

**Green Seal Standard
and Environmental Evaluation
for General-Purpose, Bathroom,
and Glass Cleaners Used for
Industrial and Institutional Purposes**

Prepared for
Green Seal, Inc.

Prepared by
University of Tennessee
Center for Clean Products and Clean Technologies
311 UT Conference Center
Knoxville, TN 37996

October 2, 2000

Table of Contents

PART 1 Green Seal Standard for General-Purpose, Bathroom, and Glass Cleaners Used for Industrial and Institutional Purposes	1-1
1.1 Scope.....	1-1
1.2 Definitions.....	1-1
1.3 Product-Specific Performance Requirements	1-2
1.4 Product-Specific Health and Environmental Requirements.....	1-2
1.4.1 Toxic Compounds.....	1-2
1.4.2 Carcinogens and Reproductive Toxins	1-3
1.4.3 Skin and Eye Irritation.....	1-3
1.4.4 Skin Sensitization	1-4
1.4.5 Combustibility.....	1-4
1.4.6 Photochemical Smog, Tropospheric Ozone Production, and Indoor Air Quality	1-4
1.4.7 Toxicity to Aquatic Life	1-4
1.4.8 Aquatic Biodegradability	1-4
1.4.9 Eutrophication	1-5
1.4.10 Packaging.....	1-5
1.4.11 Concentrates	1-5
1.4.12 Fragrances.....	1-5
1.4.13 Prohibited Ingredients.....	1-5
1.4.14 Training.....	1-5
1.4.15 Labeling Requirements.....	1-6
1.4.16 Animal Testing.....	1-6
PART 2 Survey of General-Purpose Cleaners, Bathroom Cleaners, and Glass Cleaners	2-1
2.1 How Cleaners Work	2-1
2.2 Common Ingredients.....	2-2
2.2.1 Surfactants.....	2-2
2.2.2 Builders, Saponifiers, and Chelating Agents	2-2
2.2.3 Solvents	2-3
2.2.4 Antimicrobials	2-3
2.2.5 Aerosol Propellants	2-5
2.3 Types of Cleaners	2-5
2.3.1 General-Purpose Cleaners	2-5
2.3.2 Bathroom Cleaners	2-6
2.3.3 Glass Cleaners	2-7
2.4 Packaging.....	2-7
2.5 Portion-Control Systems	2-8
PART 3 Environmental Evaluation of Industrial and Institutional Cleaners	3-1
3.1 Raw Material Extraction and Processing.....	3-1
3.1.1 Organic Ingredients	3-2
3.1.2 Inorganic Ingredients	3-4
3.1.3 Summary of the Environmental Impacts of Raw-Material Extraction and Processing.....	3-7
3.2 Chemical Manufacturing.....	3-7
3.2.1 Surfactants.....	3-7
3.2.2 Builders and Chelating Agents	3-10
3.2.3 Solvents	3-13
3.2.4 Antimicrobials	3-13
3.2.5 Aerosol Propellants	3-14
3.2.6 Other Ingredients	3-14
3.2.7 Packaging.....	3-15
3.2.8 Summary of the Environmental Impacts of Cleaning Chemical Manufacturing.....	3-15
3.3 Health and Environmental Issues in Product Distribution.....	3-16
3.4 Cleaner Use.....	3-16

3.4.1 Health and Safety	3-16
3.4.2 Environmental Impacts	3-18
3.4.3 Environmental Impacts and Ingredients	3-18
3.4.4 Summary of Environmental Impacts for Cleaner Use	3-21
3.5 Disposal.....	3-21
3.5.1 Environmental Impacts	3-21
3.5.2 Ingredients.....	3-23
3.5.3 Summary of Environmental Impacts from Disposal of Cleaners	3-28
3.6 Summary of Environmental Evaluation of Cleaning Chemicals	3-28
3.6.1 Surfactants.....	3-30
3.6.2 Builders	3-30
3.6.3 Solvents	3-30
3.6.4 Aerosol Propellants	3-30
3.6.5 Antimicrobials	3-30
3.6.6 Miscellaneous Ingredients.....	3-32
3.6.7 Packaging.....	3-32
PART 4 Existing Standards for Health and Environmental Performance	4-1
4.1 General Standards Related to Human Health	4-1
4.1.1 Toxic Compounds.....	4-1
4.1.2 Carcinogens and Reproductive Toxins	4-4
4.1.3 Skin and Eye Irritation.....	4-5
4.2 Existing Health and Environmental Performance Standards	4-6
4.2.1 Canadian Environmental Choice.....	4-7
4.2.2 Nordic Ecolabeling.....	4-8
4.2.3 Green Seal.....	4-8
4.2.4 State and Local Environmental Purchasing Programs	4-9
4.2.5 EPA Environmentally Preferable Purchasing Program Cleaning Products Pilot Project	4-14
4.2.6 ASTM Standard Guide for Stewardship for the Cleaning of Commercial and Institutional Buildings	4-14
4.2.7 Product Specifications	4-15
4.2.8 Chemical Substitutions	4-15
4.2.9 Internal Ranking Systems	4-15
4.2.10 Summary of Environmental Performance Criteria	4-16
PART 5 Performance Evaluation.....	5-1
5.1 General-Purpose Cleaners	5-2
5.2 Bathroom Cleaners	5-4
5.3 Glass Cleaners	5-5
PART 6 References	6-1
APPENDIX A: EVALUATION OF TOXICITY DATA	
APPENDIX B: HEALTH AND SAFETY DATA	

List of Tables

Table 2.1	Common surfactants.....	2-2
Table 2.2	Common builders, saponifiers, and chelating agents.....	2-3
Table 2.3	Common solvents.....	2-3
Table 2.4	Antimicrobial ingredients.....	2-4
Table 3.1	Flammable or combustible solvents.....	3-19
Table 3.2	Toxicity data for solvents.....	3-19
Table 3.3	Toxicity of antimicrobials.....	3-20
Table 3.4	Aquatic toxicity values.....	3-22
Table 3.5	Anaerobic biodegradation of common surfactants	3-23
Table 3.6	Aerobic biodegradation of surfactants in screening tests	3-24
Table 3.7	Surfactants in the environment.....	3-25
Table 3.8	Acute toxicity of surfactants to aquatic life.	3-26
Table 3.9	Aquatic toxicity of antimicrobials.	3-27
Table 3.10	Qualitative health and environmental impacts of common cleaning ingredients.....	3-29
Table 4.1	Toxicity levels in CPSC regulations.....	4-2
Table 4.2	Toxicity levels given in the TSCA prioritization methodology.....	4-2
Table 4.3	Toxicity levels given in the OSHA regulations.....	4-3
Table 4.4	Toxicity levels given in the OECD classification.....	4-3
Table 4.5	Toxicity levels given in the Globally Harmonized System classification	4-4
Table 4.6	Classification of carcinogens by the EPA.	4-4
Table 4.7	Classification of carcinogens by the IARC.....	4-5
Table 4.8	Environmental labeling/purchasing standards for industrial and institutional cleaners.....	4-7
Table 4.9	Industrial and government product specifications.....	4-15
Table 4.10	Common prohibited and unfavorable ingredients in purchasing/labeling standards.....	4-16
Table 4.11	Common health and environmental criteria.....	4-16
Table 4.12	Acute mammalian toxicity criteria.	4-17
Table 4.13	Aquatic toxicity criteria.	4-17
Table 4.14	Packaging criteria.....	4-18
Table 5.1	Specifications, required minimum cleaning efficiency, and the test methods for general-purpose cleaners.....	5-2
Table 5.2	Test methods, substrates, and soil types for general-purpose cleaners.....	5-3
Table 5.3	Cleaning efficiency specifications for bathroom cleaners.....	5-4

List of Figures

Figure 3.1	Simplified process for manufacturing ammonia	3-5
Figure 3.2	Surfactant manufacturing.....	3-8
Figure 3.3	Simplified manufacturing scheme for nonylphenol ethoxylate.....	3-9
Figure 3.4	Tetrapotassium pyrophosphate manufacturing	3-11
Figure 3.5	Ethylenediaminetetraacetic acid (EDTA) manufacturing	3-12

ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
APE	alkylphenol ethoxylates
APG	alkylpolyglycosides
APME	Association of Plastics Manufacturers in Europe
ASTM	American Society for Testing and Materials
BSCA	Building Service Contractors Association
BCF	bioconcentration factor
BCOP	bovine corneal opacity and permeability
BLS	Bureau of Labor Statistics
BOD	biological oxygen demand
BUWAL	Bundesamt fuer Umwelt, Wald und Landschaft
CGSB	Canadian General Standards Board
CDC	Centers for Disease Control
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CPSC	Consumer Product Safety Commission
CGSB	Canadian General Standards Board
CO ₂	carbon dioxide
CSMA	Chemical Specialties Manufacturers Association
DEA	diethanolamine
DOC	dissolved organic carbon
EC	effect concentration
EDTA	ethylenediaminetetraacetic acid
EO	ethoxylate
EPA	United States Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
ET	EPA's ecotoxicity database
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GSA	General Service Administration
HSDB	Hazardous Substances Data Bank
HDPE	high-density polyethylene
IARC	International Agency for Research on Cancer
IC	inhibition concentration
ISO	International Standards Organization
ISSA	International Sanitary Supply Association
K ₂ HPO ₄	dipotassium hydrogenphosphate
LAB	linear alkylbenzene

LAS	linear alkylbenzene sulfonates
LC ₅₀	lethal concentration to 50% of a population
LD ₅₀	lethal dose to 50% of a population
MJ	megajoules
MSDS	material safety data sheet
NIOSH	National Institutes of Occupational Safety and Health
NTA	nitrilotriacetic acid
NTP	National Toxicology Program
OECD	Organization for Economic Cooperation and Development
ODC	ozone-depleting compound
OSHA	Occupational Safety and Health Administration
OTA	Office of Technology Assessment
PCA	polycarbonate
PEL	permissible exposure limits
PET	polyethylene terephthalate
PCOP	photochemical oxidant production potential
PO	propylene oxide
POTW	publicly owned treatment works
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RTI	Research Triangle Institute
SDB	solvent database
SDA	Soap and Detergents Association
SAE	Society of Automotive Engineers
SM	Sanitary Maintenance
SRI	Steel Recycling Institute
STPP	sodium tripolyphosphate
TBS	tetrapropylene alkylbenzene sulfonate
TG	text guide
ThOD	theoretical oxygen demand
TRI	Toxics Release Inventory
TSCA	Toxic Substances Control Act
TURA	Massachusetts Toxics Use Reduction Act
UV	ultraviolet light
UVB	ultraviolet B light
VOC	volatile organic compound
WMO	World Meteorological Organization

INTRODUCTION

In the United States, cleaning and maintaining office, retail, commercial, industrial, educational, and healthcare facilities is a \$49-billion industry that employs 2.8 million people as maids, housekeepers, janitors, and cleaners (BSCA 1999; BLS 1999a). Cleaning is an essential part of maintaining a healthy, comfortable, and attractive indoor environment. With U.S. sales of cleaning chemicals climbing to \$6.14 billion in 1997 (ISSA and SM 1999), Green Seal believes that it is appropriate to establish an environmental labeling standard for industrial and institutional cleaning products. The standard will help users and purchasers of cleaning chemicals select products that clean effectively while minimizing negative health and environmental effects. Aberdeen Proving Ground is sponsoring this work, and Green Seal expects to pilot the standard with Aberdeen Proving Ground.

The University of Tennessee Center for Clean Products and Clean Technologies worked together with Green Seal to evaluate three classes of industrial and institutional cleaners: general-purpose cleaners, bathroom cleaners, and glass cleaners. Green Seal focused on these three cleaners because they are frequently used and, with annual sales of \$2.38 billion, they represent a large portion of the industrial and institutional cleaner market (ISSA and SM 1999). In performing this evaluation, Green Seal collected information on the ingredients of over 120 products and qualitatively examined their life-cycle environmental impacts. This evaluation is not a quantitative life-cycle assessment as defined by the Society of Environmental Toxicology and Chemistry and the United States Environmental Protection Agency (EPA).

Cleaning promotes a healthy environment. It controls harmful organisms including insects, rodents, and microorganisms that can carry or cause disease in humans. Because people spend the majority of their time indoors, a healthy indoor environment is critical to maintaining human health (Berry 1994). Cleaning also helps maintain a comfortable and attractive environment by controlling odors, soil and dirt and by contributing to orderliness. Finally, cleaning protects valuable materials by removing soils that wear away surfaces.

However, those who are responsible for maintaining a clean indoor environment may be at risk. Individuals whose jobs require the use of cleaning products may be exposed to these products for several hours a day over several years. Some cleaning chemicals can severely damage the skin and eyes, some are readily absorbed through the skin, and some are flammable. The United States Chemical Safety and Hazard Investigation Board lists liquid cleaning compounds among the top twenty causes for chemical incidents, excluding fuels (U.S. Chemical Safety and Hazard Investigation Board 1999).

Cleaning chemicals also affect building occupants and the environment. In particular, volatile cleaning chemicals may contribute to poor indoor air quality, which can cause headaches, dizziness, eye irritation, and fatigue. The extraction, manufacture, and disposal of cleaning chemicals also generate negative environmental impacts. Industrial and institutional cleaners can be toxic to aquatic life, and some ingredients

persist in the environment. Recently, a number of organizations (including EPA; the states of Vermont, Massachusetts, Minnesota, and Washington; the city of Santa Monica, California; King County, Washington; and Santa Clara County, California) have developed environmental purchasing programs for cleaning products (Barron et al. 2000). Such efforts reflect the concerns of purchasers about the effects of cleaners on users, building occupants, and the environment.

In 1993, Green Seal issued a standard for general-purpose household cleaners; this standard and accompanying environmental evaluation laid the groundwork for many of the state and local environmental purchasing programs for cleaners. Green Seal's standard for industrial and institutional cleaners builds on this previous work. The industrial and institutional standard applies to a broader range of products than the household cleaners standard (general-purpose, bathroom, and glass cleaners), and it reflects a greater concern for worker health and safety due to the greater exposure of workers to cleaning chemicals. In developing this standard and evaluation, Green Seal considered new research on cleaning chemicals, particularly on the environmental fate of alkylphenol ethoxylates and the increasing use of antimicrobials.

This document is divided into six parts. The standard, presented in Part 1, is the result of Green Seal's research to define criteria for identifying environmentally preferable industrial and institutional cleaning products. Readers may wish to review the standard first and then review Parts 2 through 5 to understand how Green Seal developed their criteria. Part 2 contains the results of Green Seal's survey of industrial and institutional cleaning products. Part 3 presents the health and environmental impacts of common cleaning ingredients. Existing health and environmental standards and purchasing programs are discussed in Part 4. Green Seal discusses cleaning performance standards and testing in Part 5.

PART 1

GREEN SEAL STANDARD FOR GENERAL-PURPOSE, BATHROOM, AND GLASS CLEANERS USED FOR INDUSTRIAL AND INSTITUTIONAL PURPOSES

1.1 Scope

This standard establishes environmental requirements for industrial and institutional general-purpose, bathroom, and glass cleaners. For purposes of this standard, general-purpose, bathroom, and glass cleaners are defined as those cleaners intended for routine cleaning of offices, institutions, warehouses, and industrial facilities. The standard does not focus on the use of cleaners in households, food preparation operations, or medical facilities.

Due to the large number of possible cleaning products, processes, soil types, and cleaning requirements, the compatibility of cleaners with surface materials is not specifically addressed in this standard. Product users should follow the manufacturers' instructions on compatibility.

Each criterion states whether it applies to the undiluted product or to the product as used.

1.2 Definitions

Bathroom cleaners. This category includes products used to clean hard surfaces in a bathroom such as counters, walls, floors, fixtures, basins, tubs, and tile. It includes products that are required to be registered under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), such as disinfectants and sanitizers, but does not include products specifically intended to clean toilet bowls.

Concentrate. This is a product that must be diluted by at least eight parts by volume water (1:8 dilution ratio) prior to its intended use.

Dispensing-system concentrates. These are products that are designed to be used in dispensing systems that cannot be practically accessed by users.

General-purpose cleaners. This category includes products used for routine cleaning of hard surfaces including impervious flooring such as concrete or tile. It does not include cleaners intended primarily for the removal of rust, mineral deposits, or odors. It does not include products intended primarily to strip, polish, or wax floors, and it does not include cleaners intended primarily for cleaning toilet bowls, dishes, laundry, glass, carpets, upholstery, wood, or polished surfaces. This category does not include any products required to be registered under FIFRA, such as those making claims as sterilizers, disinfectants, or sanitizers.

Glass cleaners. This category includes products used to clean windows, glass, and polished surfaces. This category does not include any products required to be registered under FIFRA, such as those making claims as sterilizers, disinfectants, or sanitizers.

Ingredient. Any constituent of a product that is intentionally added or known to be a contaminant that comprises at least 0.01% by weight of the product.

Ozone-depleting compounds. An ozone-depleting compound is any compound with an ozone-depletion potential greater than 0.01 (CFC 11 = 1).

Product as used. This is the most concentrated form of the product that the manufacturer recommends for a product's intended use. For example, if a manufacturer recommends a product be diluted 1:64 or 2:64 for use as a general-purpose cleaner, the product shall meet the environmental and performance requirements at a dilution of 2:64.

Primary packaging. This packaging is the material physically containing and coming into contact with the product, not including the cap or lid of a bottle.

Recyclable package. This package can be diverted from the waste stream through available processes and programs, and can be collected, processed, and returned to use in the form of raw materials or products.

Undiluted product. This is the most concentrated form of the product produced by the manufacturer for transport outside its facility.

1.3 Product-Specific Performance Requirements

Each product *as used* when diluted with water from the cold tap at no more than 50 °F, shall clean common soils and surfaces in its category effectively, as measured by a standard test method. Green Seal recommends the following test methods:

General-purpose cleaners. The product shall remove at least 80% of the particulate soil in the American Society for Testing and Materials (ASTM) D4488-95, A5.

Bathroom cleaners. The product shall remove at least 75% of the soil in ASTM D5343 as measured by ASTM D5343.

Glass cleaners. The product shall achieve at least a rating of three in each of the following Chemical Specialties Manufacturers Association (CSMA) DCC 09 categories: soil removal, smearing, and streaking.

Using standard test methods, a manufacturer can also demonstrate that its product performs as well as a nationally recognized product in its category or achieves the removal efficiency defined in this section.

1.4 Product-Specific Health and Environmental Requirements

1.4.1 Toxic Compounds

The *undiluted* product shall not be toxic to humans. Dispensing-system concentrates shall be tested as used. A product is considered toxic if any of the following criteria apply:

Oral lethal dose 50 (LD ₅₀)	≤ 2,000 mg/kg
Inhalation lethal concentration (LC ₅₀)	≤ 20 mg/L*

* If the vapor-phase concentration of the product at room temperature is less than 20 mg/L, it should be tested at its saturation concentration. If it is not toxic at this concentration, it passes the inhalation criterion.

Toxicity shall be measured on the product as a whole. Alternatively, a mixture need not be tested if existing toxicity information demonstrates that each of the ingredients complies. Ingredients that are nonvolatile do not require inhalation toxicity testing, and ingredients that are not readily absorbed through the skin do not require dermal toxicity testing (Appendix A). It is assumed that the toxicity of the individual component compounds are weighted and summed and that there are not synergistic effects (Appendix A).

The toxicity testing procedures should meet the requirements put forth by the Organization for Economic Cooperation and Development (OECD) Guidelines for Testing of Chemicals. These protocols include Acute Oral Toxicity Test (TG 401), Acute Inhalation Toxicity Test (TG 403), and Acute Dermal Toxicity Test (TG 402).

1.4.2 Carcinogens and Reproductive Toxins

The *undiluted* product shall not contain any ingredients that are carcinogens or that are known to cause reproductive toxicity. Carcinogens are defined as those chemicals listed as known, probable, or possible human carcinogens by the International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP), the U.S. Environmental Protection Agency, or the Occupational Health and Safety Administration. Chemicals known to cause reproductive toxicity are defined as those listed by the State of California under the Safe Drinking Water and Toxic Enforcement Act of 1986 (California Code of Regulations, Title 22, Division 2, Subdivision 1, Chapter 3, Sections 1200, *et seq.*).

Naturally occurring elements and chlorinated organics, which may be present as a result of chlorination of the water supply, are not considered ingredients if the concentrations are below the applicable maximum contaminant levels in the National Primary Drinking Water Standards found in 40 Code of Federal Regulations (CFR) Part 141.

1.4.3 Skin and Eye Irritation

The *undiluted* product shall not be corrosive to the skin or eyes. Dispensing-system concentrates shall be tested as used. The undiluted cleaning product shall not be corrosive to the skin, as tested using the Human Skin Construct systems (Liebsch et al. 2000; Fentem et al. 1998). The undiluted cleaning product shall also not be corrosive to the eye as tested using the bovine opacity and permeability test (BCOP) (Sina et al. 1995) after a 10-minute exposure. Green Seal will also accept the results of other peer-reviewed or standard in vitro or in vivo test methods demonstrating that the product mixture is not corrosive.

1.4.4 Skin Sensitization

The *undiluted* product shall not be a skin sensitizer, as tested by the OECD Guidelines for Testing Chemicals, Section 406. Dispensing-system concentrates shall be tested as used. Green Seal shall also accept the results of other standard test methods, such as those described in Buehler (1994) or Magnusson and Kligman (1969), as proof that the product or its ingredients are not skin sensitizers.

1.4.5 Combustibility

The *undiluted* product shall not be combustible. The product or 99% by volume of the product ingredients shall have a flashpoint above 150 °F, as tested using either the Cleveland Open Cup Tester (ASTM D92-97) or a closed-cup method International Standards Organization (ISO) 13736 or ISO 2719. Alternatively, the product shall not sustain a flame when tested using ASTM D 4206.

1.4.6 Photochemical Smog, Tropospheric Ozone Production, and Indoor Air Quality

The product *as used* shall not contain substances that contribute significantly to the production of photochemical smog, tropospheric ozone, or poor indoor-air quality. The volatile organic content of the product as used shall not exceed the following

- 1% by weight for general-purpose and bathroom cleaners
- 3% by weight for glass cleaners

The volatile organic content shall be determined by California Air Resources Board Method 310.

1.4.7 Toxicity to Aquatic Life

The product *as used* shall not be toxic to aquatic life. A compound is considered not toxic to aquatic life if it meets one or more of the following criteria:

Acute LC₅₀ for algae, daphnia, or fish ≥ 100 mg/L

For purposes of demonstrating compliance with this requirement, aquatic toxicity testing is not required if sufficient aquatic toxicity data exist for each of the product's ingredients to demonstrate that the product mixture complies. Aquatic toxicity tests shall follow the appropriate protocols in ISO 7346.2 for fish and in 40 CFR 797, Subpart B for other aquatic organisms.

1.4.8 Aquatic Biodegradability

Each of the organic ingredients shall exhibit ready biodegradability in accordance with the OECD definition except for a FIFRA-registered ingredient in a bathroom cleaner. However, all other ingredients in a FIFRA-registered bathroom cleaner must comply. Biodegradability shall be measured by one of the following methods: ISO 9439 carbon dioxide (CO₂) evolution test, ISO 10708 (two-phase closed-bottle test), ISO 10707 (closed bottle test), or ISO 7827 (dissolved organic carbon removal). Specifically, within a 28-day test, the ingredient shall meet one of the following criteria within 10 days of the time when biodegradation first reaches 10%:

Removal of dissolved organic carbon (DOC)	> 70%
Biological oxygen demand (BOD)	> 60%
% of BOD of theoretical oxygen demand (ThOD)	> 60%
% CO ₂ evolution of theoretical	> 60%

For organic ingredients that do not exhibit ready biodegradability in these tests, the manufacturer may demonstrate biodegradability in sewage treatment plants using the Coupled Units Test found in OECD 303A by demonstrating dissolved organic carbon (DOC) removal > 90%.

Testing is not required for any ingredient for which sufficient information exists concerning its biodegradability, either in peer-reviewed literature or databases or proving that the ingredient was tested in accordance with standard test procedures.

1.4.9 Eutrophication

The product *as used* shall not contain more than 0.5% by weight of total phosphorus.

1.4.10 Packaging

The primary package shall be recyclable. Alternatively, manufacturers may provide for returning and refilling of their packages.

1.4.11 Concentrates

The product must be a concentrate, except for FIFRA-registered bathroom cleaners.

1.4.12 Fragrances

Manufacturers shall identify any fragrances on their material safety data sheets (MSDSs). Any ingredient added to a product as a fragrance must follow the Code of Practice of the International Fragrance Association.

1.4.13 Prohibited Ingredients

The product shall not contain the following ingredients:

- Alkylphenol ethoxylates
- Dibutyl phthalate
- Heavy metals including arsenic, lead, cadmium, cobalt, chromium, mercury, nickel, or selenium
- Ozone-depleting compounds

1.4.14 Training

The product manufacturer, its distributor, or a third party shall offer training or training materials in the proper use of the product. These shall include step-by-step instructions for the proper dilution, use, disposal, and the use of equipment. Manufacturers shall have product labeling systems to assist non-English-speaking or illiterate personnel.

1.4.15 Labeling Requirements

The manufacturer's label shall state clearly and prominently that dilution with water from the cold tap is recommended and shall state the recommended level of dilution. The manufacturer shall also include detailed instructions for proper use and disposal and for the use of personal protective equipment.

Whenever the Green Seal certification mark appears on a package, the package shall contain a description of the basis for certification. The description shall be in a location, style, and typeface that are easily readable. Unless otherwise approved in writing by Green Seal, the description shall read as follows:

“This product meets Green Seal's standards for industrial and institutional cleaners based on its reduced human and aquatic toxicity and reduced smog production potential.”

For FIFRA-registered bathroom cleaners, replace “toxicity” with the word “impacts”.

1.4.16 Animal Testing

This section applies to Sections 1.4.1, 1.4.3, and 1.4.8. Green Seal wants to discourage animal testing and will accept the results of past peer-reviewed or standard tests demonstrating compliance with a criterion. A mixture need not be tested if existing information demonstrates that each of the ingredients complies with a criterion. Additionally, Green Seal may accept non-animal (in-vitro) test results, providing that the test methods are referenced in peer-reviewed literature and the manufacturer provides the reasons for selecting the particular test method.

PART 2

SURVEY OF GENERAL-PURPOSE CLEANERS, BATHROOM CLEANERS, AND GLASS CLEANERS

Before industrial and institutional general-purpose cleaners, bathroom cleaners, and glass cleaners could be evaluated, Green Seal needed to identify common ingredients and common classes of ingredients for each category of cleaners. To accomplish this, Green Seal gathered composition information for more than 120 products from large and small manufacturers. Some of these products cite their environmental attributes. Product manufacturers supplied MSDSs and some additional composition information. Additional information on ingredient types was obtained from manufacturer associations, trade publications, government publications, and books including Flick (1989) and Berry (1994). The products considered in this study are representative but do not include all products on the market. Appendix B contains a list of all identified ingredients.

These ingredients can be divided into the following classes:

- Surfactants – form the basis of most of the cleaners surveyed. They help dissolve soils.
- Builders – improve the performance of surfactants. These include water softeners, pH modifiers, chelating agents, and saponifiers.
- Solvents – dissolve soils such as oils and grease, making it easier to remove them. They can also reduce streaking on glass surfaces.
- Antimicrobials – kill or inactivate microorganisms on a variety of inanimate hard surface.
- Aerosol propellants – pressurized gasses used to propel a product out of a container.
- Other – includes fragrances, dyes, abrasives, deodorants, and any other substance.

This section discusses how cleaners work, common ingredients, types of cleaners, product packaging, and portion-control systems.

2.1 How Cleaners Work

Cleaners work by dissolving soils and keeping them in solution. Surfactants, builders, and solvents work together to perform these functions. Basically, cleaning solutions are either water based or solvent based, although water-based cleaners can contain such solvents as alcohols or glycol ethers. Organic soils (nonpolar soils) dissolve readily in solvent-based cleaners, whereas polar soils, such as salts, dissolve readily in water-based cleaners. Surfactants assist both polar and nonpolar soils to dissolve and break up in cleaning solutions. The structure of a surfactant has a water-loving (polar)

and a water-hating (nonpolar) end and works on the principle of like dissolves like. When a water-based cleaner containing a surfactant comes into contact with a water-insoluble soil, the nonpolar end of a surfactant dissolves in the water-insoluble soil. The water-insoluble soil becomes surrounded by the nonpolar ends of surfactant molecules. As the polar ends of the surfactant molecules are attracted to water, the water-insoluble soil breaks apart. Now the pieces of the water-insoluble soil are held in suspension by the surfactant solution and are removed with the spent cleaning solution. Builders improve surfactant performance by modifying a solution's pH and tying up hard-water salts; they also prevent suspended soils from redepositing.

2.2 Common Ingredients

2.2.1 Surfactants

A surfactant's molecule has a nonpolar (water-hating) end and a polar (water-loving) end. Surfactants lower a liquid's surface tension so a cleaning solution can penetrate and remove soils. Water will not wet a surface that is even slightly oily, but a mixture of water and surfactant will. Anionic, nonionic, and cationic surfactants are commonly found in cleaning products, although a few products contain amphoteric surfactants. The categories refer to the charge of the polar portion of the surfactant: anionic indicates a negative charge, nonionic no charge, and cationic a positive charge. Amphoteric surfactants can be anionic, nonionic, or cationic depending on the pH of the solution. Cationic surfactants are used as antimicrobials. The most common surfactants are nonylphenol ethoxylate (nonionic), linear alkylbenzene sulfonate (anionic), and alkyl dimethyl benzyl ammonium chlorides (cationic) (Table 2.1). A number of the MSDSs simply listed nonionic, anionic, amphoteric, or cationic surfactants.

Table 2.1 Common surfactants.

Surfactant Type	Examples
Nonionic	Nonylphenol ethoxylate*, alcohol ethoxylates, octylphenol ethoxylate, coconut diethanolamide (cocoamide DEA), unspecified nonionic surfactant
Anionic	Linear alkylbenzene sulfonate* (dodecylbenzene sulfonate), alcohol sulfates (lauryl sulfates), alcohol ether sulfates (lauryl ether sulfates, laureth sulfates), sodium alkyl polyether sulfonate, alkyl polyglycosides, unspecified anionic surfactant, and soap
Amphoteric	Alkylbetaine, unspecified amphoteric surfactant
Cationic	Alkyl dimethyl benzyl ammonium chlorides*, unspecified quaternary ammonium chlorides or compounds, alkylaryl dimethyl ammonium chloride, dimethyl ethyl benzyl ammonium chloride, ethylbenzene ammonium chloride, didecyl dimethyl ammonium chloride, octyl dimethyl ammonium chloride

* Most common.

2.2.2 Builders, Saponifiers, and Chelating Agents

These improve surfactant effectiveness. Builders are typically inorganic metal salts, acids, or bases and provide acidity, alkalinity, and buffering capacity. Saponifiers

convert fatty acids and glycerides to water-soluble soaps. Ethanolamines, carbonates, and silicates aid in saponification. Chelating agents including ethylenediaminetetraacetic acid (EDTA), sodium tripolyphosphate (STPP), and zeolites/polycarbonate (PCA) are used to chemically “tie up” unwanted ions, such as hard-water salts. This prevents these ions from being redeposited on a surface. Table 2.2 summarizes this class of ingredients.

Table 2.2 Common builders, saponifiers, and chelating agents.

Category	Examples
Builders	
Acids	Phosphoric acid*, acetic acid, hydrochloric acid, citric acid
Bases	Sodium hydroxide*, potassium hydroxide
Carbonates	Sodium carbonate*, sodium bicarbonate
Phosphates	Pyrophosphates, polyphosphates, phosphate esters, orthophosphates
Silicates	Sodium metasilicate*, sodium silicate
Saponifiers	Ethanolamines*, carbonates, silicates
Chelating agents	EDTA*, STPP, zeolites/PCA

*Most common.

2.2.3 Solvents

These ingredients dissolve water-insoluble soils such as oil and grease. They are also used to reduce streaking on glass surfaces. Common solvents include alcohols, glycol ethers, and terpenes, such as d-limonene and pine oil (Table 2.3).

Table 2.3 Common solvents.

Class	Examples
Alcohols	Isopropanol*, methanol, ethanol
Glycol ethers	2-butoxyethanol*, diethylene glycol ethyl ether, diethylene glycol monomethylether, 1-methoxy-2-propanol, 2-2-butoxyethoxyethanol, unspecified glycol ethers
Others	d-limonene, pine oil, tall oil, ammonia (ammonium hydroxide), terpene hydrocarbons, propylene glycol, ethylene glycol, 1,3-propanediol

*Most common.

2.2.4 Antimicrobials

These compounds, often called disinfectants or sanitizers, kill or inactivate microorganisms on hard surfaces. Green Seal identified products containing the following antimicrobials: quaternary ammonium compounds, phenols, alcohols, sodium hypochlorite, and pine oil (Table 2.4). Under FIFRA, the EPA regulates products making claims about antimicrobial activity, including products labelled as sanitizers, disinfectants, or sterilizers. FIFRA requires that products making antimicrobial claims be tested to support the claims and patterns of use (40 CFR 162.18-2). Sanitizers and disinfectants are most relevant to industrial and institutional cleaning products. A

sanitizer reduces the number of microorganisms to a safe level, typically a 99.9% to 99.999% reduction in the number of a test population of microorganism. A disinfectant is capable of destroying disease-causing bacteria, but not necessarily spores or viruses. According to the FIFRA definition, a disinfectant must be able to reduce the level of a pathogenic bacteria by 99.999% with 10 minutes of contact time. Antimicrobials begin to act as soon as they contact microorganisms.

Table 2.4 Antimicrobial ingredients.

Category	Concentration ¹	Ingredient
Quaternary ammonium compounds	0.01 - 1%	Alkyl dimethyl benzyl ammonium chlorides ² , unspecified quaternary ammonium chlorides or compounds, alkylaryl dimethyl ammonium chloride, dimethyl ethyl benzyl ammonium chloride, ethylbenzene ammonium chloride, didecyl dimethyl ammonium chloride, octyl dimethyl ammonium chloride
Phenols	2 - 5%	Ortho-benzyl parachlorophenol, ortho-phenylphenol, para-tertiary-amylphenol
Alcohols	70%	Isopropyl alcohol ² , ethanol
Sodium hypochlorite	0.5 - 5%	
Pine oil		

¹ Rutala (1996) and UC Davis (1997).

² Most common.

Quaternary ammonium compounds. The quaternary ammonium compounds were by far the most commonly identified antimicrobials (Table 2.4). Typically, concentrations ranged from 0.01 to 0.15% in their ready-to-use form; however, Green Seal identified a number of product concentrates that contained 1 to 7.5% of quaternary ammonium compound. At these levels, the quaternary ammonium compounds could cause eye and skin damage. They are odorless, non-staining, and non-corrosive to most hard surfaces and tolerate hard water and a range of pH levels. They leave a nonvolatile residue on surfaces, that controls microorganism growth for a period of time. Quaternary ammonium compounds are inactivated if they are used with an anionic surfactant.

Phenols. Only a few products contained phenols. They are tolerant of organic soils. However, they are relatively expensive and can react with plastic surfaces.

Alcohols. A number of products contained alcohols. Alcohols are antimicrobials and can enhance the antimicrobial performance of phenolic and quaternary ammonium compounds. However, alcohols must comprise 60 to 90% of a product to be effective disinfectants by themselves, and none of the products surveyed contained more than 30% alcohol.

Sodium hypochlorite. Sodium hypochlorite was identified in a few products. Sodium hypochlorite is often used alone as a disinfectant, but Green Seal did not consider disinfectants, only disinfecting cleaners. Sodium hypochlorite is highly effective and inexpensive. However, it can corrode metal surfaces and is inactivated by organic soils.

Sodium hypochlorite loses its strength with time and cannot be stored in a dilute form. It also reacts with ammonia to form toxic chlorine gas.

Pine oil. Pine oil was identified in only a few products. It is commonly used as a household disinfectant.

2.2.5 *Aerosol Propellants*

These pressurized gasses are found in aerosol cans and are used to propel a product out of the container. Common propellants include butane, isobutane, liquified natural gas, and propane.

2.3 **Types of Cleaners**

Some of the products do not fall neatly into a single category, so the products were grouped according to the manufacturers' descriptions. If the products were described by the manufacturer solely as a disinfectant, they were not included in the survey. However, if the product was described as a disinfecting cleaner, it was included in the survey. Green Seal grouped cleaners into three categories: general-purpose cleaners, bathroom cleaners, and glass cleaners. These categories are described below.

2.3.1 *General-Purpose Cleaners*

General-purpose cleaners are designed to remove a variety of soils from a range of hard surfaces. Common soils encountered in general-purpose cleaning include oils, food, wax, humus, sand, rust, soot, and street dirt. General-purpose cleaners are used to clean hard surfaces such as walls, floors, counters, fixtures, and furniture.

The majority of products are liquid cleaners, some are powders, and a few are aerosols. Many of the products contain low concentrations of volatile organic compounds (VOCs) (Green Seal 1999). A number of products are concentrates and are diluted before use. These products are available in a variety of packages, from 12-ounce trigger spray bottles to 55-gallon drums.

Common ingredients include

- Surfactants – nonylphenol ethoxylate, coco alkyldimethyl amine, and alkyl polyglycosides.
- Builders – EDTA, sodium carbonate, sodium metasilicate, and sodium hydroxide.
- Solvents – alcohols, glycol ethers, and di-limonene.
- Antimicrobials – quaternary ammonium compounds.

Flick (1989) and Hill et al. (1997) present the following formulation for general-purpose cleaners:

Powdered General-Purpose Cleaner (Flick 1989)		General-Purpose Cleaner (Hill et al. 1997)	
Ingredient	Percentage	Ingredient	Percentage
STPP or sodium carbonate	40%	Water	55 - 94%
Sodium sulfate	30%	Surfactants	5 - 10%
Surfactant	20%	Builders	1 - 29%
Sodium silicate	10%	Solvents	0 - 5%
Fragrance	-	Miscellaneous	< 1%

2.3.2 Bathroom Cleaners

Bathroom cleaners are designed to remove soils from bathroom fixtures, tile, toilets, showers, and bathtubs. Common soils encountered in bathroom cleaning include soap scum, hair, dust, sand, street dirt, oil, grease, and hard-water deposits, such as calcium and rust (Coons et al. 1987). The majority of products are liquid cleaners, and a few are aerosols. A number of products are concentrates and must be diluted before use. These products are available in a variety of packages, from 12-ounce trigger spray bottles to 55-gallon drums.

Bathroom cleaners contain disinfectants, acids, and abrasives more frequently than do general-purpose cleaners. Hydrochloric and phosphoric acid are common ingredients. The acids help to remove hard-water deposits. However, because acid cleaners can damage enamel finishes, they are not suited to all bathroom surfaces. Mild abrasives and scouring powders, including quartz and cellulose, help to remove soap scum and other soils. Common ingredients include

- Surfactants – nonylphenol ethoxylate and alkylbenzene sulfonate.
- Builders – EDTA, sodium metasilicate, and sodium hydroxide.
- Solvents – glycol ethers and alcohols.
- Antimicrobials – quaternary ammonium compounds.

Two example formulations for bathroom cleaners follow:

Non-Acid Cleaner (Flick 1989)		Acid Cleaner (Hill et al. 1997)	
Ingredient	Percentage	Ingredient	Percentage
Water	97.1%	Water	74 - 93%
Surfactant	1.5%	Solvent	2 - 9%
Sodium carbonate	0.8%	Surfactants	2 - 8%
Potassium hydroxide	0.6%	Acids	3 - 6%
		Builders	0.5 - 2%

2.3.3 Glass Cleaners

Glass cleaners are designed to remove soils from glass and other polished surfaces. Common soils include grease, oil, fingerprints, dust, and water spots. The majority of products are liquid cleaners, and a few are aerosols. A number of products are concentrates and must be diluted before use. These products are available in a variety of packages, from 12-ounce trigger spray bottles to 55-gallon drums. Glass cleaners are applied using either a trigger spray bottle or an aerosol can.

The major ingredient in liquid glass cleaners is water. Glass cleaners tend to contain a higher concentration of solvents, ranging from 1.0 to 20%. In addition, many glass cleaners contain glycol ethers (particularly 2-butoxyethanol), surfactants, and alcohol. Although aerosol glass cleaners have similar ingredients, they also contain a compressed-gas propellant. Glass cleaners rarely contain disinfectants. Common ingredients include

- Surfactants – sodium lauryl sulfate and nonylphenol ethoxylate.
- Solvents – glycol ethers (2-butoxyethanol), isopropanol, ammonia (ammonium hydroxide), and ethanol.
- Aerosol propellants – isobutane and propane.

Flick (1989) provides the following examples of non-aerosol ammonia and vinegar-based glass cleaners.

Ammonia-Based Glass Cleaner		Vinegar-Based Glass Cleaner	
Ingredient	Percentage	Ingredient	Percentage
Water	88.7%	Water	89.7%
Butoxyethanol	10.0%	Butoxyethanol	10.0%
Amonium hydroxide (28%)	1.0%	Acetic acid	to pH = 4
Surfactant	0.15%	Surfactant	0.15%
Dye	-	Dye	-

2.4 Packaging

Product manufacturers provided general information about their packaging, including types of packages and sizes. Plastic containers were the most popular. However, less than half of the manufacturers Green Seal contacted could describe the type of plastic and whether it contained recycled content.

According to the information Green Seal collected, the most common packaging for industrial and institutional cleaners is high-density polyethylene (HDPE), followed by polyethylene terephthalate (PET). According to the Soap and Detergents Association, most detergent bottles contain 25 to 50% post-consumer recycled content (SDA 1999). In the products Green Seal surveyed, the highest recycled content for HDPE was 25%

and for PET was 20%. A number of products were available in steel aerosol cans and 55-gallon steel drums. All steel products, including aerosol cans and steel drums, contain 25% recycled content (SRI 1999). Finally, a few products were packaged in polyvinyl chloride (PVC), glass, and cardboard containers.

HDPE, PET, glass, steel, and cardboard are readily recyclable. Concern still exists over residual material and aerosol can recycling; however, more programs are accepting aerosol cans. Approximately 56% of community programs accept aerosol cans along with steel cans for recycling. This 56% includes most of the large-city programs in the United States (SRI 2000). PVC is not readily recyclable. Similar products are packaged in HDPE, PET, and PVC, and no obvious reasons exist for a manufacturer's selection of a PVC package.

2.5 Portion-Control Systems

A number of product manufacturers have developed portion-control systems for their products. Green Seal identified four types of portion-control systems including an automated dispensing system, a bulb dispenser, bottles with pre-measured marks, and pre-measured pouches. All the systems enable workers to accurately measure and mix their cleaners, thereby reducing chemical usage and cost. Some of the systems reduce worker exposure to concentrated cleaners and reduce the risk of spills or splashes. Most of the systems also employ a color-coding scheme to eliminate the improper mixing of cleaning chemicals.

Automated dispensing systems and bulb systems reduce worker exposure to concentrates. Automated dispensing systems meter the cleaner and water automatically in the proper ratio. This type of system can accommodate a number of different cleaning agents at one time. Some automated systems also have a one-way valve that prevents chemicals from entering a building's water supply. Moderate to large buildings or cleaning operations typically use automated dispensing systems. Cleaning chemicals can also be dispensed by using a bulb method. For this, a valve is turned, allowing the cleaning concentrate to fill the bulb, and the bulb is then drained into a bottle and filled with water. Dispensing bulbs are suited to smaller cleaning operations.

Bottles with pre-measured marks and pre-measured dispensing pouches enable workers to properly dilute cleaning chemicals. When containers with pre-measured marks are used, cleaner is filled to the mark and then the remainder of the bottle is filled with water. Finally, some manufacturers offer their products in pre-measured pouches, which contain the proper amount of cleaning agent for a certain container. A variety of cleaning operations or buildings, especially where storage space is a problem, use these methods.

PART 3

ENVIRONMENTAL EVALUATION OF INDUSTRIAL AND INSTITUTIONAL CLEANERS

Use of environmentally preferable cleaners is part of an overall strategy to reduce pollution and health risks from cleaning operations. Training in the proper use of cleaning products is also integral to the strategy because proper use will reduce the overall consumption of cleaning chemicals and worker exposure to these chemicals. In addition, use of the appropriate tools, such as sponges and brushes, can reduce the amount of cleaning chemicals used and worker time and effort. This standard and environmental evaluation is intended to assist with the selection of environmentally preferable products. Although proper training and appropriate tools will complement product selection, this evaluation does not directly address training or tool selection.

This evaluation focuses on reducing the life-cycle environmental burdens associated with cleaning chemicals through product selection. A product's life cycle begins with the extraction of raw materials and progresses through the stages of manufacturing, use, and disposal. Each stage within a product's life cycle generates a variety of environmental burdens. This environmental evaluation qualitatively assesses the life-cycle stages of raw-material extraction, chemical manufacturing, distribution, use, and disposal for general-purpose, bathroom, and glass cleaners. The goal of this evaluation is to identify where these life-cycle impacts can best be minimized through the selection of environmentally preferable products.

Life-cycle information is not available for all cleaning ingredients. Furthermore, environmental information, such as toxicity data, generally is not available for entire products; however, this type of information is often available for individual ingredients. Therefore, the authors determined common ingredients for each category of cleaner and collected environmental data from publicly available sources for each life-cycle stage.

This part of the Green Seal standard and evaluation discusses important health and environmental impacts of cleaner ingredients, which were identified in Part 2. This part of the evaluation supports the standard, presented in Part 1. It is organized into seven sections. The first five sections correspond to the life-cycle stages: raw-material extraction, manufacturing, product distribution, use, and disposal. Section 3.6 presents a qualitative comparison of the environmental impacts of many of the ingredient classes. Section 3.7 discusses existing environmental standards for industrial and institutional cleaners.

3.1 Raw Material Extraction and Processing

The first life-cycle stage of a product includes the raw material extraction or harvesting and processing of the basic building blocks for ingredients, which can be categorized into organic and inorganic sources. The following subsections describe the sources of basic raw materials used in the manufacture of relevant building blocks and the various synthesis pathways for common ingredients found in cleaners. The most significant environmental burdens associated with these steps are then discussed.

The manufacture of any one ingredient may be a complicated process requiring both organic and inorganic building blocks. For example, one common builder, ethylenediaminetetraacetic acid (EDTA), requires ethylene, salt, and ammonia as raw materials. Ethylene is produced from natural gas or petroleum refining; chlorine is produced from salt; and ammonia is produced from natural gas. Therefore, the impacts of petroleum extraction, natural gas extraction, and salt mining should be considered with the use of this builder.

3.1.1 Organic Ingredients

A few basic raw materials form the building blocks for most of the organic ingredients in cleaners. These possible carbon sources include fats and oils from animal and plant materials, coal, petroleum, and natural gas. They are available in large quantities and could, in principle, form the basis for the manufacture of almost all organic chemicals. The price, availability, and ease of processing of the various carbon sources determine which sources are used by the organic-synthesis industry.

3.1.1.1 Fats and Oils

Process. Fats and oils are present in both animal and plant material. In 1990, world consumption of fats and oils was approximately 80 million tons, with 14% of this used for industrial purposes and the remainder used for food and feed (Stache 1996). Beef tallow, a by-product of the meat industry, is the primary source of animal fats and oils. Plant sources of fats and oils include fruits, nuts, seeds, grains, and tall oils. Tall oil is a by-product of the Kraft pulping process. Otherwise, most of these fats and oils are produced by pressing and/or solvent extraction. Coconuts and palm fruit are common plant sources for intermediates used in the manufacture of surfactants; the fats and oils derived from coconut and palm fruits contain lauric fatty acids, which are surfactant building blocks.

Fats and oils from animal and plant material primarily consist of long-chain fatty acids and the esters of glycerol, known as triglycerides. Triglycerides are converted into free acids by steam hydrolysis or into long-chain fatty alcohols by hydrogenolysis with the aid of a copper/oxide/chromium oxide catalyst (Woollatt 1985). Fatty acids and fatty alcohols are important intermediates in surfactant production (Stache 1996).

Some products extracted from plant materials are used directly in cleaning products, including pine oil and d-limonene. They are used to dissolve oils and grease. Pine oil is produced from pine trees, primarily from the southeastern United States, and d-limonene is produced from citrus peels, a by-product of fruit-juice processing.

Impacts. The production of plant material typically requires pesticides, fertilizers, and, in some cases, irrigation. These agricultural and silvacultural activities cause runoff of nutrients, sediment, and pesticides into surface waters, which harms aquatic life and reduces water quality. Fertilizer production also requires large amounts of energy and generates significant amounts of water pollution (Pittinger et al. 1991). Finally, the production of beef tallow also causes runoff of nutrients and sediment, and the production of the grain that is fed to these cattle requires pesticides and fertilizers.

3.1.1.2 Petroleum-Based Intermediates

Process. Crude oils are complex mixtures of hydrocarbons that vary in composition depending on their origin. The main components are alkanes, cycloalkanes, and a small fraction

of aromatics. Petroleum refining encompasses a broad range of processes, including fractional distillation and thermal cracking. Petrochemical intermediates, which are of greatest interest in the synthesis of organic surfactants, are short-chain olefins (primarily ethylene and propylene), ethylene oxide, aliphatic hydrocarbons, and aromatics (benzene, toluene, and xylenes).

Olefins are hydrocarbons and have at least one double bond between carbon atoms. A prime example of this type of hydrocarbon is ethylene. Ethylene can be produced, along with several co-products, by the thermal cracking of alkanes and cycloalkanes obtained through the fractional distillation of crude oil. In the United States, however, the dominant feedstock for ethylene production is ethane, which is recovered from wet natural gas (Franck and Stadelhofer 1988). Ethylene is a widely used intermediate in the petrochemical industry, yet approximately 50% of all ethylene produced is consumed in the manufacture of polymers (*Chemical Industry News* 1997).

Ethylene oxide is a cyclic compound composed of two CH₂ groups and one oxygen molecule. Almost all ethylene oxide is produced by the direct oxidation of ethylene over a silver catalyst. More than 60% of all ethylene oxide produced is hydrolyzed to ethylene glycol for use in the manufacture of terephthalic acid and as an ingredient in automotive antifreeze. Ethylene oxide is also used as an intermediate in the manufacture of many surfactants (15%) and glycol ethers (15%) (*Chemical Industry News* 1997).

Aliphatic hydrocarbons are produced in the distillation and cracking of crude oil. Aromatic hydrocarbons are manufactured by catalytic reforming of cycloalkanes. This process produces mixed aromatics in the form of benzene, toluene, and xylene. The high demand for benzene in chemical applications exceeds the ratio of aromatics produced by catalytic reforming. As a result, toluene is often converted to benzene by hydrodealkylation and disproportionation (McKetta 1997). The major uses of benzene are in the production of alkylated derivatives such as ethylbenzene (53% of total benzene) and cumene (22% of total benzene) (*Chemical Industry News* 1997).

Some building blocks can have either natural or petrochemical sources; these include alcohols and the surfactant building blocks. However, many of the major surfactants used in industrial cleaners are derived from petrochemical feedstocks including alcohol ethoxylates, alcohol ethoxylate sulfates, and linear alkylbenzene sulfonates (LAS). The alcohol component of alcohol sulfates, alcohol ethoxylates, and alcohol ethoxylate sulfates can be made from either petroleum or natural feedstocks. In fact, the principal difference between the natural-based surfactants in these groups and the petrochemical-based surfactants is the source of the alcohol portion of the surfactant. Alcohol ethoxylates and alcohol ethoxylate sulfates rely on ethylene oxide made from petroleum and natural gas for their ethoxylate portions.

Impacts. For petroleum-based ingredients, the principal environmental impacts are hydrocarbon air emissions, oil and dissolved-solids wastewater discharges, and solid and hazardous waste. Petroleum refineries release a number of hazardous air pollutants, including aldehydes, ammonia, benzo(a)pyrene, biphenyl, carbon monoxide, ethylbenzene, formaldehyde, benzene, ethylene oxide, and propylene oxide (EPA 1995a). Benzene, ethylene oxide, and propylene oxide are all listed as carcinogens by the National Toxicology Program (NTP 1998a). For ingredients derived from natural gas, the principal environmental impacts include hydrocarbon air emissions and water discharges that include oil, grease, and dissolved solids (Pittinger et al. 1991). The air emissions from petroleum and natural gas processing also

contribute significantly to the VOC loading in the lower atmosphere, which is one of the causes of photochemical smog. Both petroleum and natural gas processes are energy intensive.

3.1.1.2a Ethoxylated Alcohols

Alcohols can be derived from petroleum, natural gas, animal fat, or plant oils as primary raw materials. In the United States, 75% of ethoxylated alcohol production is based on petroleum or natural gas sources (SRI 1996). The ethoxylation of secondary alcohols with ethylene oxide is the manufacturing process for ethoxylated secondary alcohols. Ethylene oxide production is discussed in Section 3.1.1.2. The ethylene chain buildup reaction occurs at a rate similar to the ethoxylation of the alcohol. As a result, the ethylene oxide chain is built up before all alcohol has been reacted, and a polydispersed mixture containing eight ethylene oxides will contain significant amounts of other ethoxylates containing from 0 to 20 ethylene oxide units (Kirk-Othmer 1993).

An evaluation of the Toxics Release Inventory data indicates a variety of toxic chemical emissions associated with ethoxylated alcohol production. Ethylene, ethylene oxide, ethylene glycol, and methanol were common chemicals released or transferred from the facilities that manufacture ethoxylated alcohols. Emissions to air dominated on-site releases. Therefore, in addition to the impacts from the production of ethoxylated alcohols, the impacts from the production of ethylene oxide and alcohol production must be considered.

3.1.1.2b Ethylene Oxide

Ethylene oxide is produced from ethylene, which is a distillation product of either crude oil or natural gas. Potential environmental releases of chemicals from this process include ethylene oxide, benzene, ethylene, and hydrocarbons from the production of ethylene. A number of these compounds are toxic. For example, benzene and ethylene oxide are known carcinogens.

3.1.1.2c Alcohols

Alcohols are used not only as solvents in cleaners but also as intermediates for a number of surfactants and glycol ethers. The raw material source of alcohol can be either vegetable oils or a petroleum feedstock. Most alcohols derived from vegetable oils release alcohols and methyl esters to the environment; these compounds are typically VOCs. The manufacture of petroleum-based alcohols may result in the release of several hazardous air pollutants, including aldehydes, ammonia, benzene, benzo(a)pyrene, biphenyl, carbon monoxide, ethyl benzene, ethylene oxide, formaldehyde, naphthalene, and xylene. The manufacture of petroleum- and vegetable-based alcohols adds to the VOC loading in the lower atmosphere that contributes to photochemical smog. The production of petroleum-based alcohols results in water pollution and generates significant quantities of solid waste (Pittinger et al. 1991).

3.1.2 Inorganic Ingredients

Many cleaning products require one or more inorganic building blocks either directly as ingredients, as intermediates, or as ancillary materials. The most common inorganic building blocks include chlorine, sodium hydroxide, ammonia, sodium bicarbonate, sodium phosphates, and sodium silicates. Generally, the raw materials are mined and then processed to produce the building blocks or ingredients.

3.1.2.1 Chlorine/Sodium Hydroxide

Process. Chlorine and sodium hydroxide are necessary ingredients for the manufacture of a number of builders, chelating agents, and surfactants. Sodium hydroxide is used directly as a builder in some cleaning products. Chlorine and sodium hydroxide are co-products in the electrolysis of aqueous solutions of sodium chloride (salt), which is mined. In 1988, diaphragm cells (nonmercury) accounted for 76% of all United States chlorine production, mercury cells accounted for 17%, and membrane cells accounted for 5% (Burgess 1995). However, the industry is moving toward membrane-cell technology (EPA 1995b).

Impacts. The environmental impacts of salt mining and salt-brine extraction are primarily solid-waste generation and energy use (EPA 1995b). The manufacture of chlorine and sodium hydroxide results in chlorine and sodium hydroxide releases; the mercury-cell process can also generate mercury-vapor releases and mercury wastewater releases, which are major health hazards (Burgess 1995). Salt mining and extraction processes generate large quantities of solid waste (EPA 1995b).

3.1.2.2 Ammonia

Process. Ammonia is an ingredient in a number of cleaning products, and it is also used as an intermediate in the manufacture of many surfactants. Roughly, 75 to 80% of world ammonia production capacity is from steam reforming operations that use light hydrocarbon feeds. Of this percentage, 65 to 70% use natural gas as a source of light hydrocarbons. Only a small fraction of ammonia is consumed in the manufacture of surfactants and cleaners; almost 95% of the total production of ammonia is used to manufacture fertilizers, commercial explosives, and plastic fibers. Figure 3.1 presents a simplified process diagram for ammonia manufacture (Kirk-Othmer 1993).

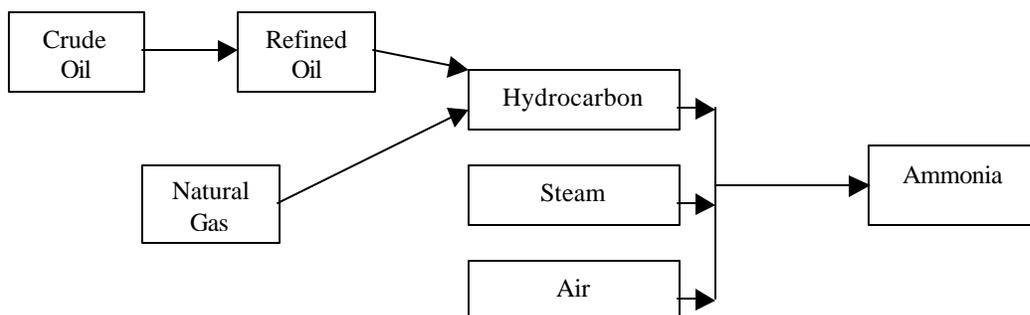


Figure 3.1 Simplified process for manufacturing ammonia (Kirk-Othmer 1993)

Impacts. Hydrocarbon and ammonia air releases are the primary impacts from the manufacture of ammonia.

3.1.2.3 Sodium Carbonate and Sodium Bicarbonate

Process. Sodium carbonate and sodium bicarbonate are common builders. In the United States, sodium carbonate comes from the mining of trona, a naturally occurring form of sodium sesquicarbonate that can be found in the Green River basin of Wyoming (McKetta 1997).

Mining techniques are similar to coal-mining practices. The process used to purify the trona and produce sodium carbonate is an extraction process that uses water as the primary solvent. Cyclone and centrifugation processes are used for the separation of the pure product. Approximately 1.5 metric tons of trona ore are required for the manufacture of 1 metric ton of sodium carbonate (Lowenheim and Moran 1975). Treating a saturated solution of sodium carbonate and water with carbon dioxide produces sodium bicarbonate, which must be dried and filtered. One metric ton of sodium bicarbonate requires approximately 690 kg of sodium carbonate and 300 kg of carbon dioxide as raw materials (Lowenheim and Moran 1975).

Impacts. The mining of trona ore for sodium carbonate creates impacts similar to those for underground coal mining in the western United States. The ore contains only about 5% impurities, so its processing is relatively clean (McKetta 1997).

3.1.2.4 Phosphates

Process. Sodium phosphates are used in the manufacture of several builders, including tetrapotassium pyrophosphate and sodium tripolyphosphate. The basic raw material requirements for producing sodium phosphates are phosphoric acid, sodium carbonate, and sodium hydroxide. Phosphoric acid is produced from phosphate rock and a mineral acid, such as sulfuric acid. Ninety-five percent of phosphoric acid produced is used to manufacture fertilizers.

Impacts. The production of phosphate chemicals requires the mining of phosphate rock. Phosphate mining in the United States is carried out predominantly in parts of North Carolina, Florida, and Idaho. One of the primary concerns with phosphate mining is the generation of large quantities of wastes that contain naturally occurring radionuclides (EPA 1985). Almost 68% of the annual waste produced by phosphate mining is estimated to have a radioactivity level of 5 picoCuries/gram for radium 226. Surface and subsurface waters can become contaminated with the constituents of phosphate mining leachate, including arsenic, cadmium, chromium, copper, lead, molybdenum, selenium, vanadium, zinc, uranium, radium-226, nitrogen, and phosphorus. The manufacture of phosphoric acid also generates process wastewater and sludge from the wastewater treatment (EPA 1995b).

3.1.2.5 Sodium Silicates

Process. Sodium silicates are common builders used in cleaners. Sodium silicates are produced by the fusion of sand and sodium carbonate in a glass furnace. Desired properties are obtained by properly adjusting the ratio of the reactants.

Impacts. The extraction impacts are similar to those of sodium carbonate. The primary environmental impact from the manufacture of sodium silicates is energy use.

3.1.2.6 Bauxite Mining, Zeolite Production

Process. Bauxite is mined, crushed, ground, and digested in a caustic solution at a high temperature and pressure to form aluminum hydroxide (Landbank 1994).

Impacts. Significant impacts associated with zeolite production include energy use during the processing of bauxite and the environmental burdens associated with aluminum mining.

3.1.3 Summary of the Environmental Impacts of Raw-Material Extraction and Processing

Petroleum-, plant-, and animal-based ingredients all have significant environmental impacts. Petroleum refining requires nonrenewable resources and generates large quantities of air and water pollutants; plant-material production contributes to sediment, nutrient, and pesticide loading of surface waters. It is difficult to compare these dramatically different impacts without quantitative life-cycle assessment data, which are not available. Furthermore, the manufacture of any one ingredient is often a complicated process requiring building blocks from several sources. For these reasons, it is difficult to determine which cleaning ingredients produce fewer environmental burdens during the raw-material extraction and processing phase (Pittinger et al. 1991). Section 3.6 summarizes the impacts from all of the life-cycle stages qualitatively.

3.2 Chemical Manufacturing

The chemical production process is the second stage of the life cycle evaluated for this standard. The production processes for general-purpose, bathroom, and glass cleaning products result in a variety of environmental burdens. This section focuses on common ingredients identified during a survey of the literature and MSDSs. It is divided into the classes of ingredients identified in Part 2 – surfactants, builders, solvents, antimicrobials, aerosol propellants, and miscellaneous ingredients. Packaging is also discussed. In some cases, Green Seal select a few ingredients to represent an entire class of ingredients with similar manufacturing processes.

The discussion of environmental burdens is based on a variety of literature sources (McKetta 1997; Kirk-Othmer 1993; Davis et al. 1992). When literature data were not available, the largest manufacturers were identified, and their SARA Title III (Emergency Planning and Community Right-to-Know Act) TRI data were examined. TRI data cover air emissions from the facility, wastewater discharges to bodies of water, and the on-site release to landfills. TRI also reports transfers to off-site publicly owned treatment works (POTWs), landfills, or other modes of land disposal. This, along with general process knowledge, provides an indication of the environmental burdens associated with a process. It should be noted that manufacturing facilities that produce ingredients used in cleaning products normally manufacture many products; therefore, directly attributing emissions to one ingredient is not possible. However, TRI data can provide an indication of the burdens associated with generating any specific ingredient.

3.2.1 Surfactants

Commercially available surfactants are not single-component products; rather, they are mixtures of molecules with identical functional groups that vary only in chain length or some other structural detail (Kirk-Othmer 1993). Figure 3.2 presents the production routes for several of the major surfactant mixtures (Pittinger et al. 1991). The complexity of surfactants makes it difficult to identify an isolated chemical species to represent all surfactants. Common anionic industrial surfactants evaluated in the development of this standard include linear alkylbenzene sulfonates (LAS), alcohol sulfates, alkylpolyglycosides (APG), and soap. Common nonionic surfactants include nonylphenol ethoxylate and cocamide diethanolamine. Cationic surfactants are discussed with antimicrobials in Section 3.2.4. This section also briefly discusses alkylbetine to represent amphoteric surfactants.

Alkylpolyglycosides. APGs are formed by the condensation polymerization of starch intermediates and fatty alcohols. The starch intermediates are derived from corn, wheat, or potatoes (Hill et al. 1997). The fatty alcohols can be derived from natural fatty acids or ethylene.

Soap. The production of soap is carried out on a large scale by the hydrolysis of triglycerides with sodium hydroxide, which produces glycerol and the sodium salt of the fatty acid (soap). The triglycerides are commonly derived from natural sources, such as beef tallow, coconut, and palm oil (Stache 1996).

Nonylphenol Ethoxylate. Nonylphenol ethoxylate manufacturing will be used to represent the class of alkylphenol ethoxylates (APEs). Nonylphenol ethoxylate is manufactured by the ethoxylation of nonylphenol with ethylene oxide. Ethylene-oxide production is discussed in Section 3.2.1.2. Nonylphenol is produced by the alkylation of phenol using propylene trimer, a derivative of (alpha)-olefin propene. Phenol can be made by several oxidation processes that use toluene and derivatives of benzene as a feedstock. The most common feedstock in phenol production process is cumene, which is manufactured by the alkylation of benzene with propene (Kirk-Othmer 1993). Figure 3.3 is a simplified process diagram for the manufacturing process of nonylphenol ethoxylate (Davis et al. 1992).

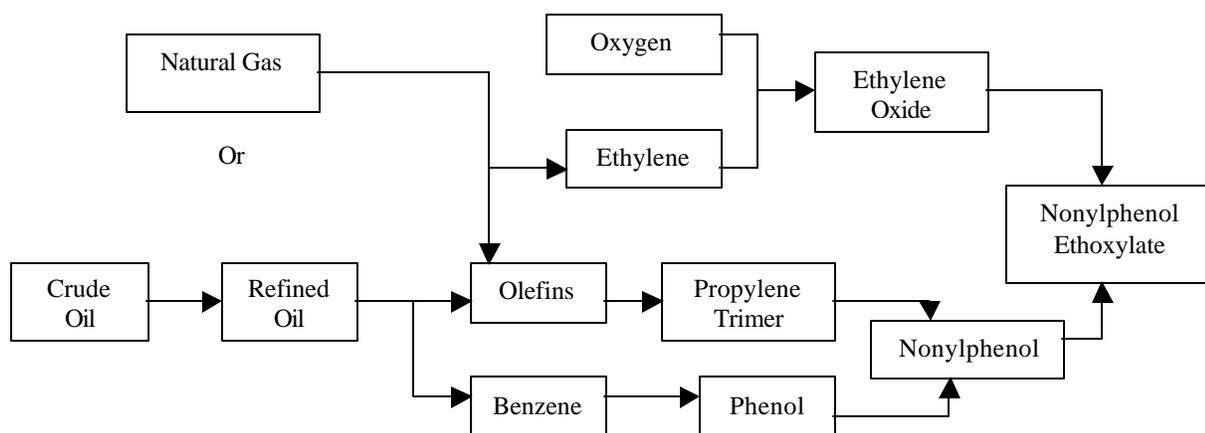


Figure 3.3 Simplified manufacturing scheme for nonylphenol ethoxylate

The production of nonylphenol ethoxylate relies on phenol, propylene, and ethylene (ethylene oxide), all of which are distillation products of crude oil or natural gas. Phenol is produced from toluene and benzene, and propylene and ethylene are produced from straight-chain hydrocarbons from the distillation of crude oil or natural gas (Davis et al. 1992). During manufacturing, ethoxylated surfactants can react with surfactant feedstocks to form 1,4-dioxane, a carcinogen, and this can be present as a contaminant (NTP 1998a; Dickey 1997). A number of these compounds, including benzene and ethylene oxide, are carcinogenic.

Cocamide Diethanolamine (DEA). Cocamide DEA is manufactured by the condensation reaction of coconut oil (lauric acid and diethanolamine). Diethanol amine is synthesized by reacting ammonia with ethylene oxide, which results in the release of ammonia and ethylene oxide, a carcinogen (NTP 1998a).

Alkylbetines. Alkylbetines are prepared from alkyldimethylamines and sodiumchloroacetate.

Overall Impacts of Surfactant Manufacturing. The manufacture of common industrial surfactants results in releases of the following chemicals: sulfuric, phosphoric, nitric, and hydrochloric acids; glycol ethers; ammonia; ethylene oxide; various alcohols; and cyclical compounds such as toluene, cumene, trimethyl benzene, and phenol. Furthermore, most surfactants rely on the petroleum refining process for paraffin compounds, aromatics, methanol, and, in part, for ethylene oxide. The production of these building blocks generates significant environmental burdens (Section 3.1.1.2). In general, surfactant manufacturing generates significant environmental burdens. However, the manufacture of alcohol sulfates, alkylpolyglycosides, and soap result in fewer burdens than the manufacture of LAS, APEs, and cocamide diethanolamine.

3.2.2 Builders and Chelating Agents

Builders and chelating agents augment the cleaning action of surfactants and provide additional cleaning and surface modification by removing hardness and binding with undesirable metal ions in solution. Builders typically comprise a large fraction of the active ingredients in many cleaners, whereas chelating agents represent a much smaller percentage of detergent formulations. Sodium bicarbonate, sodium silicates, phosphoric acid, citric acid, tetrapotassium pyrophosphate, sodium tripolyphosphate (STPP), and ethylenediaminetetraacetic acid (EDTA) are examples of builders and chelators evaluated in this work.

Sodium Bicarbonate. Treating a saturated solution of sodium carbonate and water with carbon dioxide produces sodium bicarbonate, which can be used as a buffer in cleaning products. Product separation is obtained through filtration and drying. Compared to other ingredient manufacturing processes, the manufacture of sodium bicarbonate generates relatively few environmental burdens.

Sodium Silicates. Forty percent of all silicates manufactured in the United States are consumed in the manufacture of detergents (*Chemical Industry News* 1997). Sodium silicates are produced by the fusion of sand and sodium carbonate in a glass furnace. The primary environmental impact from the manufacture of sodium silicates is energy use.

Phosphoric Acid. Phosphoric acid is produced by digesting phosphate rock (calcium phosphate) with sulfuric acid. Phosphoric acid is separated from the resulting calcium sulfate slurry by filtration (Kirk-Othmer 1993). It is also collected when phosphorus is burned in excess air when the pentoxide is hydrated.

Citric Acid. Citric acid is produced by fermentation of beet, sugar cane, or corn sugar. It is also directly extracted from citrus fruits such as pineapple waste.

Tetrapotassium Pyrophosphate. A reaction between phosphoric acid and potassium carbonate produces dipotassium hydrogen phosphate (Figure 3.4). Tetrapotassium pyrophosphate is produced by the dehydration of dipotassium hydrogen phosphate (K_2HPO_4). Menke et al. (1994) identified the main producers of tetrapotassium pyrophosphate and reported their TRI emissions, which included various acids (e.g., sulfuric and phosphoric), as well as phosphorous. The majority of the releases were air emissions or off-site transfers.

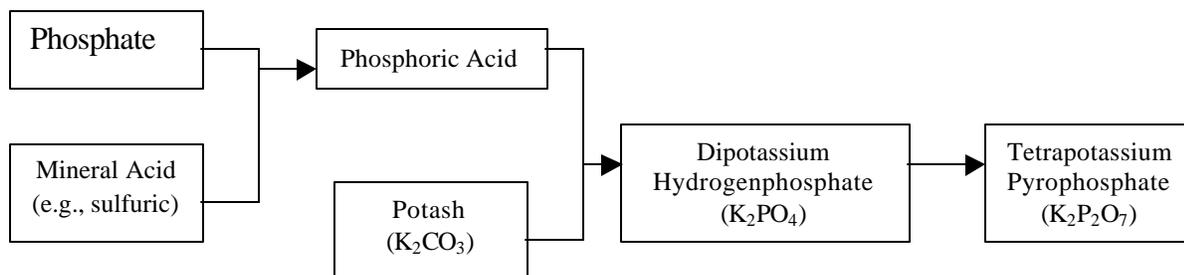


Figure 3.4 Tetrapotassium pyrophosphate manufacturing

STPP. STPP is produced by reacting phosphoric acid with sodium carbonate and sodium hydroxide. Menke et al. (1994) identified eight locations in the United States that produce STPP and found that air releases represent the vast majority of environmental releases. Only two of the eight facilities reported discharges to POTWs.

EDTA. EDTA is a chelating agent made by reacting ethylenediamine with chloroacetic acid. Ethylenediamine is produced along with other mixed amines from ethylene dichloride and ammonia. Ethylene dichloride used in the EDTA manufacturing process is produced by the chlorination of ethylene. Chloroacetic acid is produced by the chlorination of glacial acetic acid in the presence of a sulfur or red-phosphorus catalyst. More than 90% of the acetic acid used in this process is derived from either the direct liquid-phase oxidation of butane or the oxidation of acetaldehyde. Acetaldehyde is produced by the direct oxidation of ethylene (Davis et al. 1992). A simplified schematic of this process is presented in Figure 3.5. Menke et al. (1994) identified three producers of EDTA and found that air releases accounted for most of their environmental releases, with no reported releases to POTWs. Ethylenediamine is a lung irritant and a strong sensitizer, and it is manufactured from ethylene dichloride, a potential carcinogen. Releases from the manufacture of ethylenediamine include ethylene dichloride and chloroacetic acid, which is a severe skin and lung irritant (Pohanish and Greene 1996).

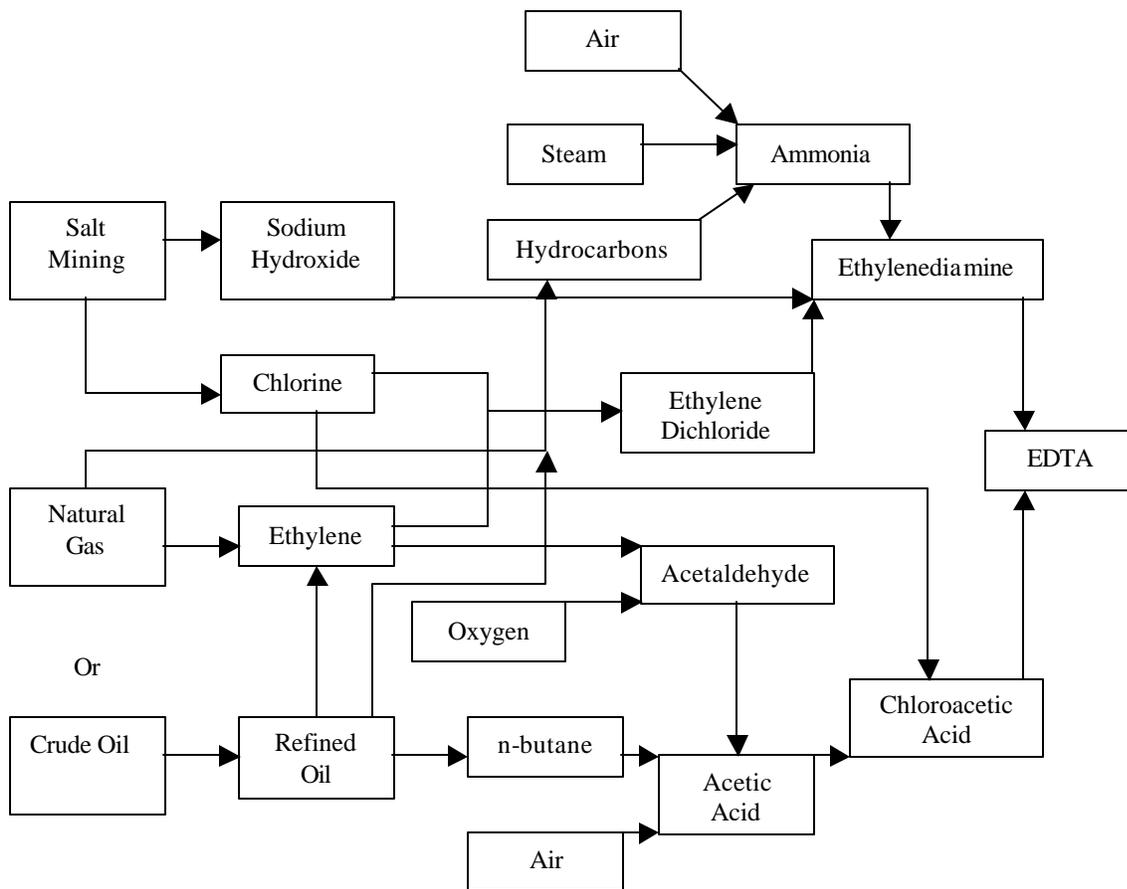


Figure 3.5 Ethylenediaminetetraacetic acid (EDTA) manufacturing

Zeolites/PCA. A common zeolite used in cleaners, zeolite A, is manufactured by reacting sodium aluminate with sodium silicate. Sodium aluminate is formed by reacting aluminum hydroxide with caustic soda. Zeolite manufacturing also requires sodium silicate (Section 3.1.2.5) and sodium hydroxide (Section 3.1.2.1). Polycarbonates are co-polymers of acrylic and maleic acids, which are derived from the oil refining process.

Overall Impacts for Builder and Chelator Manufacturing. The processing of sodium bicarbonate, sodium silicates, phosphoric acid, and citric acid has relatively fewer impacts than the processing of tetrapotassium pyrophosphate, STPP, and EDTA. Menke et al. (1994) found that the quantity of environmental releases from tetrapotassium pyrophosphate, STPP, and EDTA is high when compared with that of surfactants. Landbank (1994) reports that zeolite A/PCA and STPP are similar to each other in terms of environmental impacts generated during their production.

3.2.3 Solvents

Alcohols. See Section 3.1.1.5.

Terpenes. D-limonene, pine oil, and tall oil are all terpenes found in commercial cleaners. D-limonene is produced as a by-product in the manufacture of citrus juice (primarily orange juice) by steam distillation of the peels after pressing. Citrus oils obtained from this process are approximately 95% d-limonene. Pine oil and tall oil are made from the destructive distillation of waste wood chips in the pulp and paper industry. The extraction of d-limonene, pine oil, and tall oil generates volatile organic emissions. However, the manufacture of terpenes produces fewer environmental burdens than petroleum refining (Davis et al. 1992).

Glycol Ethers. The only commercially important route to glycol ethers is the oxide-alcohol route. In this process, glycol ethers are produced by the reactions of epoxides with anhydrous alcohols (SRI 1996). The epoxides most often used are ethylene oxide (Section 3.2.1.2) and propylene oxide. Propylene oxide is manufactured by the chlorohydrin process, in which propylene is reacted with chlorine to produce propylene chlorohydrin, or by peroxidation of propylene (SRI 1996). The propylene chlorohydrin is then dehydrochlorinated with lime or sodium hydroxide to yield propylene oxide and a salt. The selection of which epoxide and alcohol to use is determined by which glycol-ether product is desired. For example, ethylene glycol mono-n-butyl ether is manufactured from ethylene oxide and butanol; ethylene glycol monoethyl ether is manufactured from ethylene oxide and ethanol. Emissions from the manufacture of glycol ethers include alcohols, propylene oxide, and ethylene oxide (Davis et al. 1992). Ethylene oxide and propylene oxide are carcinogens.

Overall Impacts from Solvent Manufacturing. The manufacture of glycol ethers poses the greatest health and environmental impacts, particularly due to the release of toxic materials. Conversely, alcohols derived from natural sources and terpenes have the fewest toxic releases. Alcohols derived from synthetic sources have greater impacts than those derived from natural sources. However, they are intermediates in the manufacture of glycol ethers and have fewer impacts than glycol ethers.

3.2.4 Antimicrobials

Quaternary Ammonium Compounds. A number of quaternary ammonium compounds can be produced by the alkylation of tertiary fatty amines using methyl chloride, benzyl chloride, or long-chain chloroparaffins. Quaternary ammonium compounds can be produced by the quaternization of a tertiary fatty amine with benzyl chloride. Benzyl chloride is produced by chlorination of toluene. Dialkyldimethyl ammonium chloride can be produced by the quaternization of a tertiary fatty amine using methyl chloride or another chloroparaffin. The tertiary amine intermediates used in the manufacture of quaternary ammonium compounds can be derived by the reductive alkylation of a primary amine using formaldehyde. Primary fatty amines are produced by the hydrogenation of nitrile intermediates, which are made by reacting ammonia with fatty acids (Kirk-Othmer 1993).

The manufacture of quaternary ammonium compounds relies on benzyl chloride (a strong lung irritant) and methyl chloride (a potential carcinogen) or (chloroparaffins) (Pohanish and Greene 1996). Additionally, benzylchloride production requires toluene, and toluene manufacturing results in benzene releases (EPA 1995a).

Phenols. In the United States, 98% of phenol is manufactured by the cumene process, in which benzene is alkylated to cumene, which is oxidized to form cumene hydroperoxide. Cumene hydroperoxide is cleaved to form phenol and acetone (Kirk-Othmer 1993). This process results in the release of benzene, a carcinogen, and other VOCs.

Sodium Hypochlorite. See Section 3.1.2.1.

Alcohols. See Section 3.1.1.5.

Pine Oil. See Section 3.2.3.

Overall Impacts from Antimicrobial Manufacturing. Phenols and quaternary ammonium compounds have more significant environmental impacts during their manufacture than sodium hypochlorite, alcohols, or pine oil.

3.2.5 *Aerosol Propellants*

Butane, isobutane, and propane are manufactured from natural gas and petroleum. Propane is separated during fractional distillation of petroleum and during natural gas processing. Isobutane is produced from wet natural gas, which contains 0.35 mole percent isobutane, or it is recovered from the catalytic cracking process in petroleum refining (Kirk-Othmer 1993). The impacts from manufacturing these aerosol propellants are similar to those for petroleum refining and natural gas production.

3.2.6 *Other Ingredients*

Dyes. Dyes can be grouped into inorganic and organic types. Inorganic pigments are manufactured by extracting minerals from ore, including cobalt, chromium, zinc, manganese, copper, and lead. As an example, cobalt is a co-product of copper, lead, nickel, or silver mining. The ore is reduced in a furnace and then digested with hot sulfuric acid to remove copper and iron (Browning 1969). A cobalt-complex dye is formed by reacting this intermediate with sodium hydroxide and air or hydrogen peroxide (Kirk-Othmer 1993). Organic pigments can be manufactured from natural sources or synthetic sources such as petroleum intermediates. The organic pigments from natural sources are obtained by extracting the pigments either physically or chemically from plants or animals.

The manufacture of inorganic and synthetic organic pigments is energy intensive (Harsch and Schuckert 1996). The pigments themselves can be toxic; for example, a statistically higher incidence of malignant tumors has been reported in workers exposed to certain dyes and intermediates (Kirk-Othmer 1993). Alternatively, some pigments are safe enough for use in foods. EPA's Toxics Release Inventory Database for SIC code 2816 (inorganic pigment manufacturing) shows that the most significant releases are heavy metals to water and land, including chromium, zinc, manganese, barium, and lead. The reporting facilities also tended to emit hydrochloric acid, sulfuric acid, and ammonia to air.

Fragrances. Most fragrances are extracted from plant or animal sources, or they are manufactured from synthetic sources but have an identical structure to those natural plant and animal fragrances. Common natural sources include citrus, pine, cedar, eucalyptus, lavender, and mint. The fragrances are extracted mechanically or chemically (Bauer and Garbe 1985). Some active ingredients such as d-limonene and pine oil can also be used as fragrances.

Cellulose. Cellulose is used as a mild abrasive in a few cleaning products. It is manufactured by the mechanical pulping of fibrous plant materials or is a by-product of the Kraft pulping process (Kirk-Othmer 1993).

Quartz. Quartz is mined and then purified by washing and filtration (Kirk-Othmer 1993).

3.2.7 Packaging

All of the packaging options have significant upstream and process impacts that can be reduced by reuse and recycling. A few manufacturers offer returnable and refillable containers. High-density polyethylene (HDPE), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) require petroleum or natural gas as their raw materials and therefore have raw material extraction and processing impacts (Section 3.1.1.2). PVC also requires chlorine (Section 3.1.2.1). HDPE and PET have similar energy requirements, 81MJ(Megajoules)/kg and 77 MJ/kg, respectively (APME 1993, 1998). PVC production requires 66.80 MJ/kg (APME 1994). The manufacture of HDPE, PET, and PVC results in the release of hydrocarbons. However, PVC packaging represents the most significant impacts during its manufacture because PVC is based on vinyl chloride monomer, which is a known human carcinogen. Vinyl chloride and ethylene dichloride, a suspected human carcinogen, are released during PVC manufacture (EPA 1990).

Steel extraction and processing generate a significant amount of solid waste and water quality impacts (BUWAL 1996). Steel in the United States, including steel used to manufacture steel cans, contains approximately 25% recycled content, which helps to reduce its impacts. Steel extraction and manufacturing require 31.3 MJ/kg of steel (25% recycled content) (BUWAL 1996). Although steel requires less energy on a mass basis than the plastics, a steel aerosol container weighs more than a similar-sized plastic container. Although steel cans require less energy per kilogram than plastic, plastic containers are significantly lighter than steel cans.

Cardboard packaging creates wastewater, air emissions, and solid waste from paper mills. However, these effects can be reduced by using cardboard with post-consumer recycled content. Most cardboard is unbleached, so chlorinated organics are not released with the manufacture of cardboard.

Glass bottles are made from sodium carbonate and sand, and their primary impact is energy consumption. From a manufacturing standpoint, glass generates fewer burdens than plastics or metals. However, glass containers weigh eight to ten times more than similar plastic containers. During product distribution, glass containers will require more energy to transport than plastic containers, thus generating larger quantities of air emissions, water pollution, and solid waste per container (Franklin Associates 1989).

3.2.8 Summary of the Environmental Impacts of Cleaning Chemical Manufacturing

This life-cycle stage has significant health and environmental impacts, and some significant differences between ingredients and packages are apparent. Several ingredients are based on toxic intermediates, including the benzene-, ethylene oxide-, and propylene oxide-based surfactants; EDTA builders; glycol ether solvents; quaternary ammonium and phenolic antimicrobials; and inorganic and synthetic dyes. The ingredients with the fewest environmental

impacts during this life-cycle stage are sodium carbonate, sodium bicarbonate, sodium silicates, citric acid, the natural-based alcohols, and terpenes. Section 3.6 summarizes the impacts from all of the life-cycle stages qualitatively.

3.3 Health and Environmental Issues in Product Distribution

Three principal health and environmental issues are associated with product distribution: transportation emissions, VOC emissions, and worker health and safety concerns during product transfer (US Chemical Safety and Hazard Investigation Board 1999). The best health and environmental performers in this life-cycle stage are products that are concentrated, not flammable, not corrosive, and VOC free. A concentrated product reduces transportation burdens because it reduces the amount of product that needs to be transported. For these same reasons, glass containers are poor performers in this stage because they are heavier than other similar-sized containers. In addition, glass containers can break, posing a hazard to workers. Products that are not flammable or corrosive in the form in which they are transported offer fewer risks to workers handling the materials. Finally, products with low or no VOCs reduce VOC air emissions during product transfer.

3.4 Cleaner Use

The most important impacts associated with the use of cleaners include health and safety concerns for the workers and building occupants and environmental releases of the cleaners. In addition to reduction of environmental impacts through product selections, purchasers and users of cleaning chemicals should consider dispensing systems that limit worker exposure to cleaning concentrates. These are described in Section 2.4. This section describes relevant health, safety, and environmental impacts and then discusses various ingredients and their impacts. Appendix B contains health and environmental data by ingredient.

3.4.1 Health and Safety

Worker Exposure to Cleaning Chemicals. Workers are commonly exposed to cleaning chemicals through their skin and their lungs, although oral exposure is also possible. In their review of janitorial injuries in the state of Washington, Barron and Sutherland (1999) reported that 76% of janitorial injuries from chemical exposure involve skin and eye irritation or burns and 12% involve worker inhalation of chemical fumes. Barron et al. (1999) estimates that medical expenses and lost time for chemical injuries to janitors in the United States cost approximately \$75 million annually. Therefore, Green Seal wants to encourage the selection of products that are not toxic, corrosive, skin or eye irritants, or sensitizers.

Toxics. Although cleaning chemicals are not generally the most significant source of VOCs in an indoor environment, they are a significant source of VOCs to the workers who use them. This makes the inhalation toxicity of volatile cleaning chemicals an important consideration. Due to concern over worker exposure to some volatile compounds, OSHA has set permissible exposure limits (PELs) and the American Conference of Governmental Industrial Hygienists (ACGIH) has set threshold limit values for a number of solvents. Cleaning chemicals can also be absorbed through the skin, particularly some glycol ethers. Dermal toxicity of cleaning chemicals is also an important consideration. The potential for skin absorption can be greatly reduced by wearing gloves, as manufacturers generally recommend. The Consumer Product Safety Commission (CPSC) defines a toxic material as (16 CFR Part 1500.3)

$LD_{50} \leq 5 \text{ g/kg (oral)}$

$LC_{50} \leq 20,000 \text{ ppm (inhalation)}$

$LD_{50} \leq 2 \text{ g/kg (skin)}$

It is important to note that health effects occur at levels below those defined as toxic.

Corrosivity and Skin and Eye Irritation. A chemical with a pH outside the neutral range may cause injury to the skin and eyes. Although products with a pH greater than 11 or less than 2.5 pose the greatest risk for skin and eye injury (Grant 1974), pH is not the only measure of a chemical's potential for skin and eye injury.

Sensitizers. A sensitizer is a chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical. Sensitizers should be reported on MSDSs. A person can become sensitized to a cleaning chemical by inhaling it or from dermal exposure. Some of the responses to sensitizers include contact dermatitis and inflammation of the mucus membranes. According to the US Bureau of Labor Statistics, occupational skin diseases (mostly in the form of contact dermatitis) are the second most common type of occupational disease, accounting for 14% of all occupational diseases (BLS 1999b).

Flammability. The flammability of some solvents and propellants is an important safety issue. Flammable and combustible substances must be handled with extreme caution. The CPSC defines a flammable substance as one with a flashpoint between 20 and 100 °F and a combustible substance as one with a flashpoint between 100 and 150 °F (16 CFR Part 1500.3(c)(6)). OSHA defines several classes of combustible liquids. The Department of Transportation allows liquids to be tested to determine if the liquid can sustain a flame instead of relying on flashpoint. It is important to consider the combustibility of a product as a whole. For example, a dilute solution of ethanol in water would not be flammable or combustible. However, a cleaner containing high concentrations of pine oil, d-limonene, or other solvents could easily be flammable or combustible.

Indoor Air Quality. Americans on average spend 90% of their time indoors; therefore, good indoor air quality is essential to the health of building occupants (Berry 1994). Common complaints resulting from poor indoor air quality include headache, fatigue, and sluggishness and irritation of the skin, eyes, nose, throat, and lungs (Berry 1994; Bardana and Montanaro 1997). In general, the main causes of poor indoor air quality are poor ventilation, pollutants emitted outside, biological contamination due to poor moisture control, building materials, inadequate cleaning, and tobacco smoke (Berry 1994; Godish 1995; Bardana and Montanaro 1997). Cleaning and the use of cleaners promote good indoor air quality by minimizing the amount of dust, dirt, and odors that can cause a negative response in building occupants. Research Triangle Institute (RTI) (1994) assessed the effects of cleaning of indoor air quality and found that improved cleaning methods reduce the levels of biological, chemical, and particulate pollutants in the indoor environment. Additionally, cleaning removes sources of food for microorganisms and pests such as cockroaches and rodents. This reduces the potential for these organisms to cause poor indoor air quality.

On the other hand, many cleaners contain volatile ingredients, which evaporate during their use, and these VOCs cause sensory and central nervous system irritation. RTI (1994) found

that cleaning chemicals containing lower concentrations of VOCs reduce the building levels of VOCs. Individuals exposed to 5 to 25 $\mu\text{g}/\text{m}^3$ of a mixture of VOCs report an adverse response (Berry 1994; Kjaergaard 1991). In buildings, the major sources of VOCs include tobacco smoke, pesticides, and building materials such as insulation, wall and floor coverings, adhesives, and paint. Although cleaning chemicals are cited as a less significant source of VOCs, the use of VOCs in cleaners should be kept to a minimum to help maintain good indoor air quality.

3.4.2 Environmental Impacts

Photochemical Smog Production. The VOCs in a cleaner volatilize during use and can react with sunlight and atmospheric constituents to form smog and ozone. The photochemical oxidant production potential (PCOP) and the VOC content of a product can be used to estimate the amount of oxidant formed. PCOP factors for different solvents are presented in Appendix B. VOCs found in cleaners include d-limonene, glycol ethers, and alcohols.

Energy Use. A life-cycle assessment conducted by Franklin Associates for Proctor & Gamble stated that energy use for heating water used to dilute cleaning chemicals may be a significant source of environmental burdens (Kuta et al. 1992). Hot water requires either natural gas or electricity. The generation of electricity and the combustion of natural gas result in the release of greenhouse gases, acid rain precursors, and toxics. Although use instructions may not call for hot water, some users may use hot water anyway, believing that it enhances performance.

Water Use. Most of the cleaning products contain significant amounts of water or are intended to be diluted with water. The use of water is a consideration; however, no type of cleaner or set of ingredients is superior in terms of water use.

Ozone Depletion. The use of ozone-depleting compounds (ODCs) as propellants in aerosol products such as cleaners has largely been banned by Section 610 of the Clean Air Act due to concern over their role in depleting the ozone layer. When ODCs are released to the atmosphere, they do not decompose and are transported to the stratosphere, about 10 kilometers above the Earth's surface. There, ultraviolet light (UV) breaks apart the ODCs molecule and releases chlorine, fluorine, and bromine atoms. These atoms destroy stratospheric ozone. It is estimated that one chlorine atom can destroy over 100,000 ozone molecules before finally being removed from the stratosphere (WMO 1994). Furthermore, bromine atoms destroy 40 times more ozone molecules than chlorine atoms.

Because ozone filters out harmful UVB (ultraviolet B radiation, $\lambda = 280 - 320\text{nm}$) radiation, less ozone in the stratosphere means higher UVB levels at the Earth's surface. UVB radiation has been linked to skin cancer, cataracts, and damage to certain crops and marine organisms. Although some UVB radiation reaches the Earth's surface even without ozone depletion, its harmful effects increase as a result of this problem (WMO 1994).

3.4.3 Environmental Impacts and Ingredients

Surfactants. The commonly used surfactants are relatively nontoxic for humans although some may irritate the skin, mucous membranes, and eyes (Bartnik and Kunstler 1987; Berry 1994). Sodium dodecyl sulfate is listed as a skin sensitizer (HSDB 1999). Furthermore, the NTP has tested cocoamide diethanolamine for carcinogenicity and found an increased incidence of liver and kidney tumors in mice (NTP 1998b). Cocoamide diethanolamine contains

diethanolamine, and the NTP has also reported clear evidence of carcinogenic activity of diethanolamine in male and female rats. Surfactants are not volatile and would not be expected to cause indoor air quality problems.

Builders and Chelating Agents. Some commonly used builders can be particularly irritating to skin, eyes, mucous membranes, and lungs. These include sodium hydroxide and phosphoric acid (HSDB 1999). Some builders are used to adjust the pH of a solution, and alkaline or acidic cleaners can damage skin and eyes. The pH of a product is one indication of whether it is likely to cause skin or eye damage, but pH is not the only factor.

Solvents. A number of solvents can pose particular health concerns for workers, particularly in terms of flammability, toxicity, and skin irritation. A number of the solvents are flammable or combustible in their pure form (Table 3.1). These solvents would need to be present at relatively high concentrations to make the entire product flammable.

Table 3.1 Flammable or combustible solvents.

Acetic acid	d-limonene	Isopropyl alcohol
Butoxyethanol	Ethanol	1-Methoxy 2-propanol
Dipropylene glycol monomethyl ether	Ethylene glycol diethyl ether	Pine oil

Many solvents are volatile and evaporate readily; therefore, the main exposure route for workers is inhalation, but absorption through the skin is also possible. Table 3.2 summarizes toxicity and skin irritation data for a number of solvents.

Table 3.2 Toxicity data for solvents.

Chemical	LD ₅₀ Oral (mg/L)	LD ₅₀ Skin (mg/L)	LC ₅₀ Inhalation (ppm)	Skin & Eye Irritation	Sensitizer	Source
1-Methoxy -2-propanol	5,660	13,000	25,800/4H			DB
2-(2-n-Butoxyethoxy) ethanol	5,600	4,120	-			DB
2-Ethyl-hexyloxyethanol						
2-Propoxy -2 propanol	2,800	3,550		Med		
Butoxyethanol	470	220	450/4H	Low		DB
Dibutyl phthalate	8,000	20,000				HSDB
Diethylene glycol monoethyl ether	550	8,500	-	Low		DB
Dipropylene glycol monomethyl ether	5,135	9,500	>1213	Med		DB
d-limonene	4,400	-	-	High	Y	DB
Ethanol	3,310	1,060	5,620/1H mus	High (eyes)		
Isopropyl Alcohol	5,045	12,800	4,671/8H	Low	Y	DB
Pine oil	5,170					
Propylene glycol	22,000	20,800	>Sat/8H	Med		DB
Trimethylene glycol	4,773	>20,000	-			DB, Ecotox

DB: Solvent Substitution Database (<http://www.ncms.org>).

Ecotox: EPA ecological toxicity database (<http://www.epa.gov/ecotox>).

According to the CPSC definition of “toxic”, several of the solvents are toxic in their pure form. However, cleaning products contain significant amounts of water, and products containing some concentration of these solvents would not necessarily be considered toxic. It is interesting to note that butoxyethanol is more toxic by all routes than any of the other solvents commonly identified in cleaners.

Another way to examine the relative toxicity of solvents is to consider the OSHA PELs. The lower the PEL, the greater the level of concern. OSHA National Institute of Occupational Safety and Health (NIOSH) has set permissible exposure limits (PELs) for butoxyethanol at 25 ppm (skin) and 121 mg/m³ (air). The OSHA PEL for dibutyl phthalate is 5 mg/m³ (air). Although dipropylene glycol monomethyl ether and 1-methoxy-2-propanol are less toxic than butoxyethanol, OSHA is concerned about worker exposure and has set the PEL at 100 ppm. Isopropyl alcohol is the only other solvent with an OSHA PEL, which is set at 400 ppm.

Antimicrobials. The main impact during the use phase for antimicrobials is the risk of skin and eye injuries, particularly if the concentrates contain a large percent of sodium hypochlorite, pine oil, or quaternary ammonium compounds. However, toxicity and the presence of VOCs are also important. A 5% solution of sodium hypochlorite is highly irritating (HSDB 1999). A 10% solution of alkyldimethylbenzyl ammonium chloride is a primary irritant, and concentrations as low as 0.1 to 0.5% are irritating to the eyes and mucous membranes (HSDB 1999). Green Seal identified a few concentrated products that listed 5 to 10% concentrations of quaternary ammonium compounds, and several with concentrations between 2 and 5%. Sodium hypochlorite cannot be stored at a dilute concentration because it will lose its antimicrobial activity. Pine oil is discussed under solvents.

Table 3.3 presents toxicity data for antimicrobials. Alkyldimethylbenzyl ammonium chloride is more toxic than the other antimicrobials; however, it would not necessarily make a product toxic at a typical use concentration of 0.1%. The phenols are volatile and considered moderately toxic (HSDB 1999). EPA considers o-phenylphenol a probable carcinogen. Finally, workers should never add sodium hypochlorite to any cleaning product because it can react with ammonia (an ingredient in a number of products) to release toxic chloramines.

Table 3.3 Toxicity of antimicrobials.

Compound	Oral LD₅₀ (mg/kg)¹	Dermal LD₅₀ (mg/kg)²	Source
Alkyldimethylbenzyl-ammonium chloride	100 - 700		HSDB
o-phenylphenol	2,480		HSDB
Para-tertiary amylphenol	1,950		
Ethanol	7,060	> 20,000	SDB
Isopropyl alcohol	5,045	12,800	SDB
Sodium hypochlorite	5,800		HSDB

Aerosol Propellants. A number of aerosol propellants are flammable, including isobutane, butane, and propane. The product users must exercise caution in the use and storage of these products. Aerosol cleaning products containing ODCs should no longer be manufactured according to Section 610 of the Clean Air Act.

Miscellaneous Ingredients. None of the identified ingredients are likely to have significant effects during this life-cycle stage.

Packaging. Glass packages have a potential to break and expose workers to the cleaning chemicals, as well as to broken glass. Other than the potential for breaking, none of the packages have any impacts during the use phase.

3.4.4 Summary of Environmental Impacts for Cleaner Use

Some ingredients, depending on their concentration, have the potential to cause skin and eye damage to workers. The ingredients of greatest concern include sodium hydroxide, phosphoric acid, and sodium hypochlorite; however, the pH of the solution is a more important factor than the presence of any specific ingredients. Other ingredients of concern in this stage include VOCs and flammable chemicals. Section 3.6 summarizes the impacts from all the life-cycle stages qualitatively.

3.5 Disposal

Typically, the volatile components of cleaners, such as alcohols or glycol ethers, evaporate during the use phase. The residual cleaner is either removed with a rag or sponge or disposed down the drain. As the rags and sponges are cleaned, the residual cleaner and dirt are removed and become part of the wastewater stream. This wastewater contains soils from the cleaned surfaces (such as solids, oil, and grease), as well as residual cleaning agents. All spent cleaning solutions must be treated in a POTW or other wastewater treatment system before being discharged. Both the cleaners themselves and the soil from the cleaned surfaces can produce negative aquatic impacts. The most significant environmental issues associated with the disposal of cleaners are poor biodegradation, aquatic toxicity, bioconcentration, eutrophication, and endocrine disruption. A brief discussion of each environmental impact is presented, followed by a discussion of the ingredient classes. Appendix B contains a summary of all available toxicity data.

3.5.1 Environmental Impacts

3.5.1.1 Biodegradation

If the ingredients in a cleaner do not degrade, they can reach levels that are toxic for aquatic life; they can also create foaming problems and interfere with treatment operations at a POTW. Biodegradation is the destruction of a compound by the biological action of living organisms. For cleaning ingredients, the most relevant biological action is the action of microorganisms in wastewater treatment plants and in receiving waters. There are two ways to consider biodegradation: primary and ultimate biodegradation. Primary biodegradation occurs when the compound of interest is altered by biological action; this is measured by the change in concentration of that compound. Ultimate biodegradation is the complete conversion of the original compound of interest to carbon dioxide, water, and mineral salts. This can be measured by the removal of carbon, the evolution of CO₂, or oxygen consumption (Swisher 1991; Hutzinger 1985).

Biodegradation can occur aerobically, in the presence of oxygen, or anaerobically, in the absence of oxygen. Some compounds are readily biodegradable with aerobic organisms but are resistant to biodegradation by anaerobic organisms. Several types of tests are used to measure

biodegradability, from simple bottle tests to tests that attempt to simulate sewage treatment plant conditions. In selecting a test method, Green Seal aims to choose a test that would fail a compound that will not biodegrade in the environment and would pass a compound that will be degradable in the environment. The International Standards Organization (ISO) has published a number of tests for measuring ultimate biodegradability in aquatic environments. The Organization for Economic Cooperation and Development (OECD) developed a definition for a readily biodegradable compound that states that a compound is readily biodegradable if, in a 28-day test, it biodegrades by 60% or more within 10 days of the time when biodegradation first reaches 10%. (Santa Monica, California uses the OECD definition of ready biodegradability in its purchasing criteria.)

3.5.1.2 Aquatic Toxicity

Wastewaters that are toxic can harm fish and other aquatic organisms, posing aesthetic problems, as well as possible contamination of drinking water sources. A common measure of aquatic toxicity is the concentration at which a certain percent of an organism dies within a certain time frame. For example, “LC₅₀ (fish, 96h)” is a common measure of aquatic toxicity that denotes the concentration at which 50% of fish die in 96 hours.

There are no aquatic toxicity standards for chemical mixtures such as cleaners. EPA has published a guidance document for conducting cleaner technologies substitutes assessments (EPA 1996a). The assessment provides criteria for evaluating the aquatic toxicity of chemicals used in various manufacturing processes (Table 3.4).

Table 3.4 Aquatic toxicity values.

Chronic/Acute Toxicity	Value	Rating
Chronic Values	# 0.1 mg/L	High toxicity
	> 0.1 to # 10 mg/L	Moderate toxicity
	>10 mg/L	Low toxicity
Acute Values	# 1.0 mg/L	High toxicity
	> 1.0 to # 100 mg/L	Moderate toxicity
	>100 mg/L	Low toxicity

3.5.1.3 Bioconcentration

Bioconcentration is the elevated concentration of a chemical in an organism compared to the concentration in the surrounding environment. Some chemicals are taken up by small aquatic organisms and increase in the food chain as these organisms are consumed by larger animals. A bioconcentration factor (BCF) is a measure of a compound’s tendency to bioaccumulate. It is defined as the ratio of the concentration of the test substance in the fish or other organism to the concentration in the surrounding medium (i.e., water). The Canadian Environmental Choice Program defines a compound with a BCF > 100 as persistent. However, EPA’s Cleaner Pilot project defines products with a BCF < 1,000 as preferable in terms of food chain exposure. Alkylphenol ethoxylates (APEs) and o-phenyl phenol have BCFs greater than 100 (Appendix B).

3.5.1.4 Eutrophication

Eutrophication is caused by the discharge of nutrient-rich wastes into bodies of water. These wastes cause algae blooms and subsequent dissolved-oxygen depletion as the algae dies. This reduction in dissolved oxygen harms aquatic life and leads to fish kills. Phosphates are one cause of eutrophication in surface waters (Ford 1993). Many times phosphate discharges from industry are a local issue, such as in the Great Lakes region. Some POTWs can treat phosphates at an additional charge to industry. There are a number of regulations and programs that address the phosphate content of laundry detergents and cleaners. Green Seal selected a phosphate limit of 0.5% because it effectively limits the quantity of phosphates and it coincides with many state purchasing programs.

3.5.1.5 Endocrine Disruption

Chemicals that mimic or block the activities of hormones are known as endocrine disrupters. These compounds have a number of effects such as decreased fertility in birds, shellfish, and mammals (Colburn 1996). No recognized list of endocrine disrupters exists, and no standard test method for determining if a chemical is an endocrine disrupter exists. However, there is evidence that alkylphenol ethoxylate surfactants and dibutyl phthalate act as endocrine disrupters; this evidence was considered in the development of the standard.

3.5.2 *Ingredients*

3.5.2.1 Surfactants

Biodegradation. Tables 3.5 and 3.6 summarize the biodegradability of a number of surfactants. In general, surfactants with linear structures are more biodegradable than surfactants with branched structures. Tetrapropylene alkylbenzene sulfonate (TBS), *i*-nonylphenol 9 ethoxylate, and the ethylene oxide/block propylene copolymers exhibit the poorest ultimate biodegradability.

Table 3.5 Anaerobic biodegradation of common surfactants (Swisher 1991; Hill et al. 1997).

Surfactants	Extent	Time	Analysis
LAS	20%	3 days	MBAS
C ₁₅₋₁₆ - α -olefin sulfonates	31 - 43%	28 days	MBAS
Coco-ethoxylate alcohol sulfate	53 - 67%	28 days	MBAS
Alkylpolyglycoside	> 96%	unknown	unknown

Table 3.6 Aerobic biodegradation of surfactants in screening tests (Swisher 1991; Hill et al. 1997).

Surfactants	Primary Biodegradation	Ultimate Biodegradation	
	BiAS Removal	Closed Bottle Test (% ThOD)	OECD Screen Test (% C-removal)
Anionic surfactants			
LAS	95	65	73
TBS	8 - 25	0 - 8	10 - 13
C ₁₄₋₁₈ α -Olefin sulfonates	99	85	85
sec.-C ₁₃₋₁₈ -Alkane sulfonates	96	73	80
C ₁₆₋₁₈ -Fatty alcohol sulfates	99	91	88
C ₁₂₋₁₅ -Oxo alcohol sulfates	99	86	--
C ₁₂₋₁₄ -Fatty alcohol diethylene-glycol ether sulfates	98	100	--
C ₁₆₋₁₈ - α -Sulfo fatty acid methyl esters	99	76	--
Nonionic surfactants			
C ₁₆₋₁₈ -Fatty alcohols 14 EO	99	86	80
C ₁₂₋₁₄ -Fatty alcohols 30 EO	99	27	--
C ₁₂₋₁₄ -Fatty alcohols 50 EO	98	--	--
C ₁₂₋₁₈ -Fatty alcohols 6 EO 2PO	95	83	69
C ₁₂₋₁₈ -Fatty alcohols 5 EO 8PO	70	15	--
C ₁₂₋₁₄ -Fatty alcohols 10 PO	50 - 63	21	11
C ₁₃₋₁₅ -Oxo alcohols 7 EO	93	62	--
i-Nonylphenol 9 EO	6 - 78	5 - 10	8 - 17
n-C ₈₋₁₀ - Alkylphenols 9 EO	84	29	-
C ₁₂₋₁₈ -Amines 12 EO	88	33	--
Alkylpolyglycocide		73 - 88	90 - 94

BiAS: Bismuth-active substance; ThOD: Theoretical oxygen demand; C-removal: carbon removal; LAS: linear alkylbenzene sulfonate; TBS: tetrapropylene alkylbenzene sulfonate; EO: ethylene oxide or ethoxylate unites; PO: propylene oxide units

A number of studies have examined the presence of common surfactants in the environment (Table 3.7). Surfactants that persist in the environment have the potential to reach levels harmful to aquatic life. In Europe, some countries became concerned over the levels of alkylphenol ethoxylates (APEs) in some of their rivers and over research showing that APEs act as endocrine disrupters. In fact, Germany and Switzerland banned the use of APEs in cleaning products, and they are currently being phased out in the United Kingdom, Belgium, the Netherlands, and Sweden. APEs will be discussed in more detail in the following section.

Table 3.7 Surfactants in the environment (concentration in ppm).

	APE	LAS	(C₁₈) Me₂Nt
In household and municipal sewage ¹			
- receiving waters, US	0 - 0.5		
Surface waters & groundwaters			
- river, Illinois ¹	0.001 - 0.005	0.01	
- river, U.S. ¹		0.01 - 0.03	
- estuary, U.S. ¹		0.001 - 0.005	
- river, Ohio ¹	0 - 0.5		
- river, U.S. ¹			0.04 - 0.08
- river, U.S. ¹			0.01 - 0.04
- river, Mississippi ²		0.0001 - 0.028	
- rivers, U.S. (90% of 30 locations) ³	0.003 - 2.96		
- river, Indiana ¹	0.0012		
- rivers, U.S. (26 locations) ³		0.010 - 0.300	
Sediment			
- rivers, U.S. (90% of 30 locations) ⁴	< 0.390		
-river, Mississippi ⁴		0.01 - 20	
- rivers, U.S. (15 locations) ³		16 - 322	

APE: Alkylphenol ethoxylate and metabolites; LAS: Linear alkylbenzene sulfonate; (C₁₈) x Me₂ Nt: a dialkyldimethyl quaternary ammonium compound

¹ Swisher (1991).

² Tabor and Barber (1996).

³ Rappaport and Eckhoff (1990).

⁴ Naylor et al. (1992).

APEs. Dickey (1997) published a comprehensive review of the environmental impacts of APEs and discussed options for replacing them. APEs are not readily biodegradable in standard tests (Schwartz and Vaeth 1987; SRI 1996). In addition to incomplete biodegradability, APEs are initially metabolized into nonylphenol, octylphenol, nonylphenol monocarboxylic acid, and octylphenol monocarboxylic acids, which tend to be less biodegradable, more toxic, and more persistent (Dickey 1997; Ahel et al. 1993, 1994). Although APEs are removed effectively (99%) by tertiary wastewater treatment, they are poorly removed by primary wastewater treatment plants (12%) (Fedinger et al. 1995). Furthermore, instead of being mineralized completely to CO₂, water, and mineral salts, these compounds tend to adsorb to sludge and sediment, where their half life has been estimated at 60 years (Shang et al. 1999). Heinis et al. (1999) also reports the persistence of APEs in sediment. APEs and their metabolites have been detected in surface waters and sediments in the United States and Europe (Table 3.4). Finally, APEs can be magnified through the food chain; the BCF for nonylphenol ethoxylate is 300 in fish and up to 10,000 in algae (Dickey 1997).

An increasing amount of evidence is being published that APEs and their metabolites are endocrine disrupters, and their effects have been documented in aquatic life. Although a comprehensive analysis of APEs is presented in Dickey (1997), some more recent data are summarized here. The Illinois EPA lists p-nonylphenol and p-octylphenol (metabolites of nonylphenol and octylphenol ethoxylate, respectively) as a known and a probable endocrine disrupters, respectively (Illinois EPA 1997). Ashfield et al. (1998) reported that female juvenile rainbow trout exposed to 30 µg/L exhibited growth reduction and increased ovary size. Exposure to nonylphenol mono-carboxylic acid, a nonylphenol ethoxylate metabolite, at 1 to 10 µg/L caused a significant reduction in ovary size. Miles-Richardson et al. (1999) reported increased testicular lesions and necrotic spermatazoa at a concentration of 1.1 and 3.5 µg nonylphenol/L. Jobbling and Sumpter (1996) reported that fish exposed to nonylphenol or octylphenol at 0.5 to 0.65 µg/L showed changes in their production of vitellogenin, an egg yolk protein normally produced by female fish.

Because of the evidence that APEs are persistent and act as endocrine disrupters, APEs should not be an ingredient in an environmentally preferable cleaner. Therefore, the standard will exclude products containing them.

Aquatic Toxicity. Table 3.8 summarizes the aquatic toxicity of common surfactants (Talmage 1994; Hill et al. 1997; Schwarz and Vaeth 1987). It is difficult to draw conclusions about the relative toxicity of the surfactants because the results of toxicity testing vary depending on the species tested and the temperature.

Table 3.8 Acute toxicity of surfactants to aquatic life¹.

Surfactants	Fish LC ₅₀ (mg/L)	Daphnia LC ₅₀ (mg/L)	Algae (growth inhibition) NOEC (mg/L)
LAS	3 - 10	8 - 20	30 - 300
C ₁₄₋₁₈ -α-Olefin sulfonates	2 - 20	5 - 50	10 - 100
Fatty alcohol sulfates	3 - 20	5 - 70	60
Alcohol ether sulfates	1.4 - 20	1 - 50	65
Alkane sulfonates			
Soaps	6.7 - 150	--	10 - 50
Fatty alcohol EO/PO adduct	0.5 - 1	0.3 - 1	--
Alkylpolyglycoside	LC ₀ * = 3.7	38 - 48	10
Alkylphenol ethoxylates			
- C ₉			
7 EO	3.2	4.1 (96hr)	
9 EO	1.6		
Alcohol ethoxylates			
- C ₉₋₁₀			
2.5 EO	5 - 7		
5 EO	8 - 9		
6 EO	5.4		
- C ₁₂₋₁₅			
7 EO	0.48		

LAS: linear alkylbenzene sulfonate; EO: ethylene oxide or ethoxylate units

¹ Schwarz and Vaeth 1987; Hill et al. 1997; Talmage 1994

3.5.2.2 Builders

Eutrophication caused by the disposal of phosphates is one significant issue associated with the disposal of builders. Another is EDTA, which has poor biodegradability (Hinck et al. 1997; Kaluza 1998; Nortemann 1999). In the modified OECD test, only 20% of dissolved organic carbon was removed after 19 days, and anaerobic biodegradation of EDTA is negligible (HSDB 1999). EDTA also remobilizes heavy metals in the sediment of polluted waters (Bordas and Bourg 1998). However, the mobilization of heavy metals depends on the concentration of EDTA and heavy metals; the pH and redox potential of the water; and the presence of competitive ligands and precipitating anions (Oude 1992; Gonsinor et al. 1997). Landbank (1984) reports that zeolites, which tend to precipitate during water treatment, can significantly increase the amount of wastewater treatment sludge. The other builders are relatively inert and would not be expected to cause significant problems during disposal.

3.5.2.3 Antimicrobials

Table 3.9 summarizes the available toxicity data for antimicrobials. A cleaning product containing a typical use concentration of 0.1% of either of the quaternary ammonium compounds listed in Table 3.9 would be considered toxic to aquatic life according to EPA (1996b) guidance. A product containing a similar dilution of o-phenylphenol would not be considered toxic. However, o-phenylphenol is considered a carcinogen by EPA, and it has a BCF ranging from 15 to 607; therefore, it could be magnified through the aquatic food chain. Sodium hypochlorite and the alcohols are relatively nontoxic to aquatic life at their use concentrations. The alcohols would probably evaporate in a wastewater treatment plant.

Table 3.9 Aquatic toxicity of antimicrobials.

Compound	Fish LC ₅₀ (mg/L) ¹	Daphnia LC ₅₀ (mg/L) ²	Source
Alkyldimethylbenzyl-ammonium chloride		0.039	HSDB, ET
Didecyl dimethyl ammonium chloride	0.47 (24h)	0.059	HSDB, ET
o-phenylphenol	3.4		HSDB
Ethanol	11,100	3,715	SDB
Isopropyl alcohol	4,200	1,099	SDB
Sodium hypochlorite	5.9	2.1	HSDB, ET

ET: ECOTOX; HSDB: Hazardous Substances Data Bank; SDB: Solvent database (no date)

¹ Flathead minnow, 96-hour test unless otherwise noted.

² 48-hour test. Daphnia are small freshwater invertebrates.

3.5.2.4 Miscellaneous Ingredients

The disposal of dyes containing heavy metals is the most significant concern due to their persistence. The other ingredients should have minor impacts. The disposal of dibutyl phthalate, sometimes used as a solvent, can lead to endocrine system effects. The Illinois EPA lists dibutyl phthalate as a suspected endocrine disrupter (Illinois EPA 1997).

3.5.2.5 Packaging

Disposal of packaging is one of the significant life-cycle stages for industrial and institutional cleaners. Although empty plastic or cardboard containers pose few environmental impacts in a landfill, their incineration can cause hazardous air emissions and toxics in ash. In

addition, landfill space and incineration capacity are limited in the United States. Of the plastic containers, PVC containers pose the greatest hazards if incinerated. Combustion of PVC can cause the formation of dioxins, which are released to the air and in solid waste. Recycling significantly reduces environmental impacts from disposal, as well as from raw materials extraction and processing. HDPE, PET, and cardboard recycling programs are well established in this country. PVC recycling is rarely practiced, and PVC containers can contaminate PET recycling processes. Concern still exists over residual materials. However, aerosol cans are now accepted at 56% of community recycling programs (SRI 2000), and Bhimarapu and Karydas (1996) reported that recycling aerosol cans poses little risk even if an occasional can that is not empty is recycled.

3.5.3 Summary of Environmental Impacts from Disposal of Cleaners

The disposal of cleaning chemicals generates significant environmental impacts, particularly for surface waters and aquatic life. Although most surfactants are relatively nontoxic, APEs do not biodegrade readily. Additional concerns exist over APE's ability to disrupt the endocrine system. Among builders, phosphates have the greatest impact on streams due to eutrophication. Among antimicrobials, quaternary ammonium compounds tend to be toxic to aquatic life, and phenolic antimicrobials can bioaccumulate in the aquatic food chain. Finally, packaging that is not recycled depletes landfill space, and the combustion of PVC releases dioxins. Section 3.6 summarizes the impacts from all life-cycle stages qualitatively.

3.6 Summary of Environmental Evaluation of Cleaning Chemicals

Table 3.10 summarizes the qualitative health and environmental impacts of a number of cleaning ingredients. The plus sign indicates relatively fewer impacts; the minus sign indicates relatively greater impacts and zero indicates impacts similar to others.

Table 3.10 Qualitative health and environmental impacts of common cleaning ingredients.

	Manufacturing	Distribution	Use	Disposal
<i>Surfactants</i>				
Linear alkylbenzene sulfonate	-	+	+	-
Alcohol sulfates	+	+	+	+
Alkylpolyglycosides	+	+	+	+
Soap	+	+	+	+
Nonylphenol ethoxylate	-	+	+	-
Cocoamide diethanolamine	-	0	-	0
<i>Builders</i>				
Sodium hydroxide	0	-	-	0
Sodium carbonate/bicarbonate	+	+	+	+
Phosphoric acid	0	-	-	-
Citric acid	+	0	0	+
Sodium silicates	+	-	0	+
Sodium tripolyphosphate	0	+	0	-
Zeolites/PCA	0	+	0	0
EDTA	-	0	0	-
<i>Solvents</i>				
Alcohols	0	-	0	0
Terpenes	0	-	-	0
Glycol ethers	-	-	-	0
<i>Aerosol Propellants</i>				
Hydrocarbons	-	-	-	-
<i>Antimicrobials</i>				
Quaternary ammonium compounds	-	0	-	-
Phenols	-	-	-	-
Alcohols	0	-	-	0
Sodium hypochlorite	0	-	-	0
Pine oil	+	-	-	0
<i>Miscellaneous ingredients</i>				
Dyes	- to 0	0	0	- to +
Fragrances	0	0	-	0
<i>Packaging</i>				
HDPE	0	0	NR	0
PET	0	0	NR	0
PVC	-	0	NR	-
Aerosol cans	-	-	NR	-
Cardboard	0	0	NR	0
Glass	+	-	-	0

NR: Not relevant.

3.6.1 Surfactants

Most surfactants except for soap are manufactured, at least in part, from synthetic sources, and differences in the raw material extraction and processing of surfactant building blocks is difficult to discern because of the complex and varied intermediates. However, distinctions exist in the manufacturing and disposal stages. APEs, LAS, and cocoamide diethanolamine generate more toxic releases during their manufacture than soap, alkylpolyglycosides, and alcohol sulfates. In addition, the NTP has found evidence of cocoamide diethanolamine's potential carcinogenic activity (NTP 1998b). Furthermore, APEs and LAS do not biodegrade as well as soap, alkylpolyglycosides, and alcohol sulfates. Finally, concerns exist over the role of APEs as endocrine disrupters.

3.6.2 Builders

Builders can have significant health impacts during product use as well as during manufacture and disposal. A number of builders modify pH, and products with a pH outside the neutral range can irritate or damage the skin and eyes. Phosphates and EDTA have greater impacts during disposal than other builders because phosphates are one cause of eutrophication, and EDTA can mobilize persistent toxics in the sediment. Furthermore, EDTA generates greater burdens during its manufacture than the other builders. Landbank (1994) published a life-cycle comparison of phosphates and zeolites/PCA and reported that phosphates and zeolites/PCA have approximately equivalent life-cycle environmental burdens. However, a good deal of controversy exists over some of the assumptions in the study.

3.6.3 Solvents

Solvents impose their greatest impacts during manufacture and use. During manufacturing, glycol ethers have the greatest impacts among the solvents, and some of the glycol ethers are the most toxic during the use phase. Terpenes and alcohols derived from natural sources have the fewest impacts during manufacturing. The manufacture and use of any of the common solvents cause the release of VOCs, which can irritate workers, degrade indoor air quality, and contribute to urban smog. Therefore, the use of solvents in cleaning products should be limited.

3.6.4 Aerosol Propellants

The use and storage of flammable gasses under pressure are the greatest concern associated with aerosol propellants. These propellants are also VOCs and contribute to poor air quality. Cleaning products containing hydrochlorofluorocarbons are no longer sold due to their effect on the ozone layer. Many products are available in non-aerosol forms, so the need for aerosol propellants in cleaning products is unclear.

3.6.5 Antimicrobials

Antimicrobials have their greatest impacts during their manufacture, use, and disposal. Quaternary ammonium compounds and phenols have the greatest impacts during their manufacture. All antimicrobials can damage worker skin and eyes, depending on concentration. The alcohols and phenols are VOCs, which can be harmful to workers who inhale them. Alcohols and phenols also degrade indoor air quality and contribute to urban smog. Finally,

quaternary ammonium compounds can be toxic to aquatic life, depending on their concentrations.

Increasingly, antimicrobials are being added to all types of cleaning products. While the use of antimicrobials or some form of disinfection is clearly necessary for food preparation surfaces and for some surfaces in hospitals, controversy exists over the benefits of disinfecting environmental surfaces in the home, office, or other institutional settings. Additionally, disagreement exists over whether adding antimicrobials to cleaning products is beneficial. In this subsection, Green Seal reviews available data on whether disinfecting environmental surfaces is necessary and whether antimicrobials should be incorporated into cleaning products.

Is disinfecting environmental surfaces necessary? Microorganisms, including bacteria, fungi, and viruses, are present on nearly all surfaces in our environment. Some of these microorganisms are capable of producing infection in humans, and people generally believe that using a disinfectant or disinfecting cleaner will reduce the potential for the spread of disease. However, the benefits of this practice are unclear for the following reasons:

- The benefits of disinfecting are well established for food preparation surfaces and for surfaces in hospitals that may come into contact with broken skin or mucous membranes (CDC 1985; Rutala 1996; Russell et al. 1999). Although microorganisms are present on walls, floors, and other environmental surfaces, they are rarely associated with the transmission of infections, even in hospital settings. Therefore, extraordinary attempts to disinfect or sterilize these environmental surfaces are rarely necessary (CDC 1985). Levy (1998) states that there is no evidence that disinfecting environmental surfaces, such as floors, walls, and furniture, decreases the spread of disease in households. Research is clearly needed to determine if there are public health benefits to disinfecting environmental surfaces.
- Cleaning on a regular basis, without the use of disinfectants, is an effective method for eliminating most microorganisms. Cleaning also removes the source of food microorganisms need in order to reproduce. According to Russell et al. (1999), disinfectants are not necessary for eliminating most microorganisms on floors, walls, ceilings, furniture, and sinks; standard cleaning is sufficient. The CDC also recommends only routine cleaning and removal of soil for general housekeeping activities in hospitals.

Should antimicrobials be part of an industrial and institutional cleaning product? More controversy exists as to whether antimicrobials should be included in cleaning products. Some manufacturers state that antimicrobials are necessary to protect public health, and they believe antimicrobials must be included in cleaners to conserve labor and labor expenses. Other manufacturers and the city of Santa Monica, CA believe that cleaning and disinfecting are two separate activities. They cite two reasons for separating cleaning from disinfecting:

- A surface must be clean or relatively clean prior to disinfecting. Although antimicrobials are inactivated by organic soil, some antimicrobials are more sensitive than others. For example, sodium hypochlorite is inactivated by the presence of organic soil; however, quaternary ammonium compounds and phenols are more tolerant of organic soils.
- Workers must exercise care when using disinfecting cleaners to avoid recontaminating areas as they are attempting to disinfect. For example, using a soiled rag, sponge, or mop could

recontaminate a surface that is being disinfected. In addition, workers must follow the directions carefully to ensure that the antimicrobial has had sufficient contact time to achieve good bacterial kill. Krilov et al. (1996) report that improved cleaning and disinfection can be used effectively as part of an infection control program in a school.

Summary. The use of antimicrobials presents a challenge because Green Seal aims not only to reduce the use of unnecessary ingredients but to protect public health. After considering the literature, product formulations, and discussions with purchasers, users, and formulators, Green Seal has decided to consider general-purpose and glass cleaners that are required to be registered under FIFRA outside the scope of the standard. However, bathroom cleaners that are required to be registered under FIFRA will be considered within the scope of the standard.

3.6.6 Miscellaneous Ingredients

Dyes can have significant environmental impacts during their manufacture and disposal. However, dyes can assist workers in identifying cleaning products, thereby reducing the potential for accidentally mixing incompatible chemicals. Because dyes containing heavy metals have significant environmental impacts, Green Seal has prohibited heavy metals in a product.

Fragrances can have impacts during their manufacture and use. Nearly all manufacturers stated that fragrances were necessary because they reduce the need for cleaning and mask the scent of unpleasant-smelling ingredients. The International Fragrance Association has developed a code of practice for fragrances, and Green Seal recommends that manufacturers follow this code of practice.

3.6.7 Packaging

Most cleaners are packaged in plastic containers, although some are packaged in aerosol containers and a few are packaged in glass. Packaging impacts occur during raw material extraction and processing, manufacturing, and disposal life-cycle stages; recycling reduces all these impacts. Although HDPE and PET plastics are recycled at rates of approximately 25% (EPA 1996b), PVC is not being recycled to any significant extent. In addition, PVC has greater toxic impacts during its manufacture than other types of plastics.

Aerosol cans are accepted in 56 to 57% of community recycling programs, but concerns exist about residual materials in the containers (SRI 2000). In addition, the propellants are flammable and contribute to reduced indoor air quality.

PART 4

EXISTING STANDARDS FOR HEALTH AND ENVIRONMENTAL PERFORMANCE

4.1 General Standards Related to Human Health

In establishing a certification program for cleaners, it is important to ensure that the product does not present a threat to human health. Human-health standards include toxicity, carcinogenicity, reproductive toxicity, and skin and eye irritation. This section reviews human health standards Green Seal can use in the development of an environmental labeling standard for industrial and institutional cleaners. Section 3.8 discusses existing environmental standards for industrial and institutional cleaners.

4.1.1 Toxic Compounds

There are numerous regulations that list chemicals as hazardous, but these classifications often include specifications in addition to systemic toxicity in mammals. Agencies that have derived systems for classifying chemicals as toxic based on mammalian toxicity include the CPSC, Toxic Substances Control Act (TSCA), OSHA, and OECD.

These classification systems are based on the results of toxicity tests using laboratory animals. An acute LD₅₀, as used in these regulations, is the calculated concentration of a substance, expressed in mass of the substance per mass of the animal, that will kill 50% of the individuals within an exposed group of white rats within 14 days, when administered orally as a single dose. An acute inhalation LC₅₀, as used in these regulations, is the calculated concentration of a substance in air (gas, vapor, aerosol, fume, or dust) that will kill 50% of the individuals within an exposed group of white rats when inhaled continuously for one hour, or less if death occurs first. The acute LD₅₀ for skin absorption is the calculated concentration of a substance, expressed in mass of the substance per mass of the animal, that will kill 50% of the individuals within an exposed group of rabbits when administered in continuous contact with bare skin for 24 hours.

Some agencies have developed criteria based on subchronic exposure as compared to acute exposure. The LD₅₀ and LC₅₀ values for these types of exposures are based on multiple exposures over an extended period of time, which is defined by the type of study. Therefore, the LD₅₀ values are calculated based on the mass of substance applied per mass of the animal, averaged over the number of days the animals was exposed. Similarly, the LC₅₀ value is calculated based on the time of exposure, and the final value is expressed as the mass of substance applied per mass of the animal per day.

The CPSC has adapted the definitions of highly toxic compounds from the Federal Hazardous Substances Act (Pub. L. 86-613, 74 Stat. 372-81 [15 U.S.C. 1261-74]) and has also established definitions for toxic compounds (16 CFR Part 1500.3). These criteria are based on the results of acute toxicity tests (Table 4.1).

The TSCA Interagency Testing Committee to Prioritize Chemicals for Testing has developed criteria for classifying (Walker 1995). These criteria have been developed for both acute and subchronic toxicity data (Table 4.2).

Table 4.1 Toxicity levels in CPSC regulations.

Toxicity Ranking	Measure	Species
Highly toxic	$LD_{50} \leq 50$ mg/kg (oral)	White rats
	$LC_{50} \leq 200$ ppm (inhalation)	White rats
	$LC_{50} \leq 2$ mg/L (inhalation dust or aerosol)	White rats
	$LD_{50} \leq 200$ mg/kg (skin)	Rabbits
Toxic	50 mg/kg < $LD_{50} \leq 5$ g/kg (oral)	White rats
	200 ppm < $LC_{50} \leq 20,000$ ppm (inhalation)	White rats
	2 mg/L < $LC_{50} \leq 200$ mg/l (inhalation dust or aerosol)	White rats
	200 mg/kg < $LD_{50} \leq 2$ g/kg (skin)	Rabbits

Table 4.2 Toxicity levels given in the TSCA prioritization methodology.

Type of Exposure	Toxicity Ranking	Measure
Acute	Extremely Toxic	$LD_{50} < 50$ mg/kg (oral)
		$LD_{50} < 1$ mg/kg (dermal)
		$LD_{50} < 5$ mg/L (inhalation)
	Very Toxic	$LD_{50} = 50 - 500$ mg/kg (oral)
		$LD_{50} = 1 - 50$ mg/kg (dermal)
		$LD_{50} = 5 - 50$ mg/L (inhalation)
	Moderately toxic	$LD_{50} = 500 - 5,000$ mg/kg (oral)
		$LD_{50} = 50 - 500$ mg/kg (dermal)
		$LD_{50} = 50 - 500$ mg/L (inhalation)
	Slightly Toxic	$LD_{50} > 5,000$ mg/kg (oral)
		$LD_{50} > 500$ mg/kg (dermal)
		$LD_{50} > 500$ mg/L (inhalation)
Subchronic	Extremely Toxic	$LD_{50} < 1$ mg/kg/day (oral)
		$LD_{50} < 0.2$ mg/kg/day (dermal)
		$LD_{50} < 0.1$ mg/L (inhalation)
	Very Toxic	$LD_{50} = 1 - 10$ mg/kg/day (oral)
		$LD_{50} = 0.2 - 1$ mg/kg/day (dermal)
		$LD_{50} = 0.1 - 1$ mg/L (inhalation)
	Moderately Toxic	$LD_{50} = 10 - 100$ mg/kg/day (oral)
		$LD_{50} = 1 - 10$ mg/kg/day (dermal)
		$LD_{50} = 1 - 10$ mg/L (inhalation)
	Slightly Toxic	$LD_{50} > 100$ mg/kg/day (oral)
		$LD_{50} > 10$ mg/kg/day (dermal)
		$LD_{50} > 10$ mg/L (inhalation)

The OSHA regulations concerning the definitions of human health hazards defined highly toxic and toxic chemicals using the criteria listed in Table 4.3 (29 CFR Part 1910.1200, App A). For the purposes of defining toxic compounds, acute toxicity test results are used. OSHA recognizes the importance of chronic toxicity studies; however, no defining standards were developed because of the range and diversity of toxic endpoints (Table 4.3).

Table 4.3 Toxicity levels given in the OSHA regulations.

Toxicity Ranking	Measure
Highly Toxic	LD ₅₀ < 50 mg/kg (oral)
	LD ₅₀ < 200 mg/kg (dermal)
	LD ₅₀ < 5 mg/L (inhalation of mist, fume, or dust)
	LD ₅₀ < 200 ppm (inhalation of gas or vapor)
Toxic	LD ₅₀ = 50 - 500 mg/kg (oral)
	LD ₅₀ = 200 - 1,000 mg/kg (dermal)
	LD ₅₀ = 2 - 20 mg/L (inhalation of mist, fume, or dust)
	LD ₅₀ = 200 - 2,000 ppm (inhalation of gas or vapor)

The OECD has developed criteria for classifying chemicals as very toxic, toxic, and harmful are based on the results of acute toxicity tests (Table 4.4).

Table 4.4 Toxicity levels given in the OECD classification.

Toxicity Classification	Measure	Species
Very toxic	LD ₅₀ ≤ 25 mg/kg (oral)	Rat
	Less than 100% survival at 5 mg/kg (oral)	Rat
	LC ₅₀ ≤ 0.25 mg/L/4 hr (inhalation)	Rat
	LD ₅₀ ≤ 0.5 mg/L/4 hr (inhalation aerosols or particulates)	Rat
	LD ₅₀ ≤ 50 mg/kg (dermal)	Rat or rabbit
Toxic	25 < LD ₅₀ ≤ 200 mg/kg (oral)	Rat
	100% survival at 5 mg/kg but evident toxicity (oral)	Rat
	0.5 < LC ₅₀ ≤ 2 mg/L/4 hr (inhalation)	Rat
	0.25 < LC ₅₀ ≤ 1 mg/L/4 hr (inhalation aerosols or particulates)	Rat
	50 < LD ₅₀ ≤ 400 mg/kg (dermal)	Rat or rabbit
Harmful	200 < LD ₅₀ ≤ 2,000 mg/kg (oral)	Rat
	100% survival at 50 mg/kg but evident toxicity (oral)	Rat
	Less than 100% survival at 500 mg/kg (oral)	Rat
	2 < LC ₅₀ ≤ 20 mg/L/4 hr (inhalation)	Rat
	1 < LC ₅₀ ≤ 5 mg/L/4 hr (inhalation aerosols or particulates)	Rat
	400 < LD ₅₀ ≤ 2,000 mg/kg (dermal)	Rat or rabbit

The Globally Harmonized System has developed an integrated hazard classification system. They divide the hazards into five classes, with class 5 being relatively low acute toxicity but may present a danger to vulnerable populations (Table 4.5).

Table 4.5 Toxicity levels given in the Globally Harmonized System classification (OECD 1998).

	Class 1	Class 2	Class 3	Class 4	Class 5
Oral (mg/kg)	5	50	300	2,000	5000
Dermal (mg/kg)	20	200	1,000	2,000	
Vapors (mg/L)	0.5	2.0	10	20	

For the purposes of this standard, Green Seal recommends the Globally Harmonized System and OECD criteria for not harmful because they were developed by an international organization. The oral toxicity criterion is $LD_{50} > 2,000$ mg/kg, and the toxicity criterion for inhalation of gas or vapor is $LC_{50} > 20$ mg/L.

4.1.2 Carcinogens and Reproductive Toxins

Four organizations that evaluate and classify chemicals based on the overall level of evidence of their carcinogenic effect are EPA, IARC, the California Department of Health Services, and the U.S. Department of Health and Human Services' National Toxicology Program (NTP). EPA devised a classification scheme with five categories; the scheme is summarized in Table 4.6 (OTA 1987). The classification scheme of the IARC is summarized in Table 4.7 (OTA 1987).

Table 4.6 Classification of carcinogens by the EPA.

Group A - Human Carcinogen	Sufficient evidence from epidemiologic studies to support a causal association between exposure to the chemicals and cancer.
Group B - Probable Human Carcinogen	B1: Limited evidence from epidemiologic studies, and sufficient evidence from animal studies. B2: Inadequate or no data from epidemiologic studies, and sufficient evidence from animal studies.
Group C - Possible Human Carcinogen	Limited evidence in animals in the absence of human data.
Group D - Not Classifiable as to Human Carcinogenicity	Inadequate human and animal data or no data.
Group E - Evidence of Noncarcinogenicity for Humans	No evidence of carcinogenicity in at least two adequate animal tests in different species or in both adequate epidemiologic and animal studies.

Table 4.7 Classification of carcinogens by the IARC.

Group 1	The agent is carcinogenic to humans: sufficient evidence of carcinogenicity in humans.
Group 2A	The agent is probably carcinogenic to humans: limited evidence of carcinogenicity in humans and sufficient evidence in animals.
Group 2B	The agent is possibly carcinogenic to humans: limited evidence in humans in the absence of sufficient evidence in animals. Inadequate evidence in humans (or no data) but sufficient evidence in animals.
Group 3	The agent is not classifiable as to its carcinogenicity to humans: agents are placed in this category when they do not fall into any other group.
Group 4	The agent is probably not carcinogenic to humans: evidence suggests a lack of carcinogenicity in humans and in animals. In some cases, evidence suggests lack of carcinogenicity in animals without human data where other supporting evidence exists.

California, under the Safe Drinking Water and Toxic Enforcement Act of 1986, is required to list chemicals known to cause cancer or reproductive toxicity. In listing chemicals, the state relies on other authoritative bodies, such as EPA and IARC, and its own panel of experts. Under the law, a chemical is considered to cause cancer if there is sufficient evidence in either humans or animals. A chemical is considered to cause reproductive toxicity when there is either human evidence or when studies in animals indicate that an association between the toxic agent and reproductive effects in humans is biologically plausible (California Code of Regulations, Title 22, Division 2, Subdivision 1, Chapter 3, Sections 12000, *et seq.*).

The NTP publishes the *Annual Report on Carcinogens*, which is a consensus list of chemicals that are either known or reasonably expected to cause cancer in humans. Several federal agencies are represented in the group that determines the chemicals for the report, including EPA, OSHA, the Food and Drug Administration, the Agency for Toxic Substances and Disease Registry, and the National Cancer Institute (NTP 1998a).

Chemicals that are suspected of causing cancer or reproductive toxicity may be subject to regulations governing releases to the environment or the workplace, but most have not been specifically regulated. For instance, until the 1991 Clean Air Act Amendments, only seven hazardous air pollutants had been regulated. OSHA has lagged even further behind in adopting workplace standards for most carcinogens. Even with regulatory controls in place, however, risks remain from the use and release of these chemicals.

Green Seal recommends that the products do not contain any known, probable, or possible carcinogens as defined by IARC, NTP, EPA, or OSHA.

4.1.3 Skin and Eye Irritation

The CPSC, OSHA, OECD, and the cosmetics industry have developed criteria for skin and eye irritation. The CPSC defines an irritant as a compound that is not a corrosive but induces a local inflammatory reaction in normal living tissue as a result of immediate, prolonged, or repeated contact (16 CFR Part 1500.3). It states that skin irritants should be defined using the Draize skin test with rabbits (16 CFR Part 1500.42). The CSPC defines corrosive as any substance that, in contact with living tissue, will cause destruction of tissue by chemical action

(16 CFR Part 1500.3). It uses the Draize test method to determine corrosivity and states that, when the compound is tested on the intact skin of the albino rabbit, the structure of the tissue at the site of contact is destroyed or changed irreversibly in 24 hours or less.

OSHA uses the same criteria as CPSC and references the CPSC definitions and protocols in defining skin and eye irritants (29 CFR Part 1910.100, App A).

The OECD considers a material corrosive to the skin if, using the results of animal testing, the material produces destruction of skin tissue (namely, visible necrosis through the epidermis and into the dermis) in one or more of three tested animals after exposure up to a four-hour duration [OECD Test Guide (TG) 404]. Corrosive reactions are typified by ulcers, bleeding, bloody scabs, and, by the end of observation at 14 days, discoloration due to blanching of the skin.

The OECD considers a material corrosive to the eye if it causes irreversible effects on the eye including persistent corneal opacity, discoloration of the cornea, adhesion, and interference with the function of the iris or other effects that impair sight. In this context, persistent lesions are considered those that are not fully reversible within an observation period of normally 21 days (OECD, TG 405). The OECD also recommends searching the literature and considering skin irritation test results before testing eye irritation/corrosion to avoid any unnecessary animal testing.

The cosmetics industry generally uses the Kay and Calandra criteria for classifying materials in terms of their eye irritation properties (Kay and Calandra 1962). The scoring of the various tests is based on the severity of the reaction. The rating for a product is increased if the reactions caused are beyond simple erythema and edema, e.g., necrosis, escharosis, or hemorrhage.

Recently, EPA, OSHA, and the CPSC have endorsed the use of synthetic skin for skin corrosion testing to reduce animal testing. Furthermore, peer-reviewed non-animal test methods for skin and eye corrosion have been developed. These include the Human Skin Construct systems (Liebsch et al. 2000; Fentem et al. 1998) for skin irritation/corrosion and the bovine corneal opacity and permeability test (BCOP) (Sina et al. 1995) for eye irritation/corrosion. The BCOP method has been tested on cleaning products and has been shown to agree well with the results of Draize testing (Swanson et al. 1995).

Green Seal would like to reduce animal testing; therefore, it recommends the Human Skin Construct systems test (Liebsch et al. 2000; Fentem et al. 1998) for skin corrosion and the BCOP test (Sina et al. 1995) for eye corrosion.

4.2 Existing Health and Environmental Performance Standards

Green Seal identified a number of environmental labeling, purchasing, and stewardship standards for industrial and institutional cleaners (Table 4.8). The Canadian Environmental Choice Program was the only national labeling program with an environmental labeling standard for industrial and institutional cleaners. However, many national programs have standards for household cleaners, including Green Seal in the United States, the Canadian Environmental Choice program, the German Blue Angel program, the Nordic Ecolabeling program, the EU Ecolabeling program, and the Austrian Environmental Shield program. The city of Santa

Monica, California; the states of Massachusetts, Minnesota, Vermont, and Washington; and King County, Washington have developed purchasing standards for industrial and institutional cleaners. Barron et al. (1999) developed chemical substitution recommendations for janitorial chemicals as part of a pilot project to evaluate pollution prevention opportunities in the janitorial industry. A few government specifications for cleaners contain environmental criteria. Finally, some manufacturers have developed their own internal environmental ranking systems. Green Seal also searched but did not identify any military specifications for general-purpose, bathroom, or glass cleaners.

Table 4.8 Environmental labeling/purchasing standards for industrial and institutional cleaners.

Type of Organization	Organizations	Standard
City	Santa Monica, CA	Purchasing
County	King County, WA	Purchasing
State	Massachusetts, Minnesota, Vermont, Washington	Purchasing
Federal	EPA	Purchasing
International	Canadian Environmental Choice, Nordic Swan	Labeling
Other	ASTM SAE 1550B and GSA	Stewardship guide Product specifications

The international labeling standards and the city, county, and state purchasing programs defined criteria for selecting environmentally preferable products. The EPA environmental purchasing program for cleaners and the ASTM guide for environmental stewardship present a framework for selecting products and managing cleaning operations rather than setting criteria. Most programs developed lists of prohibited ingredients and supplemented this with either a point-based ranking system or additional criteria for other environmental attributes. A point-based system defines criteria and scoring ranges. The product's scores for each criterion are totaled, and all products with a score above a certain level are considered preferable. For example, a product with a pH range between 5 and 9 would receive the maximum score, such as 5, and a product with a pH above 12 or below 2.5 would receive a score of 0. This score would be added to the scores for other attributes, such as toxicity, flammability, VOC content, etc.

The remainder of this section outlines and summarizes the Canadian environmental labeling standard, Green Seal's environmental labeling standard for household cleaners, purchasing standards, product specifications, and stewardship standards. Each standard's criteria are listed alphabetically, and their order does not reflect the relative importance of the various criteria.

4.2.1 Canadian Environmental Choice

This program defines criteria for a number of categories, and those products meeting all criteria can be certified. The categories include the following

- Aquatic toxicity: the whole product must have an inhibition concentration (IC_{50}) > 200 mg/L (minimum dilution) and IC_{50} > 10 mg/L (concentrate) as measured on ceriodaphnia, selenastrum, or photobacterium. The product cannot contain more than 0.1% of any ingredient that is very acutely toxic, acutely toxic and not readily biodegradable, or bioaccumulating and not readily biodegradable. A very acutely toxic ingredient has an LC_{50}

or effect concentration (EC_{50}) < 100 mg/L for fish, daphnia, or algae. A bioaccumulative compound has a BCF > 100.

- Biodegradability: readily biodegradable.
- Concentration limits: 1% EDTA, 5% nitrilotriacetic acid (NTA), 5% total phosphorus, and 10% VOC content
- Corrosivity: product cannot cause irreversible damage to the skin. Its pH must be between 2.0 and 13.
- Flashpoint: must be greater than 61 °C (140 °F).
- Prohibited: aromatic solvents, APEs, butoxy ethanol, carcinogens, chlorinated solvents, and ODCs.

4.2.2 Nordic Ecolabeling

This standard defines criteria for industrial cleaning and degreasing agents. The criteria include the following

- Aquatic toxicity: prohibits compounds that are very toxic to the aquatic environment (Fish LC_{50} (96 hr), daphnia EC_{50} (48 hr), or algae IC_{50} (72 hr) < 1 mg/L). The criteria place further limits on the combination of toxicity, biodegradability, and potential for bioaccumulation.
- Concentration limits: 5g NTA/L and 2 g phosphorus/L.
- Dyes: must be cosmetic or food-grade.
- Prohibited: APEs, chlorinated packaging, EDTA, fragrances, halogenated organics, LAS, petroleum-based solvents, and phthalates.

4.2.3 Green Seal

This publicly reviewed standard defines criteria for general-purpose household cleaners; to be certified, a product must meet all criteria. Green Seal published its criteria along with an environmental evaluation, and this laid the groundwork for many of the city and state environmental purchasing standards. The criteria include the following

- Aquatic toxicity: the product must have an EC_{50} > 10 mg/L for daphnia (48 hr), algae (96 hr), or daphnia (14 day) or an LC_{50} > 10 mg/L for fish.
- Biodegradability: readily biodegradable.
- Concentration limits: heavy metals 0.5 mg/L except cadmium 0.1 mg/L and mercury 0.02 mg/L, 0.5% phosphates, and 10% VOCs.
- Packaging: no aerosol cans unless a recycling program exists wherever the product is sold; no secondary packaging unless the product is a concentrate; no packaging dyes or additives

to which lead, cadmium, mercury, or hexavalent chromium has been added; and lead, cadmium, mercury, and hexavalent chromium packaging content cannot exceed 100 ppm.

- Prohibited: carcinogens and reproductive toxins.
- Toxicity: LD₅₀ (oral) > 5,000 mg/kg; LC₅₀ (dermal) > 2,000 mg/kg; LC₅₀ (inhalation) > 20,000 ppm.
- Other: the product cannot contain disposable towelettes.

4.2.4 State and Local Environmental Purchasing Programs

In 1993, Santa Monica, California developed a two-tier ranking system to identify environmentally preferable products. Many of the other purchasing programs developed similar systems. These systems require all products to meet a set of pass/fail criteria and then be ranked on additional attributes. Massachusetts, Vermont, and Washington developed similar systems with slightly different criteria. Minnesota's standard relies entirely on a relative ranking system, and King County, Washington uses pass/fail criteria exclusively. After these programs identify environmentally preferable products, they field test the best products. Final product selection is based on the results of the environmental ranking, pilot testing, and cost. In addition to the criteria highlighted in the following sections, most state programs also require that manufacturers comply with a number of state and federal regulations. A summary of each purchasing program follows.

The City of Santa Monica, California

The city of Santa Monica developed a two-tier ranking system, which was recently refined.

Pass/fail criteria:

- Biodegradability: meets the OECD definition of readily biodegradable.
- Prohibited: aerosol cans, APEs, carcinogens, disinfectants in cleaners, mutagens, ODCs, teratogens, and the Emergency Planning and Community Right-to-Know Act (EPCRA) Title III Section 313 Toxics Release Inventory (TRI) chemicals.
- VOC content: must not exceed 10% for general-purpose cleaners, 5% for bathroom and tile cleaners, and 8% for glass cleaners. Aerosol products are allowed to have a slightly higher VOC content.

Relative ranking criteria:

- Aquatic toxicity: prefer products with the lowest overall aquatic toxicity.
- Dyes and fragrances: prefer none or food-grade dyes and fragrances.
- Employee training: prefer vendors that offer employee training.
- Flashpoint: prefer a flashpoint above 200 °F.

- Packaging: prefer concentrated products and plastic types 1 - 5.
- pH: prefer 6.1 < pH > 8.0: least preferable 2.5 > pH or pH > 12.5.
- Skin and eye irritation: prefer nonirritating products. A variety of different tests are acceptable.
- Toxicity: prefer LD₅₀ (oral) > 5,000 mg/kg, LD₅₀ (dermal) > 4,300 mg/kg, and LC₅₀ (inhalation) > 10,000 ppm.
- VOC content: prefer none or trace.
- Other attributes: the vendors may provide information about other attributes of their product, and such attributes are considered in the selection process. For example, some products are manufactured locally (which reduces transportation impacts); some are produced by minority-owned businesses or manufactured from renewable resources.

Massachusetts

The state of Massachusetts developed a two-tier ranking system similar to that of Santa Monica.

Pass/fail criteria:

- Phosphates: must not exceed 0.5% by weight for most products.
- Prohibited: carcinogens, ODCs, and chemicals on the Massachusetts Toxics Use Reduction Act (TURA) list, which includes most of the Emergency Planning and Community Right-to-Know Act (EPCRA) Title III Section 313 TRI and CERCLA.
- VOC content: must not exceed 10% for general-purpose cleaners, 5% for bathroom and tile cleaners, and 8% for glass cleaners. Aerosol products are allowed to have a slightly higher VOC content. Other products must not exceed the legal limit according to Massachusetts law.

Relative ranking criteria:

- Alkylphenol ethoxylates: prefer none.
- Biodegradability: prefer readily biodegradable.
- Corporate environmental impacts : an environmental program for company operations that takes the company beyond compliance.
- Dyes and fragrances: prefer none or food grade or a product that is available with and without dyes.
- Flashpoint: prefer flashpoints > 200 °F; least preferable < 140 °F.

- Skin and eye irritation: prefer nonirritating products as measured by one of a variety of test methods.
- Packaging: prefer concentrates, no aerosol cans, recyclable packaging materials, packages with recycled content, and refillable containers.
- pH: prefer $4.0 < \text{pH} < 9.0$, and least preferable: $2.5 > \text{pH}$ or $\text{pH} > 11.5$.
- Phosphates: prefer lowest concentration.
- VOC content: prefer lowest VOC content.
- Other: prefer a product that contains no listed or characteristic Resource Conservation and Recovery Act (RCRA) waste.

Minnesota

Minnesota's purchasing program uses the following relative ranking criteria:

- Dyes and fragrances: prefer no synthetic fragrances or dyes.
- Flashpoint : prefer flashpoint > 200 °F; least preferable < 140 °F.
- Ingredients: prefer no carcinogens under IARC, NTP, or ACGIH and no ODCs.
- pH: prefer $2 < \text{pH} < 12.5$.
- Packaging: prefer no aerosol cans, containers without excess packaging, packages with 20% post-consumer recycled content, refillable containers, concentrated product, and containers that minimize exposure to the concentrate.
- Phosphates: prefer less than 0.5 % by weight.
- Toxicity: Minnesota based its human toxicity criteria on 29 CFR 1910.1200, Appendix B, Health Hazard Definition

Criteria	Preferable	Least Preferable
Oral LD ₅₀	≥ 500 mg/kg	≤ 50 mg/kg
Dermal LD ₅₀	$\geq 1,000$ mg/kg	≤ 200 mg/kg
Inhalation LC ₅₀	$\geq 2,000$ ppm	≤ 200 ppm

- Toxicity: prefer chemicals not listed in the Minnesota Toxics Index. This index was developed using a multimedia fate model, chemical properties, and toxicity data to estimate the hazard potential of a number of chemicals. Minnesota's Toxic Index includes those chemicals with the greatest hazard potential (Pratt et al. 1993).
- Other: prefer products derived from plant matter.

Vermont

The state of Vermont developed the following pass/fail and relative ranking purchasing criteria.

Pass/fail:

- Prohibited: carcinogens, mutagens, ODCs, teratogens, and TRI chemicals.
- VOC content: must not exceed 10% for general-purpose cleaners, 5% for bathroom and tile cleaners, and 8% for glass cleaners.

Relative ranking:

- Aquatic toxicity: prefer EC_{50} daphnia (48h), LC_{50} fish (96h), or EC_{50} algae (96h) $> 2,000$ ppm.
- Biodegradability: prefer readily biodegradable products.
- Corporate environmental impacts: prefer cruelty-free product testing, pollution prevention program, and vendors with a corporate environmental statement.
- Flashpoint : prefer > 200 °F; least preferable < 140 °F.
- pH: prefer $5 < \text{pH} < 9.5$; least preferable $\text{pH} < 2.0$ or $\text{pH} > 12.5$.
- Potential for exposure to users: prefer vapor pressure < 6 mmHg, evaporation rate < 3.0 %, and volatile content except water < 10 %.
- Packaging: prefer non-aerosol cans; post-consumer, recycled-content container; minimized packaging; recyclable container; and concentrated product.
- Toxicity: prefer products that are less toxic when compared to similar products.
- Other: prefer renewable ingredients.
- Other: products that have Green Seal approval will automatically meet a number of the criteria.

Washington

The state of Washington developed the following pass/fail and relative ranking purchasing criteria.

Pass/fail:

- Aquatic toxicity: EC_{20} daphnia (48h), EC_{20} fish (96h), EC_{20} algae (96h), EC_{20} daphnia (21d) $> 1,000$ mg/L.
- Biodegradability: readily biodegradable.
- Flashpoint: greater than 140 °F.

- pH: $2 < \text{pH} < 12.5$.
- Prohibited: APEs, carcinogens, mutagens, ODCs, teratogens, and TRI chemicals.
- VOC content: must not exceed 10%.
- Other: no product can be a hazardous waste for reasons such as ignitability, corrosivity, reactivity, or toxicity.

Relative ranking:

- Dyes and fragrances: prefer no synthetic dyes or fragrances.
- Packaging: prefer a vendor with a container management plan such as reusing, recycling, or re-filling containers. Prefer a concentrated product, dispensing equipment to minimize exposure, non-aerosol containers, 35% or greater post-consumer content, plastic types 1 - 7.
- Phosphates: prefer less than 0.5% by weight.
- Skin, eye irritation, and lung irritation: prefer products that do not require a warning label for skin, eye, or lung irritation.
- Toxicity:

Prefer

LD₅₀ (oral) > 5,000 mg/kg
 LD₅₀ (dermal) > 4,300 mg/kg
 LC₅₀ (inhalation) > 10,000 ppm

Least Preferable

LD₅₀ (oral) < 500 mg/kg
 LD₅₀ (dermal) < 430 mg/kg
 LC₅₀ (inhalation) < 1,000 ppm

- Training programs: prefer vendors with training programs for workers who use their product.
- VOC content: prefer none or trace amount.
- Other: prefer ingredients produced from renewable resources.

King County, Washington

King County developed a set of pass/fail criteria for its purchasing program:

- Aquatic toxicity: LC₂₀ ≥ 1,000 ppm.
- Biodegradability: readily biodegradable.
- Flammability: nonflammable.
- pH: must be $2.0 < \text{pH} < 12.5$.

- Prohibited: butyl cleaners, carcinogens, chlorinated fluorocarbons, chlorinated solvents, dichloroethane, mutagens, and no chemicals listed in Washington’s state dangerous waste regulations.
- Skin irritation: non-irritating.
- Other: vendors must accept the no-charge return of all 55-gallon drums used for their products.

4.2.5 EPA Environmentally Preferable Purchasing Program Cleaning Products Pilot Project

The goal of this project was to help purchasers identify products that would reduce human health and safety concerns in the buildings overseen by the General Service Administration’s (GSA) Public Building Service. Green Seal identified a number of attributes and developed a product attribute matrix for products in the GSA’s Biodegradable Cleaner/Degreaser Catalogue. In order to be in the matrix, GSA required that products be readily biodegradable according to the OECD definition and that the product have a low toxicity as defined by the following

LD ₅₀ (oral)	> 50 mg/kg (rat)
LD ₅₀ (dermal)	> 200 mg/kg (rabbit)
LC ₅₀ (inhalation)	> 2 mg/L

Other than these requirements, the matrix system leaves the evaluation of preferability to the purchaser. The attributes include the following

- Air pollution potential as measured by VOC content.
- Skin irritation potential.
- Food chain exposure as measured by a product’s BCF. Products with a BCF < 1,000 are preferable.
- The presence of fragrances.
- The presence of dyes.
- Reduced or recyclable packaging.
- Product has features to minimize exposure to the concentrate.

4.2.6 ASTM Standard Guide for Stewardship for the Cleaning of Commercial and Institutional Buildings

This guide presents stewardship principles for managing facility cleaning processes (ASTM E1971 1998). It outlines how to develop a stewardship plan, and it provides recommendations for worker training and communication of worker safety and environmental impacts. However, the guide focuses on general management considerations and does not provide specific criteria for product selection, environmental impacts, or worker safety.

4.2.7 Product Specifications

The Society of Automotive Engineers (SAE) specification and a number of federal product specifications set requirements for pH, flashpoint, and/or biodegradability. Table 4.9 summarizes the requirements. A few of the federal product specifications have been cancelled recently (denoted by *).

Table 4.9 Industrial and government product specifications.

Specification	Requirement
SAE 1550B, aircraft hard surface cleaner	Flashpoint > 70 °C (158 °F)
P-C-1891, porcelain and ceramic tile cleaner	$7.0 \leq \text{pH} \leq 10.0$
P-D-1747C, general-purpose detergent A-A-3156, spray on, wipe off detergent*	pH < 12.8
P-D-225, solvent type detergent	90% biodegradable, flashpoint > 90 °C (194 °F)
P-D-220D, general-purpose detergent	$5.0 < \text{pH} < 10.5$
A-A-70B, glass cleaner*	Flashpoint > 49 °C (120 °F)

* Cancelled.

4.2.8 Chemical Substitutions

Barron et al. (1999) developed recommended chemical substitutions as part of a pilot project to evaluate pollution prevention opportunities in the janitorial industry in California. They make specific recommendations about preferred ingredients and ingredients to avoid or to use with caution. For example, they recommend using glass cleaners formulated with isopropanol or other less hazardous ingredients as opposed to those containing butoxyethanol. They also recommend general-purpose cleaners formulated with linear alcohol ethoxylates, citric acid, or other less hazardous ingredients over those formulated with alkylphenyl ethoxylates, ethanolamine, or butoxyethanol.

4.2.9 Internal Ranking Systems

A number of companies have developed their own lines of environmentally preferable products, and some companies specialize in formulating environmentally preferable products. Many of these companies define their environmentally preferable products as those with a neutral pH, low VOC content, ready biodegradability, and/or renewable ingredients. Green Seal identified two companies, Rochester Midland and ServiceMaster®, that developed more comprehensive criteria for environmentally preferable cleaners. Rochester Midland developed the following criteria for its EnviroCare® product line:

- Prohibited – phosphates, carcinogens, and ODCs.
- Skin and eye irritation – no worse than slight irritation using the Draize test.
- Toxicity – LD₅₀ > 5,000 mg/kg.
- VOC content – complies with all state regulations.

- Other – preference for ingredients from renewable natural resources.

ServiceMaster® developed a point-based ranking system that considered biodegradation, pH, and the content of heavy metals, phosphorus, ODCs, VOCs, carcinogens, chlorine, and renewable resources. A product that scores 80% of the maximum score is eligible to receive a butterfly which indicates it is an environmentally preferable product.

4.2.10 Summary of Environmental Performance Criteria

The existing environmental purchasing standards have a number of similar health and environmental criteria, including prohibited ingredients, toxicity, flammability, corrosivity, biodegradability, and packaging. Some of the agencies prohibited a number of ingredients with their pass/fail criteria, and others preferred products without certain ingredients using their relative-ranking criteria (Table 4.10). Table 4.11 summarizes other common criteria. These tables are followed by discussions of acute mammalian toxicity standards, aquatic toxicity standards, corrosivity standards, and packaging standards.

Table 4.10 Common prohibited and unfavorable ingredients in purchasing/labeling standards. The program prohibits the ingredient unless otherwise noted.

Ingredient	Organization	Ingredient	Organization
Carcinogens	C, GS, KC, SM, MA, MN ¹ , VT, WA	Mutagens	KC, SM, VT, WA
APEs	C, N, SM, MA ¹ , WA	Teratogens	SM, VT, WA
ODCs	C, SM, MA, MN ¹ , VT, WA	TRI	SM, MA ² , VT, WA

C: Canada; GS: Green Seal; KC: King County, WA; MA: Massachusetts; MN: Minnesota; N: Nordic Ecolabeling; SM: Santa Monica; VT: Vermont; WA: Washington

APE: alkylphenol ethoxylates; ODCs: ozone depleting substances; TRI: toxic release inventory chemicals

¹ The program prefers products without these ingredients.

² Prohibits ingredients on the Massachusetts TURA list, which contains most of EPCRA 313, TRI, and CERCLA.

Table 4.11 Common health and environmental criteria.

Criterion	Organization
High flashpoint	C, FS, MA, MN, SAE, SM, VT, WA
Ready biodegradability	EPA*, GS, FS, KC, MA, SM, VT, WA
Low VOC content	GS, SM, MA, VT, WA
Restriction on phosphates	C, GS, MA, MN, N, VT, WA
Corporate environmental program	MA, MN, VT
No or only food-grade dyes or fragrances	MA, MN, N, WA
Employee training program	SM, MA, VT, WA
Ingredients derived from natural sources	MN, VT

C: Canada; FS: federal specifications; GS: Green Seal; KC: King County, WA; MA: Massachusetts; MN: Minnesota; N: Nordic Ecolabeling; SAE: SAE 1550B; SM: Santa Monica; VT: Vermont; WA: Washington

* Required to be in the GSA catalogue.

Toxicity. A number of standards set criteria for acute mammalian toxicity and aquatic toxicity in order to reduce health impacts to workers and environmental impacts to surface waters (Table 4.12, Table 4.13). Vermont has a relative ranking criterion for comparing the mammalian toxicity of similar products, but it does not set toxicity cutoffs. The city of Santa Monica, California and the state of Washington have a relative ranking criterion for comparing aquatic toxicity of similar products, but they also do not set cutoffs.

Table 4.12 Acute mammalian toxicity criteria.

Criterion	Organization	Note
LD ₅₀ (oral) > 5,000 mg/kg	Rochester Midland ¹ , Santa Monica, CA and Washington	Preferable
LD ₅₀ (dermal) > 4,300 mg/kg		
LC ₅₀ (inhalation) > 10,000 ppm		
LD ₅₀ (oral) > 500 mg/kg	Minnesota	Preferable
LD ₅₀ (dermal) > 1,000 mg/kg	EPA ²	Pass/fail
LC ₅₀ (inhalation) > 2,000 ppm		
LD ₅₀ (oral) > 50 mg/kg (rat)		
LD ₅₀ (dermal) > 200 mg/kg (rabbit)		
LC ₅₀ (inhalation) > 2 mg/L		

¹ Oral toxicity criterion only.

² Required to be in the GSA catalogue.

Table 4.13 Aquatic toxicity criteria.

Criteria	Organization	Note
IC ₅₀ > 200 mg/L (minimum dilution) and IC ₅₀ > 10 mg/L (concentrate)	Canada	Pass/fail
EC ₅₀ daphnia (48h), LC ₅₀ fish (96h), EC ₅₀ algae (96h), EC ₅₀ daphnia (14d) > 10 mg/L	Green Seal	Pass/fail
LC ₂₀ > 1,000 ppm	King County, WA	Pass/fail
EC ₂₀ daphnia (48h), EC ₂₀ fish (96h), EC ₂₀ algae (96h), EC ₂₀ daphnia (21d) > 1,000 mg/L	Washington	Pass/fail
EC ₅₀ daphnia (48h), LC ₅₀ fish (96), or EC ₅₀ algae (96h) > 2,000 ppm	Vermont	Preferable

Corrosivity, Skin, Eye, and Lung Irritation. Many of the standards set preferences for products with a neutral pH and for products that are not skin, eye, or lung irritants. Some programs defined a neutral pH more narrowly than others. However, most programs prohibited or rated products as least favorable if the pH was below 2 to 2.5 or above 12 to 13 due to the potential risk to workers and the potential for regulation as a characteristic hazardous waste. Washington based skin, eye, and lung irritation on the presence of a caution or warning label. In addition to a criterion for pH, Massachusetts and Santa Monica, California prefer products that are not skin or eye irritants as determined by test methods.

Packaging. A number of purchasing criteria focused on various ways of minimizing worker exposure and waste through improved packaging (Table 4.14). Washington, Minnesota, and Massachusetts also preferred vendors with programs that reuse, refill, or recycle their containers. The Nordic Ecolabeling and the Green Seal household cleaner standard prohibit PVC packaging and secondary packaging except for concentrates. King County, Washington required vendors to accept the empty 55-gallon drums of their products at no charge.

Table 4.14 Packaging criteria.

Preferable	Organization
Concentrate	SM, WA, MA, MN
Non-aerosol containers	MA, WA, MN
Recycled content containers ¹	WA, MN, MA
Recyclable packaging ²	MA, WA, SM
Packaging minimizes worker exposure	WA

¹ Recycled content differed by program.

² If plastic, types 1 - 5 for SM and 1 - 7 for WA.

PART 5

PERFORMANCE EVALUATION

Cleaning performance is an important aspect of environmental certification. An environmentally preferable cleaner that does not clean well causes purchasers and users to lose faith in certified products. Furthermore, the environmental benefits of a “green” cleaner will likely be lost if a user requires a much larger quantity than with another brand. A certified cleaner should perform in the range of other products on the market. The goal of this section is to determine a minimum level of cleaning performance and to recommend a test method for each product category.

The performance criterion in this certification standard is intended to set a minimum level of performance that is adequate for each type of cleaning. In order to determine the minimum performance level, the authors talked to manufacturers and searched specifications from national and international standards organizations, trade associations, government, and the military. During these discussions, a number of manufacturers and the Canadian Environmental Choice Program stated that a cleaner must perform significantly better than water. According to the Canadian General Standards Board 2-GP-11M, distilled water removes less than 35% of a standard soil from a surface and a reference cleaning product removes at least 80% of the soil (CGSB 2-GP-11M 1988).

Standard test methods provide an objective and reproducible indication of a product’s cleaning ability; this is critical for a national standard, such as the one being developed. A number of factors affect cleaner performance, including water supply and soil type. Manufacturers may sell slightly different formulations in different parts of the country because of these differences. For instance, some areas of the country have water containing high levels of minerals such as calcium, magnesium, and iron, which can inhibit a cleaner’s performance. In addition to its location, the activities occurring within a building define the types of soils that are present. For instance, a seaside hotel, a city bus station, and a manufacturing plant will all have different types of soil.

Most of the contacted manufacturers test their products in the field in addition to laboratory testing. Laboratory tests include standard test methods or a company’s own test methods. Field testing is important to ensure purchasers that the product they are considering will perform well in their cleaning environments. The city of Santa Monica and the states of Massachusetts, Minnesota, Vermont, and Washington field tested the products that met their environmental criteria before selecting which products to purchase.

The performance criteria in this standard are not substitutes for field testing but will provide an indication of whether a product performs in the range of other products. We examined all known specifications and performance standards to recommend an adequate level of cleaning performance, test method, and soil type. However, our survey of test methods and soil types is not complete; it is only intended to provide an overview of standard test methods. Most of the test methods and soil types would provide a reasonable indication of cleaning performance, and there is no universal soil or test that represents all cleaning situations. Therefore, Green Seal will recommend a test method but will accept the results of other standard test methods. In keeping with the ISO guidelines, Green Seal prefers to recommend standard test

methods from international standards organizations, followed by national standards organizations, government, military, and trade associations (ISO 14024 1998). The rest of this section details how the performance criteria were selected for each product category.

Note that a number of the government specifications discussed in this section have been canceled recently. This is part of the government’s policy of streamlining its purchasing to allow purchasing agents more flexibility. However, the products purchased by the government are likely to still meet the cleaning performance criteria.

5.1 General-Purpose Cleaners

General-purpose cleaners are intended to clean a variety of soils on a variety of surfaces including walls, floors, and countertops. Green Seal’s goal is to select a representative test method and soil type and to determine a reasonable minimum level of performance. Green Seal identified a number of standards and specifications for general-purpose cleaners (Table 5.1). The two most common methods of determining adequate performance were to

- Require that a product perform as well as a reference product.
- Require that a product remove a certain percentage of soil.

Table 5.1 Specifications, required minimum cleaning efficiency, and the test methods for general-purpose cleaners.

Standard/Specification	Minimum Cleaning Efficiency	Test Method
Canadian Environmental Choice ECP-57 for industrial and commercial cleaners	Adequately compared to reference product	CGSB-2-GP-11M
Green Seal GS-08 for general-purpose household cleaners	80%	ASTM 4488, A5 ASTM 4488, A2
Fed. P-D-220D (1978) for general-purpose detergents	80%	Fed 536/6701
Fed. P-D-225A (1975) for general-purpose detergents	80%	Fed 536/6701
GSA A-A-3156 (1998) for general-purpose detergents (spray on, wipe off)	80%	ASTM 4488, A5
GSA A-A-201A for cleaning compounds for floor cleaning machine	95%	ASTM D3206
SAE AMS 1550B for water-based hard surface cleaners	Perform adequately	
GSA A-A-1992 (1984) for powdered cleaning compounds for hard surface floor	As well as reference product	Fed. P-D-1747

CGSB: Canadian General Standards Board; ASTM: American Society for Testing and Materials; SAE: Society of Automotive Engineers

Table 5.1 shows that a minimum removal efficiency of 80% is a common requirement. All test methods use a straight-line washability apparatus to simulate cleaning and a photometer or visual inspection to determine cleaning efficiency. The test methods also employ a variety of soils and substrates (Table 5.2).

Table 5.2 Test methods, substrates, and soil types for general-purpose cleaners.

Test Method	Substrate	Soil Type
CGSB 2-GP-11M	White vinyl tile	Iron oxide, kerosene, stoddard solvent, white petroleum jelly SAE 10 lubricating oil, hydrogenated vegetable shortening
ASTM D4488, A2	Painted masonite wallboard	Vegetable shortening, lard, vegetable oil, carbon black
ASTM D4488, A3	Linoleum	Vegetable oil, mineral oil, turbine base oil, jet turbine fuel, metallic brown oxides, naphthenic hydrocarbon solvent
ASTM D4488, A3	White latex painted masonite board, white vinyl tile, or stainless steel	Grease with charcoal Wax, or Graphite powder
ASTM D4488, A5	White vinyl tiles	^{1,2} Natural humus, paraffin oil, used motor oil, Portland cement, silica, lampblack carbon, iron oxide, clay, steric acid, oleic acid, or Kerosene, stoddard solvent, paraffin oil, motor oil, vegetable shortening, olive oil, linoleic acid, squalene, octadecene
ASTM D4488-5, A6	White enamel painted stainless steel	Paint thinner, vegetable oil, mineral oil, carbon black, graphite powder
Fed. 536/6701 (1975)	White vinyl	Metallic brown, odorless kerosene, stoddard solvent, white mineral oil, lubricating oil, vegetable shortening
Green Seal GS-08 ASTM D4488, A2	Painted masonite wallboard	Crayon, ball-point pen, pencil
Fed. P-D-1747C (1983)	Vinyl	Kerosene, mineral oil, oleic acid, petroleum ether, Sanders-Lambert urban soil, water, morpholine.

¹ The GSA A-A-3156 (1998) specification eliminates the use of the motor oil in the soil.

² This soil mixture is also used by the U.S. Navy to represent urban soil.

Two specifications use reference cleaning compounds.

GSA A-A-1992 (1984) Reference Formula ¹		CGSB 2-GP-11M (1988) Reference Formula ²	
Ingredient	Wt%	Ingredient	Wt%
Sodium sesquicarbonate	82.5	Sodium tripolyphosphate, anhydrous	40.0
Tetrasodium pyrophosphate	17.0	Sodium sulfate anhydrous	29.5
Diammonium phosphate	0.5	Alkyl benzene sulfonate	23.5
		Sodium metasilicate, pentahydrate	7.0

¹ A 0.5% by weight solution in synthetic hard water.

² A 2.0% by weight solution in synthetic hard water.

Recommended criterion. After all these standards/specifications and test methods were examined, ASTM D4488 (1995) was identified as a reasonable test method; no international standard was identified. Alternatively, manufacturers may demonstrate that their product achieves 80% removal efficiency or performs as well as a recognized national brand using a standard test method.

5.2 Bathroom Cleaners

Bathroom cleaners are intended for use on ceramic tile, sinks, and bathroom fixtures. Common soils encountered in bathroom cleaning include soap scum, dust, sand, street dirt, oil, grease, hair, and hard-water deposits such as calcium and rust. Green Seal identified three performance standards/specifications for industrial bathroom cleaners, federal specification P-C-1891 (1996), ASTM D5343 (1997), and CSMA DCC-16 (1995).

P-C-1891 (1976) is a federal specification for porcelain and ceramic tile cleaning compounds. This specification defines three types of cleaning compounds. Type I is a single-phase liquid detergent or emulsion in an aerosol bottle; type II cleaner is a free-flowing liquid that contains detergents, builders, and abrasives; and type III is an acid-solution cleaner. Table 4.3 shows the minimum cleaning requirements. The specification did not define a minimum removal efficiency for type III cleaners. The removal efficiency is estimated by visual inspection.

ASTM developed a standard test method for measuring the cleaning performance of ceramic tile cleaners. This method, ASTM D5343 (1997), uses a synthetic soap scum applied to a ceramic tile, which is cleaned with a straight-line washability apparatus. The cleaning efficiency is measured with a photovolt reflectometer or visually by a panel of judges. If the cleaning efficiency is measured visually, the standard recommends ranking the soil removal between 0 and 5, with 0 corresponding to virtually no soil removal and 4 corresponding to 75% removal.

The CSMA developed a standard test method for evaluating the performance of bathroom cleaners. CSMA DCC-16 presents two tests; both use synthetic sebum and soap as soils although the soil and substrate differ. The soil removal can be measured visually or with a reflectometer. CSMA DCC-16 states that a product that cannot achieve an average removal rate of 25% does not have acceptable soap-scum removal properties.

Table 5.3 Cleaning efficiency specifications for bathroom cleaners.

Cleaner	Cleaning Efficiency	Substrate	Soil
P-C-1891 type I	50%	White porcelain	Vegetable shortening, lard, cooking oil
P-C-1891 type II	75%	White porcelain	Vegetable shortening, lard, cooking oil
CSMA DCC-16		Black ceramic	Soap, shampoo, black clay, synthetic sebum
CSMA DCC-16	>25%	White Formica	Hard water, soap, graphite powder, synthetic sebum
ASTM D5343		White ceramic	Synthetic sebum, metal stearates, carbon black, and dirt

Recommended criterion. After these standards/specifications and test methods were examined, ASTM D5343 (1997) was identified as an appropriate test method because it was developed by a national standards organization. The certification standard will require 75% soil removal as measured by ASTM D5343 (1997) or another standard test method. Alternatively, manufacturers may demonstrate that their product performs as well as a nationally recognized brand.

5.3 Glass Cleaners

Glass cleaners are designed to remove such soils as grease, oil, fingerprints, dust, and water spots from glass and other polished surfaces. Green Seal identified three specifications and one test method for glass cleaners. GSA A-A-40A (1980a) and GSA A-A-40B (1998) commercial item descriptions for liquid glass cleaners specify that products perform at least as well as a reference glass cleaner as measured by CSMA DCC-09 (1995). The GSA A-A-14 (1980b) commercial item description for glass cleaning scouring powders specifies that products must remove a test soil completely and not scratch the glass as measured by visual inspection.

The reference cleaner contains 4.0% isopropanol, 4.0% dipropylene glycol monomethyl ether, 1.0% ammonium hydroxide (28% in water), 0.1% Pluronic F 108, and 90.0% distilled water. DCC-09 tests cleaning, streaking, and smearing performance with a Gardner straight-line washability apparatus on a glass panel soiled with a mixture of mineral oil, clay, synthetic sebum, and perchloroethylene. Performance is rated visually for each category (cleaning, streaking, and smearing) on a four-point scale, with four being the best performance and one being poor performance.

Recommended criterion. The product must remove soil well with only slight smearing or streaking (achieve a rating of three in each category) as tested by CSMA DCC-09 or another standard test method. Alternatively, manufacturers may demonstrate that their product performs as well as a nationally recognized brand.

PART 6

REFERENCES

- Ahel, M., et al. 1993. Bioaccumulation of the lipophilic metabolites of non-ionic surfactants in freshwater organisms. *Environmental Pollution* **79**:273-248.
- Ahel, M., et al. 1994. Behavior of a alkylphenol polyethoxylate surfactants in the aquatic environment II: Occurrence and transformation in rivers. *Water Research* **28**(5):1143-1152.
- APME (Association of Plastics Manufacturers in Europe). 1993. *Eco-profiles of the European Plastics Industry*, Report 3: Polyethylene and Polypropylene, Brussels.
- APME (Association of Plastics Manufacturers in Europe). 1994. *Eco-profiles of the European Plastics Industry*, Report 4: Polyvinyl chloride, Brussels.
- APME (Association of Plastics Manufacturers in Europe). 1998. *Eco-profiles of the European Plastics Industry*, Report 16: PET film production, Brussels.
- Ashfield, L.A., et al. 1998. Exposure of female juvenile rainbow trout to alkylphenolic compounds results in modifications to growth and ovosomatic index. *Environmental Toxicology and Chemistry* **17**(3): 679-686.
- ASTM (American Society for Testing and Materials) D4488. 1995. Standard guide for testing cleaning performance of products intended for use on resilient flooring and washable walls.
- ASTM (American Society for Testing and Materials) D5343. 1997. Standard guide for evaluating cleaning performance of ceramic tile cleaners.
- ASTM (American Society for Testing and Materials) E1971. 1998. Standard guide for stewardship for the cleaning of commercial and institutional buildings.
- Bardana, E. and A. Montanaro (eds). 1997. *Indoor Air Pollution and Health*. New York, Basel, Hong, Kong:Marcel Dekker.
- Bartnik, F. and K. Kunstler. 1987. Biological Effects, Toxicology and Human Safety, Chapter 9 in *Surfactants Consumer Products: Theory, Technology, and Application*. Edited by J. Falbe, Springer Verlag, Heidelberg.
- Barron, T. and L. Sutherland. 1999. Environmentally preferable janitorial products: issues and opportunities. *Pollution Prevention Review*, Autumn.
- Barron, T., C. Berg and L. Bookman. 1999. *How to Select and Use Safe Janitorial Chemicals*. U.S. EPA Region IX, Pollution Prevention Incentives for States.
- Barron, T., D. Raphael and S. Sutherland. 2000. Purchasing environmentally preferable janitorial products. *Pollution Prevention Review*, Winter.
- Bauer, K. and D. Garbe. 1985. *Common Fragrance and Flavor Materials*. Weinheim, Germany:VHC Verlag.
- Berry, M.A. 1994. *Protecting the Built Environment: Cleaning for Health*. ISBN: 0-9635715-0-8, Chapel Hill, NC: Tricomm 21st Press.
- Bhimavarapu, K. and D. Karydas. 1996. *Recycling Aerosol Cans: a Risk Assessment*. Prepared for the Chemical Specialties Manufacturers Association.
- BLS (Bureau of Labor Statistics). 1999a. *Occupational Employment Statistics*
http://stats.bls.gov/oes/national/oes_serv.htm

- BLS (Bureau of Labor Statistics). 1999b. Nonfatal occupational illness by category of illness, private industry 1994-1998.
- Bordas, F. and A.C.M. Bourg. 1998. Effect of complexing agents (EDTA and ATMP) on the remobilization of heavy metals from a polluted river sediment. *Aquatic Geochemistry* 4:201-214.
- Browning, E. 1969. *Toxicity of Industrial Metals*,. 2nd ed. New York: Appleton-Century-Crofts.
- BSCA (Building Service Contractors Association). 1999. The cleaning industry: profile and projections. *Services Magazine*, October.
- Buehler, E.V. 1994. Occlusive patch method for skin sensitization in guinea pigs: the Buehler method. *Food and Chemical Toxicology* 32: 97-101.
- Burgess. 1995. *Recognition of Health Hazards in Industry*. New York: John Wiley & Sons, Inc.
- BUWAL (Bundesamt fuer Umwelt, Wald und Landschaft). 1996. *Environmental Inventory for Packaging Materials*. Bern, Switzerland.
- CDC (Centers for Disease Control). 1985. *Guideline for Handwashing and Hospital Environmental Control*. Hospital Infections Program, Center for Infectious Diseases.
- CGSB (Canadian General Standards Board) 2-GP-11M. 1988. Methods of testing and analysis of soaps and detergents: cleaning efficiency.
- Chemical Industry News*. 1997. Chemical Profiles. New York: Schnell Publishing.
(<http://www.chemexpo.com/news/newsframe.html>)
- Colburn, T., D. Dumanoski and J. Peterson Myers. 1996. *Our Stolen Future*. New York: Penguin Books.
- Coons, D.M., et al. 1987. Performance in Detergents, Cleaning Agents, and Personal Care Products. Chapter 5 in *Surfactants in Consumer Products; Theory, Technology, and Application*. Edited by J. Falbe, Heidelberg: Springer Verlag.
- CSMA (Chemical Specialties Manufacturers Association). 1995. DCC-09 Test method for glass cleaners.
- CSMA (Chemical Specialties Manufacturers Association). 1995. DCC-16 Test method for bathroom cleaners.
- Davis, G.A., et al. 1992. *Household Cleaners: Environmental Evaluation and Proposed Standards for General Purpose Household Cleaners*. University of Tennessee, Center for Clean Products and Clean Technologies, prepared for Green Seal, Inc.
- Dickey, P. 1997. *Troubling bubbles: The Case for Replacing Alkylphenol Ethoxylate Surfactants*. Washington Toxics Coalition.
- EPA (Environmental Protection Agency). 1985. *Wastes from the Extraction and Beneficiation of Metallic Ores, Phosphate Rock, Blasts, Overburden from Uranium Mining, and Oil Shale*. Office of Solid Waste.
- EPA (Environmental Protection Agency). 1990. *Toxic Air Pollutant Emission Factors – A Compilation for Selected Air Toxics Compounds and Sources*, 2nd Edition.
- EPA (Environmental Protection Agency). 1995a. *Profile of the Petroleum Refining Industry*. Office of Compliance, EPA/310-R-95-013.
- EPA (Environmental Protection Agency). 1995b. *Profile of the Inorganic Chemical Industry*. EPA Office of Compliance. EPA 310-R-95-004.

- EPA (Environmental Protection Agency). 1996a. *Cleaner Technologies Substitutes Assessment: A Methodology and Resource Guide*. Office of Pollution Prevention and Toxics, Washington, DC, EPA 744-R-95-002.
- EPA (Environmental Protection Agency). 1996b. *Characterization of Municipal Solid Waste in the United States*. Office of Solid Waste.
- Federal Specification P-D-225A. 1975. Federal specification for solvent-type general-purpose detergent.
- Federal Specification P-C-1891. 1976. Federal specification for porcelain and ceramic tile cleaning compound.
- Federal Specification P-D-220D. 1978. Federal specification for general-purpose detergent.
- Federal Specification P-D-1747C. 1983. Federal Specification for general-purpose (spray on, wipe off) detergent.
- Federal Standard Test Method 536/6701. 1975. Test method for cleaning efficiency.
- Fedinger, N.J., et al. 1995. Measurement of alkyl ethoxylate surfactants in natural waters. *Environmental Science & Technology* **29**(4):856-863.
- Fentem, J.H., et al. 1998. The ECVAM international validation study on in vitro tests for skin corrosivity. *Toxicology In Vitro* **12**:471-482.
- Flick, E.W. 1989. *Advanced Cleaning Product Formulations*. Westwood, NJ: Noyes Publications.
- Ford, T.E. 1993. *Aquatic microbiology*. Boston: Blackwell Scientific Publications.
- Franck, H.G. and J.W. Stadelhofer. 1988. *Industrial Aromatic Chemistry*. New York: Springer-Verlag.
- Franklin Associates. 1989. *Comparative Energy & Environmental Impacts for Soft Drink Delivery Systems*, Final Report (Marek).
- Godish, T. 1995. *Sick Buildings Definition, Diagnosis, and Mitigation*. Boca Raton, Ann Arbor, London: Lewis Publishers.
- Gonsior, S. J., et al. 1997. The effects of EDTA on metal solubilization in river sediment/water systems. *Journal of Environmental Quality* **26**:957-966.
- Grant, W. Morton. 1974. *Toxicology of the Eye*, 2nd Edition. Springfield, IL: Charles C. Thomas.
- Green Seal. 1999. Industrial and Institutional Cleaners. *Choose Green Report*.
- GSA (General Services Administration) A-A-40A. 1980a. Commercial item description for liquid and aerosol glass cleaner.
- GSA (General Services Administration) A-A-14. 1980b. Commercial item description for glass cleaning scouring powder.
- GSA (General Services Administration) A-A-1992. 1984. Commercial item description for hard surface floor (powdered heavy duty) cleaning compound.
- GSA (General Services Administration) A-A-40B. 1998. Commercial item description for liquid glass cleaner.
- GSA (General Services Administration) A-A-3156. 1998. Commercial item description for general-purpose (spray on, wipe off) detergent.
- Harsch, Matthias and Manfred Schuckert. 1996. *Ganzheitliche Bilanzierung der Pulverlackiertechnik im Vergleich zu anderen Lackiertechnologien*, Universität Stuttgart.

- Heinis, L.J. et al. 1999. Persistence and distribution of 4-nonylphenol following repeated application to littoral enclosures. *Environmental Toxicology and Chemistry* **18**(3):363-375.
- Hill, et al. 1997. *Alkyl Polyglycosides: Technology Proportions, and Applications*. New York: VCH.
- Hinck, M.L., J. Furguson and J. Puhaakka. 1997. Resistance of EDTA and DPTA to aerobic biodegradation. *Water Science and Technology* **35**(2-3):25-31.
- HSDB (Hazardous Substances Data Bank). 1999. Peer-reviewed toxicity data from the National Libraries of Medicine. <http://sis.nlm.nih.gov/sis1/>
- Hutzinger, O. (ed). 1985. Reactions and Processes. In: *The Handbook of Environmental Chemistry*, Vol. 2C, Berlin: Springer-Verlag.
- Illinois EPA. 1997. *Endocrine Disruptors Strategy*.
- ISO (International Standards Organization). 1998. Final draft international standard 14024, environmental labels and declarations – Type I environmental labeling – principles and procedures.
- ISSA (International Sanitary Supply Association) and SM (Sanitary Maintenance). 1999. *Report on Sanitary Supply Distributor Sales*.
- Jobbling, S. and P. Sumpter. 1996. Detergent components in sewage effluent are weakly estrogenic to fish: an in vitro study using rainbow trout hepatocytes. *Aquatic Toxicology* **27**:361-372.
- Kaluza, U., P. Klingelhofer and K. Taeger. 1998. Microbial degradation of EDTA in an industrial wastewater treatment plant *Water Research* **32**, 9: 2843-2845.
- Kay, J.H. and J.C. Calandra. 1962. Interpretation of eye irritation tests. *Journal of the Society of Cosmetic Chemists* **13**(6):281-289
- Kirk-Othmer. 1993. *Encyclopedia of Chemical Technology*, 4th Edition.
- Kjaergaard, S.K., et al. 1991, Human reactions to a mixture of indoor volatile organic compounds, *Atmospheric Environment* **25A**:1417-1426.
- Krilov, L.R., et al. 1996. Impact of an infection control program in a specialized preschool. *American Journal of Infection Control* 167-173.
- Kuta, C.C., et al. 1992. Life-cycle – putting things into perspective. Presented at Soap and Detergents Association Annual Meeting, Boca Raton. FL.
- Landbank. 1994. *The Phosphate Report*. Landbank Environmental Research & Consulting.
- Levy. 1998. The challenge of antibiotic resistance. *Scientific American* **3**:46-53.
- Liebsch, M., et al. 2000. The ECVAM prevalidation study on the use of EpiDerm for skin corrosivity testing. *ATLA* **28**:(in press).
- Lowenheim, F.A. and M.K. Moran. 1975. *Faith, Keys and Clark's Industrial Chemicals*, 4th Edition. New York:John Wiley & Sons, Inc.
- Magnusson, B. and A.M. Kligman. 1969. The identification of contact allergens by animal assay. The guinea pig maximization test. *Journal of Investigative Dermatology* **52**:268-276.
- McKetta. 1997. *Encyclopedia of Chemical Processing and Design*. New York:Marcel Dekker Inc.

- Menke, D.M. et al. 1994. *Demonstration of Alternative Cleaning Systems*. U.S. EPA, National Risk Management Research Laboratory, Cincinnati, OH.
- Miles-Richardson, S.R. et al. 1999. Effects of waterborne exposure to 4-nonylphenol and nonylphenol ethoxylate on secondary sex characteristics and gonads of fathead minnows. *Environmental Research Section* **A80** S122-S137.
- Naylor, G.G. et al. 1992. Alkylphenol ethoxylates in the aquatic environment. *Journal of the American Oil Chemists Society* **69**:695-703.
- Nortemann, B. 1999. Biodegradation of EDTA. *Applied Microbiology and Biotechnology* **51**:751-759.
- NTP (National Toxicology Program). 1998a. *Eight Annual Report on Carcinogens*. U.S. Department of Health and Human Services, Research Triangle Park, NC.
- NTP (National Toxicology Program). 1998b. Fact Sheet on the toxicology and carcinogenesis studies of diethanolamine and fatty acid diethanolamine condensates. U.S. Department of Health and Human Services, Research Triangle Park, NC.
- OECD (Organization for Economic Cooperation and Development). 1998. *Harmonized Integrated Hazard Classification System for Human Health and Environmental Effects of Chemical Substances*.
- OTA (Office of Technology Assessment). 1987. *Identifying and Regulating Carcinogens*. OTA-BP-H-42, Washington, DC, November.
- Oude, N.T. (ed.) 1992. *Detergents*, Volume 3 of the Handbook of Environmental Chemistry. New York:Springer Verlag.
- Pittinger, C.A., et al. 1991. *Environmental Life Cycle of Detergent-Grade Surfactant Sourcing and Production*.
- Pohanish, R.P. and S.A. Greene (eds.) 1996. *Hazardous Materials Handbook*. New York:Van Nostrand Reinhold.
- Pratt, C. et al. 1993. An indexing system for comparing toxic air pollutants based upon their potential environmental impacts. *Chemosphere* **27**(8):1359-1379.
- Rappaport, R.A. and W.S. Eckhoff. 1990. Monitoring linear alkyl benzene sulfonate in the environment, 1973-1986, *Environmental Toxicology and Chemistry*, Vol 9.
- RTI (Research Triangle Institute). 1994. Indoor environment characterization of a non-problem building: assessment of cleaning effectiveness. Prepared for the US EPA Environmental Criteria and Assessment Office, RTI, Research Triangle Park, NC.
- Russell, A.D., W.B. Hugo and G.A.J. Ayliffe. 1999. *Principles and Practice of Disinfection, Preservation, and Sterilization*, Great Britain:University Press.
- Rutala, W.A. 1996. APIC guidelines for selection and use of disinfectants. *American Journal of Infection Control* **24**:313-342.
- Schwarz, G. and E. Vaeth. 1987. Analysis of surfactants and surfactant formulations. Chapter 7 in *Surfactants in Consumer Products: Theory, Technology and Application*. Edited by J. Falbe, Heidelberg:Springer Verlag.
- SDA (Soap and Detergents Association). 1999. Recycle it. <http://www.sdahg.org/environment/recycleit2.html>
- Shang, D.Y., et al. 1999. Persistence of nonylphenol ethoxylate surfactants and their primary degradation products in sediments near a municipal outfall in the Strait of Georgia, British Columbia, Canada. *Environmental Science and Technology* **33**:366-1372.

- Sina, J.F., et al. 1995. A collaborative evaluation of seven alternatives to the Draize eye irritation test using pharmaceutical intermediates. *Fundamental and Applied Toxicology* **26**:20-31.
- SOLVDB. No date. National Center for Manufacturing Sciences Solvent Substitution Database.
<http://solvdb.ncms.org/whatfind.htm>
- SRI (Steel Recycling Institute). 1996. *Chemical Economics Handbook*. SRI Consulting, Menlo Park, CA.
- SRI (Steel Recycling Institute). 1999. Buy recycled with recyclable steel.
<http://www.recycle-steel.org/buy/index.htm>
- SRI (Steel Recycling Institute). 2000. Personal communication with M. Rizzuto of SRI. January 6, 2000.
- Stache, H.W. (ed) 1996. *Anionic Surfactants: Organic Chemistry*. Surfactant Science Series, Volume 56. New York:Marcel Dekker.
- Swanson, J., et al. 1995. Prediction of ocular irritancy of full-strength cleaners and strippers by tissue equivalent and bovine corneal assays. *Journal of Toxicology Cutaneous and Ocular Toxicology* **14**(3)179-195.
- Swisher, R.D. 1991. *Surfactant Biodegradation*, 2nd Edition. New York:Marcel Decker.
- Tabor, F. and L.B. Barber. 1996. Fate of linear alkylbenzene sulfonate in the Mississippi River. *Environmental Science & Technology* **30**:161-171.
- Talmage, S. 1994. *Environmental and Human Safety of Major Surfactants, Alcohol ethoxylates and Alkylphenol Ethoxylates*. Boca Raton:Lewis Publishers.
- UC Davis (University of California Davis). 1997. Selecting chemical disinfectants, Safety Net # 41.
<http://ehs.ucdavis.edu/sftynet/bio/sn-51.html>
- US Chemical Safety and Hazard Investigation Board. 1999. *The 600k Report: Commercial Chemical Incidents in the United States 1987-1996*, Special Congressional Summary.
- Walker, J.D. 1995. Estimation methods used by the TSCA Interagency Testing Committee to prioritize chemicals for testing: exposure and biological effects scoring and structure activity relationships., *Toxicology Modeling* **1**(2):123-141.
- WMO (World Meteorological Organization). 1994. *Scientific Assessment of Ozone Depletion*. World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 37.
- Woollatt, E. 1985. *The Manufacture of Soaps, Other Detergents and Glycerine*. New York:John Wiley & Sons.