 3.8. Most aqueous cleaning agents contain one or more surfactants to aid the cleaning process and to facilitate water rinsing.

Key considerations when selecting a surfactant package include the pH of the solution, the soils to be removed, the water source identified, and the foaming properties that are compatible with the cleaning application selected.

Stabilizers and Inhibitors

Stabilizers and corrosion inhibitors[4] are often included in a cleaning agent formulation. Solvent stabilizers serve to prevent solvent breakdown and to chemically inhibit reactions that may degrade solvent properties. They are used as pH acceptors, metal inhibitors, and antioxidants. Stabilizers commonly found in hydrocarbon solvent blends are listed in Table 3.8.

Many of these stabilizers are present at volumetrically inconsequential levels to be considered upon disposal, however when the solvents are distilled for reuse, sump life may be shortened due to lack of a sufficient stabilizer. Major manufacturers of hydrocarbon solvents take great care to ensure that even trace components meet specification, especially with recycled material.

Inhibitors are defined as agents that slow or interfere with a chemical reaction. In a cleaning agent, they are materials that when added to a fluid, decrease the corrosion rate of a metal. This is accomplished

TABLE 3.8   Hydrocarbon Stabilizers

1,4-Dioxane	2-Methyxy phenol	Pentene oxide	Butoxy methyl oxirane
1,3-Dioxolane	Morpholine	Furanidine	Diisopropylamine
Nitromethane	Thiazoles	*Sec*-Butanol	Butadiene oxide
1,2-Butylene oxide	Glycidyl acetate	Amyl alcohol	Methyl pyrrole
Oxolane	Stearates	Trioxane	Epichlorohydrin
Triethylamine	Ethyl acetate	Aniline	Cyclohexene oxide
1,4-Epoxybutane	Propanol	Isocyanates	

TABLE 3.9 Inhibitors

Hexamine	Silicates	Phenylenediamine
Hydrazine	Nitrites	Carboxylates
Ascorbic acid	Chromates	Dimethylethanolamine
Zinc oxide	Morpholine	Condensation products of aldehydes
Sulfonates	Phosphates	Monoethanolamine
Complex amines	Triazoles	Triethanolamine

by the formation of a passivation layer or thin film, by inhibiting oxidation or reduction of the redox system, or by scavenging the dissolved oxygen. Inhibitors may be grouped as water soluble, water displacing, or emulsion chemistries.

The most practical inhibitor chemistries provide indoor protection up to 6 months. These compounds are compatible with aqueous cleaning agents and often the inhibitor package is formulated directly into the cleaner composition. The amount of inhibitor present in the bath dictates the length of protection enjoyed. Sometimes inhibitors are added sump-side to enhance protection of an existing composition or to provide inhibition to a rinse solution. Some examples are listed in Table 3.9.

Barrier films like paints, lacquers, and oils are also used for short- or long-term corrosion during storage.

Conditioners

Aqueous cleaning agents contain water or are designed to be diluted further with water prior to use. Use solutions may contain up to 99% water. For the most part, aqueous concentrates are made with distilled or deionized water to minimize the amount of dissolved solids added to the mixture.

Water that contains dissolved minerals will leave a residue upon evaporation. Minerals such as calcium (Ca) or magnesium (Mg) can react with carbonates and soaps to form insoluble scum and scale. To prevent this reaction from occurring, cleaning agents are formulated with sequestering agents or chelators, materials used to tie up the offending elements.

Water hardness varies considerably across the United States and the world. Figure 3.9 shows a map[5] of these variations. Water solids will increase dramatically over time, doubling every 4 weeks. These accumulated solids can cause spotting on polished surfaces and can cause scale build up in the washing equipment and on plumbing surfaces. Chlorides, sulfates, and dissolved copper act as catalysts and can enhance the corrosion potential of the water.

Depending on the water source used, hard water salts or other solids may need to be managed for optimum performance. Common chelating materials used to condition aqueous cleaning fluids are listed in Table 3.10. Conditioners may be selected based on their performance at managing hard water salts or they may be chosen for their ability to manage metal oxides. Often a combination of components is used depending on the cleaning job involved.

Water conditioners and metal chelators control oxidation and scale formation. They may, however, interfere with subsequent effluent treatment if heavy metals are involved. The local POTW may have regulations concerning the use of chelation materials; it is best to check with local officials concerning waste disposal issues.

pH Modifiers

pH[6] is a measure of acidity or basicity of a solution that contains water. It is the co-logarithm of the activity of dissolved hydrogen (H^+) ions. The pH scale is not an absolute scale; it is relative to a set of standard solutions whose pH is established by international agreement. It is generally thought that "p" is a constant that stands for "negative logarithm." "H" stands for hydrogen. It can be measured potentiometrically if
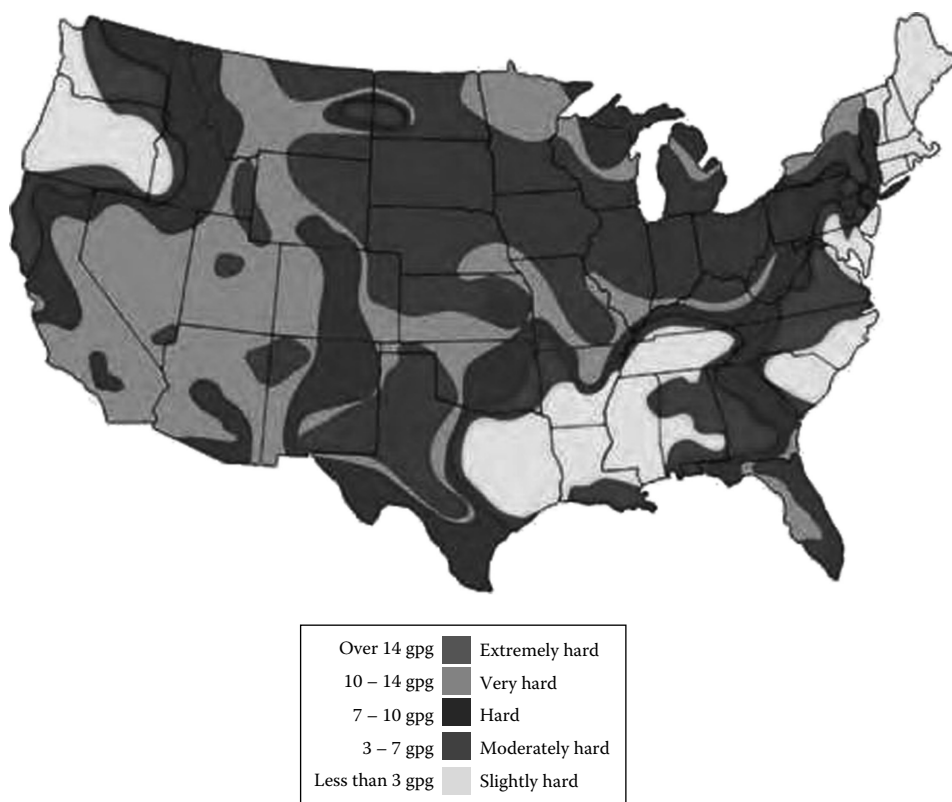
Over 14 gpg ▨ Extremely hard
10 – 14 gpg ▨ Very hard
7 – 10 gpg ■ Hard
3 – 7 gpg ▨ Moderately hard
Less than 3 gpg ▨ Slightly hard

FIGURE 3.9   Water hardness, map of the United States.

TABLE 3.10   Common Conditioners and Sequestration Rates

Conditioner	Calcium Ion Sequestration Rate, mg/g	Calcium Carbonate Sequestration Rate, mg/g	Iron Sequestration Rate, mg/g
EDTA, 30%	41	103	
NTA	63	158	
HEEDTA, 41%	48	120	14.5
STPP	52	250	
ATMP, 50%	183	325–590	
Sodium gluconate	13	33	334
Sodium glucoheptanate	22	55	393

Notes: All percentages are expressed in w/v. EDTA, ethylenediamine tetraacetic acid; NTA, nitrilotriacetic acid; HEEDTA, hydroxyethyl ethylenediamine triacetic acid; STPP, sodium tripolyphosphate; ATMP, amino tri(methylene phosphonic acid).

an electrode is calibrated with a solution of known hydrogen ion concentration. pH paper and indicator solutions can be used for rough estimates of pH. The simplest (although not complete) differential between an acid and a base is that an acid is a proton donor and a base is a proton acceptor.

Pure water is said to have a neutral pH of 7. Solutions with a pH less than 7 are acidic and liquids having a pH greater than 7 are basic. Materials that do not contain water cannot be measured by pH; K_b value is used instead.

Aqueous cleaning agents contain acids or alkalinity builders depending on the pH and application of the cleaner. Neutral cleaners will have a pH in the 5–9 range. Acid cleaners will have a pH less than 5. Alkaline cleaners will have a pH greater than 9. Organic or mineral acids are used to lower the pH while alkalinity builders and hydroxides are added to raise the pH.

Acid cleaners are used to remove inorganic soils like rust, scale, and metal oxides, usually by solubilizing or chemically digesting the soils. Some acids have more than one pK_a because they are polyprotic; they have more than one proton per molecule. These cleaners may contain mild organic acids, caustic mineral acids, or a combination of acids selected to target a specific set of soil conditions. Some of these acids are listed in Tables 3.11 and 3.12. As a general rule, strong acids have a low pH and a low pK_a while weak acids have a higher pH and a higher pK_a value. Multiple pK_a values offer a wider range of strength and buffering potential, thus making them effective on a broader range of soils while providing greater soil holding potential, resulting in longer bath life.

Alkaline cleaners contain bases, alkalis, or hydroxides. A base is any chemical compound that, when dissolved in water, gives a solution having a pH greater than 7. It is the opposite of an acid; the hydronium ion (H_3O^+) concentration is reduced. An alkali[7] is a basic ionic salt of an alkali metal or alkaline earth metal that is water soluble and forms hydroxide ions (OH^-). A strong base hydrolyzes completely raising the pH toward 14. In chemistry hydroxides refer to any inorganic compounds that contain the hydroxyl group. While acids are "corrosive," strong bases are "caustic," capable of burning, corroding, dissolving, or eating away by chemical action.

Some general properties of alkaline cleaners include the following:

1. They are moderately concentrated with a pH 10 or greater.
2. Some concentrated solutions may cause caustic burns.

TABLE 3.11   Mineral Acids

Acid Type	Acid	Formula	pH, 1.0 M Approx.[a]	pK_a[b]
Mineral	Sulfuric	H_2SO_4	<1	−3, 1.99
	Phosphoric	H_3PO_4	1.5	2.15, 7.20, 12.35
	Hydrochloric	HCl	<1	−4
	Hydrofluoric	HF	<1	3.2
	Nitric	HNO_3	<1	−1
	Chromic	H_2CrO_4	<1	0.74, 6.49

[a] All pH values are based on 1 M solutions at ambient temperature.
[b] pK_a is the acidity constant or acid dissociation constant, a quantitative measure of the strength of an acid; a logarithmic scale $-\log 10\ K_a$.

TABLE 3.12   Organic Acids

Acid Type	Acid	Formula	pH, 1.0 M Approx.[a]	pK_a[b]
Organic	Citric	$C_6H_8O_7$	2.2	3.13, 4.76, 6.40
	Acetic	$C_2H_4O_2$	2.4	4.75
	Sulfamic	H_3NSO_3	1.2	1.04
	Boric	H_3BO_3	5.1	9.27, 12.7, 13.8
	Ascorbic	$C_6H_8O_6$	3	4.10
	Formic	H_2CO_2	1.9	3.75
	Carbonic	H_2CO_3	2.1	6.37, 10.25

[a] All pH values are based on 1 M solutions at ambient temperature.
[b] pK_a is the acidity constant or acid dissociation constant, a quantitative measure of the strength of an acid; a logarithmic scale $-\log 10\ K_a$.

3. They are slippery to the touch due to saponification of fatty acids on the skin.
4. They are water soluble.
5. They are measured on the pH scale.

Ammonia and amine materials are bases but not alkalis.

Alkalinity builders are a group of basic materials used to raise the pH of a cleaning agent. They are commonly found in aqueous and some oxygenated hydrocarbon compositions to provide detergency. Some of the commonly used builders include those listed in Table 3.13. The formulator can select the alkalinity builder package best suited for the performance objectives of the cleaning agent. Often a combination of compounds is built into a composition to provide optimum detergency on the substrates involved. Alkalinity builders are selected based on the substrates involved, the soils being removed and the regulatory concerns governing the cleaning process.

Amines are a class of organic compounds containing nitrogen that are derived from ammonia (NH_3) when one or more of the hydrogen atoms is/are replaced with an alkyl group. They may be primary, secondary, tertiary, or complex depending on the number of hydrogen atoms replaced.

Amine-based cleaning agents are alkaline having a pH ranging from 7.5 to 13. Amine-based cleaners can fall in the neutral pH range, generally classified as having a pH up to 9. And neutral pH cleaners can contain a limited amount of alkalinity builders as well. In fact, most do. Each will chemically react with organic acids to form amine soaps. When used in aqueous and semiaqueous compositions, these materials are used to saponify or neutralize acidic soils such as flux, paste, animal and vegetable oils, grease, etc. They also contribute to pH control, buffering, and corrosion inhibition. Unlike mineral or metallic soaps formed during saponification with hydroxides, organic amine soaps have a higher hydrophilic-lipophilic balance (HLB) and therefore are more water-soluble and easier to rinse with water.

Alkaline salts commonly used in the formulation of cleaning agents include phosphates, carbonates, and silicates. Sodium chloride and sodium sulfate are occasionally used as filler materials in powdered

TABLE 3.13   Alkalinity Builders

Alkalinity Builder	Chemical Formula	pH, 1 M Approx.	pK_b[a]
Calcium hydroxide	$Ca(OH)_2$	12.2	2.43, 1.4
Lithium hydroxide	LiOH	14	−0.36
Potassium hydroxide	KOH	>13	0.5
Sodium hydroxide	NaOH	>13	0.2
Tetra ammonium hydroxide	Mixture	>13	0.0
Ammonia	NH_3	11.6	4.75
Triethanolamine	$C_6H_9NO_3$	10.5	6.2
Diethanolamine	$C_4H_{11}NO_2$	11.0	4.75
Monoethanolamine	C_2H_7NO	11.7	4.5
2-Amino-2-methyl-1-propanol	$C_4H_{11}NO$	11.5	9.8
Sodium carbonate	Na_2CO_3	11.6	6.4, 10.3
Potassium carbonate	K_2CO_3	11.6	6.37, 10.25
Sodium silicate	Na_2SiO_3	11–12.5	Not available
Potassium silicate	K_2SiO_3	11.7	1.92
Sodium metasilicate	Na_2SiO_3	13	1.0
Sodium tripolyphosphate	$Na_5P_3O_{10}$	9.8	Not available
Tetrapotassium pyrophosphate	$K_4P_2O_7$	10–11	Not available
Trisodium phosphate	Na_3PO_4	12–14	2.23

Note: The values given in Tables 3.11 through 3.13 were taken from various books and Internet sources. pH values are based on 1 M solutions.

[a] pK_b is the alkalinity constant or alkalinity dissociation constant; a quantitative measure of the strength of the base solution ($-\log 10\ K_b$).

compositions and some aqueous blends. These cleaning agents may range from neutral to highly alkaline, all are nonvolatile and do not contribute to reportable volatile organic compounds (VOC). All of these cleaners require water rinsing for complete removal of all product residues. Typical properties are listed in Tables 3.14 through 3.16.

Inorganic hydroxides include the sodium and potassium salts. They are highly basic and corrosive. Some nonferrous alloys including aluminum and zinc are attacked by free hydroxides. Hydroxides are hygroscopic and nonvolatile with no VOC. When mixed with fatty acids, they form mineral or metallic soaps and they require water rinsing for complete removal of all product residues. Some typical properties are listed in Table 3.17.

TABLE 3.14   Phosphates

MW	Common Name	Formula	pH, 1%	pH, 0.1%	P_2O_5/P, %	H_2O, %
380	TSP-12	$Na_3PO_4 \cdot 12H_2O$	11.77	11.23	18.7/8.16	52.1
182	TSP. H_2O	$Na_3PO_4 \cdot H_2O$	11.62	11.41	39.0/17.0	0
164	ANHYD. TSP	Na_3PO_4	11.75	11.43	43.3/18.9	0
120	ANHYD. MSP	NaH_2PO_4	4.66	5.15	59.2/25.8	0
142	ANHYD. DSP	Na_2HPO_4	9.05	8.16	50.0/21.8	0
368	TRIPOLY	$Na_5P_3O_{10}$	9.74	9.70	58.0/25.3	0
266	PYRO	$Na_4P_2O_7$	10.00	9.92	53.3/23.3	0
330	TKPP	$K_4P_2O_7$	10.08	9.82	43.0/18.8	0

Note: MW, molecular weight.

TABLE 3.15   Carbonates

MW	Common Name	Formula	pH, 1%	pH, 0.1%	CO_2, %	Na_2O, %
106	Light ash	Na_2CO_3	10.84	10.73	41.5	58.5
106	Dense ash	Na_2CO_3	11.05	10.82	41.5	58.5
84	Bicarbonate	$NaHCO_3$	8.13	8.19	52.5	37.0
226	Sesquecarbonate	$NaHCO_3 \cdot 2H_2O$	9.85	10.05	38.9	41.2
138	Potassium carbonate	K_2CO_3	11.15	10.73	31.9	68.1 K_2O

Note: MW, molecular weight.

TABLE 3.16   Silicates

MW	Common Name	Formula	pH, 1%	pH, 0.1%	SiO_2, %	Na_2O, %
122	Metasilicate	Na_2SiO_3	12.17	11.66	49.1	50.8
212	Metasilicate pentahydrate	$Na_2SiO_3 \cdot 5H_2O$	12.15	11.5	28.3	29.2
184	Orthosilicate	Na_4SiO_4	12.29	11.83	32.6	67.4
252	Sesquisilicate $\cdot 5H_2O$	$Na_3HSiO_4 \cdot 5H_2O$	12.12	11.61	23.8	36.9

Note: MW, molecular weight.

TABLE 3.17   Hydroxides

MW	Common Name	Formula	pH, 1%	pH, 0.1%	Na_2O, %
40	Caustic soda	NaOH	12.40	12.06	77.4
56	Caustic potash	KOH	12.45	12.02	83.9 K_2O

Note: MW, molecular weight.