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Specialty Liquid Household Surface Cleaners

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I. INTRODUCTION

Household hard surface cleaners are defined in this discussion as formulations, powder or liquid, used to clean hard surfaces in the home, excluding dishes. Therefore, cleaners used on "soft" surfaces in the home — upholstery and carpet cleaners, fabric stain cleaners, etc. — are not discussed here. Also excluded from this discussion are household products that are used primarily as treatments rather than cleaners *per se* — polishes, floor waxes, tarnish removers, and drain cleaners (decloggers). Also not included are air fresheners, which are not cleaners but are often included in market analysis as part of the household cleaning market. Metal cleaners, surface descalers, and other such industrial liquid cleaners will not be discussed. The formulation of liquid bleach products is an art in itself so bleach will be discussed here briefly as an adjunct to all-purpose cleaning.

Household surface cleaners are now moving to added benefits beyond simple cleaning of the hard surface. Added benefits for cleaners are well established in other areas (e.g., conditioning with shampooing, softening with laundering, tartar control with tooth brushing) but such advantages are arriving late for hard surface cleaning.

This list of benefits can be described as changes made to the surface beyond cleaning, where something is left behind on the surface to give it desired properties beyond being clean. Cleaning only removes soil, therefore returning the surface to its native state, including whatever wear-and-tear the surface has incurred. Only very recently has treatment of the surface beyond cleaning been incorporated into household cleaners. This development is mostly taking place in bathroom/toilet cleaners and not so much in other areas of the house. (Polishes are, of course, the main surface modifiers in other areas of the household, but their main purpose is the surface modification and not cleaning. As noted before, they are therefore not part of this discussion.)

The other recent development in cleaners is the use of ingredients with "name recognition." In the personal care area, certain ingredients such as alphahydroxy acids or aloe are recognized by consumers as having specific benefits for the skin. In the case of aloe, this is the result of long years of folk tradition and word of mouth. In the case of alphahydroxy acids, this is the result of intensive advertising and education on the part of cosmetic companies. The aura around an ingredient can be achieved either way, or by a combination of ways; the point is that consumers recognize the ingredient and infer their own ideas of how that ingredient improves the performance of the product. Examples of such ingredients in the hard surface cleaning area are orange oil (for cleaning) and Teflon® (for surface improvement). These will be described in more detail in the discussion of product areas where they play the largest role.

The starting point for this discussion is the history of the development of household cleaners [1]. Powder cleaners will be covered briefly as part of the evolution of this field of cleaners. In general, powder cleaners tend to have large market share in developing countries, while liquid all-purpose cleaners and cream cleansers dominate in Western Europe, and liquid cleaners, especially those dispensed through trigger sprayers, enjoy popularity in North America and Australia and New Zealand. Therefore, this discussion, especially with respect to recent developments, focuses on developments in North America and Western Europe [2]. The area of household cleaning may be seen as one of the most challenging for the formulator, as the household cleaning regime can be said to have the most varied chemistry of any cleaning field. This is in response to the variety of cleaning tasks in the home, and the demands of the consumer.

To illustrate the problem for the product developer, one only has to enumerate the soils and surfaces. The soils can vary from simple dust and hair to dirt, hard water spots, and fingerprints to hardened grease, soap scum, and excrement. Although the usual household cleaning tasks are concentrated in only two rooms of the house, kitchen and bathroom, the number of different surfaces encountered are many. In the U.S., for example, there may be Formica®, ceramic tiles, grout, lacquered wood, vinyl flooring, painted surfaces, brass, stainless steel, enamel, porcelain, aluminum, chrome, glass, marble, methyl methacrylate, and other types of plastics. All of these materials may occur within only two rooms of the same home!

From a scientific point of view, one can see that these surfaces run the gamut from high-energy (ceramic and metal) to low-energy (plastic) surfaces. Soils, also, can vary, from very nonpolar (motor oil) to very polar (lime scale), and combinations of everything in between. The tenacity of the soil adherence will therefore vary according to the combination of soil and surface. In general, the better the soil wets the surface, the better the adherence. It is a well accepted principle of adhesion that two substances in intimate contact with each other tend to adhere very well, this being a necessary (but not sufficient) condition. High-energy surfaces tend to be easy to wet, making them generally easy to soil. An example is the relative tenacity of soap scum on ceramic as opposed to plastic surfaces (so called "fiberglass" bath enclosures that are made of methyl methacrylate or other acrylates).

Once wetting has occurred, the soil can then "bond" to the surface. What is often forgotten in adhesion is that van der Waals forces can be strong enough to account for the adhesion of soils to surfaces. Simple dispersion forces are about 5 kcal/mol, and hydrogen bonds between 4 and 40 kcal/mol, whereas covalent bonds can be as weak as 15 kcal/mol [3]. It can be seen from these numbers that if good molecular contact is made between the soil and surface, a bond can be made. This is especially easy if the soil is liquid or deposited from a liquid medium. Of course, the contributions of other mechanisms such as electrostatic attraction tend to strengthen the bond between soil and surface, if they are present. (Also, if the surface tends to be rough, then there also exists the possibility of purely mechanical adhesion, with the soil physically located in nooks and crannies of the surface.) If an attempt is made to break an adhesive boundary, a likely course is that one or the other of the materials tends to break within itself. Therefore, in cleaning, the soil can be broken down into successively thin layers removed from the surface, unless the fundamental bond between the soil and the surface can be compromised. Very thin layers can be even more difficult to remove than the original thicker layer [4]. For household cleaning this would imply that the most tenaciously held soil is that most intimately in contact with the surface and this should be the target of truly efficacious cleaning. Upper layers of the soil are relatively easy, by this analysis, to remove compared to the fundamental layer. In the beginning of cleaning history, the soil was simply abraded off, which inevitably damaged the unsoiled areas of the surface. In recent times, the discovery of more chemical, rather than mechanical, means of removing soil has greatly improved this situation.

A well-formulated modern cleaner avoids abrasion as a primary mechanism of cleaning and depends on more chemical rather than mechanical means. This has obvious advantages in terms of wear and tear on the surface. However, care must also be taken to make sure that chemical compatibility with the surface is also observed. For instance, acid cleaners generally have advantages in cleaning soap scum residues, but these would not be good cleaning formulations to use on a marble bathroom sink. Even though the acid will not greatly damage the structural integrity of the sink, it would surely remove the polished shine of the stone surface, minutely dissolving and therefore pitting and roughening the calcium carbonate. Therefore, a good knowledge of the chemical susceptibility of various household surfaces is necessary to the successful formulator.

Implements should also be considered in the components of the cleaning task. Much of the abrasiveness of the early cleaning process came not from the cleaner but from the implement, often a heavy scrub brush. Consumers in developed markets have a wide variety of implements to use in the cleaning process including cellulose sponges, brushes, cleaning cloths, paper towels, and plastic and metal scrubbing pads. The first three of these are also used in developing markets. These implements supply different amounts of abrasion to the soiled surface during the cleaning process and can blur the differences between cleaning formulations if the implement is highly abrasive.

Cleaning is generally accomplished in three steps: wetting, penetration, and removal. In some ways, water may be looked upon as the primary cleaning element. Given enough time, enough volume, and the right temperature, water is capable of cleaning almost any soil/surface combination. However, the times involved can be of the order of days, or the temperatures required close to boiling. The volumes of water also needed to rid the surface of the soil are also increasingly a concern nowadays.

Cleaning solutions can be viewed as water with ingredients added to speed the cleaning action, decrease the water volume, or lower the temperature at which effective water-based cleaning takes place. Organic solvents are, of course, very effective cleaners, particularly for nonpolar (greasy) soils, but the most effective solvents can have toxicity concerns [5]. (Various chlorinated solvents were long used by the electronics industry to degrease circuit boards, but due to increasing health and environmental concerns there is now a large patent literature on safer cleaning formulations.) Solvents are largely used in household cleaners as important, but not predominant, ingredients, except in glass cleaners and pine cleaners.

In pine cleaners, the pine oil component can be in the 15 to 30% range, and in glass cleaners, the solvent far exceeds the amount of surfactant in the formulation. However, even in these types, water is still the predominant ingredient, as it is in the rest of the household cleaners.

Surfactants, of course, lower the surface tension of water, thereby increasing the wetting of the soil by the cleaning solution. This is especially important for hydrophobic soils like grease. Solvents help the cleaning solution to penetrate into the soil, softening it, sometimes even partially dissolving the soil. (Surfactants also help to incorporate hydrophobic ingredients like solvents into water-based formulations by solubilizing them.) Other active ingredients, acids, bleaches, alkaline compounds, etc., can then more effectively react with the soil to change its composition to make it more liquid, less polymerized, more tenacious, etc., and easier for the cleaning solution to remove. The surfactant then helps to emulsify or otherwise lift the soil from the surface into the cleaning solution. The mechanical action of wiping or scrubbing also aids the wetting, penetration, and lifting of the soil by spreading, roughening, and breaking up the soil. The cleaning solution is then removed, leaving a clean surface. The best cleaners are effective at performing these tasks on even the most fundamental layers of soil, restoring the surface to its original state.

A further challenge for the formulator is the incorporation of surface-modifying ingredients into the cleaner. The ingredient must be stabilized into the formulation, but must destabilize to be deposited on the surface. Also, the deposition of the surface-protective agent cannot interfere with the cleaning process.

A cleaning task for the consumer will usually be one or two soils on any one of the surfaces. In addition, besides removing the soil, one must consider the safety of the chemical strategy used to remove the soil on the underlying surface. This has grown to become a more desired benefit in recent time [6]. Germ killing is also considered part of the household surface cleaning task by many consumers, especially on bathroom or food preparation surfaces. To meet some of these target concerns, the chemistry of the cleaner may be focused, but this can also limit the useful scope of the product.

As will be seen in this discussion, the evolution of cleaners developed from simple soap powders to liquid formulations to products that are more specialized. "All-purpose cleaners" are the backbone of this development. Along with specialized formulas for specific cleaning problems, in some cases these products are augmented by specialized packaging. Generally, the packaging contributes more to the convenience of the product than the efficacy.

This is especially true of the new product form that has taken a large share of the market in North American and to an even larger extent in Europe. This product form is the wipe. Wipes have existed for a number of years in the personal care area (particularly as baby wipes) but have only recently become a preferred form in household cleaning. The structure and the formulation around this form is covered in the appropriate sections of this chapter.

The trend in the U.S. and Europe has continued over the years to more "niche" products as toilet bowl cleaners and dedicated bathroom cleaners. These types of products tend to show the greatest growth, and have maintained this high growth position for about ten years [7,8]. Abrasive-type cleaners have been more or less flat for ten years. Liquid all-purpose cleaners continue to sell well. Spray cleaners, bathroom cleaners, and toilet bowl cleaners all increased dramatically in 1999 and then more or less had a fairly constant level for three years. It may be that the sales were then also similar the following three years (2002 to 2004), but Wal-Mart data were no longer available. The largest part of the decrease in the sales numbers is due probably to the subtraction of Wal-Mart's contribution to the sales volume. The jump in bathroom cleaner sales in 1999 may be due in part to the launch of shower rinsing products. Toilet bowl cleaners have also seen a large increase in novelty and types in the same period. Glass cleaners probably include not only glass cleaners and ammonia cleaners (a very minor part of the market) but also the glass and surface sprays. (All-purpose sprays are probably included in the all-purpose cleaners category.) These spray versions can sometimes be considered "niche" products themselves, and can account for as much as 33% of the all-purpose cleaner segment. In Europe also special-purpose cleaners, such as bathroom cleaners, were the largest growth segment [9] until the launches of household cleaning wipe products in the late 1990s, growing from $578 million in 1997 to $1.8 billion in 2002 [10]. Glass cleaner wipes sales (in dollars) grew 405% in the U.S. from 2000 to 2001, and 344% from 2001 to 2002, and all-purpose cleaner wipes were up 85% and 14% in the same periods [11]. U.S. sales trends for various cleaning products are shown in Figure 13.1.

All-purpose cleaners have been launched in "ultras" — formulas that give double or triple the cleaning strength of the formulas already common in the marketplace. This has already happened in Europe and North America. These products use less packaging, occupy less storage space, and give consumers more flexibility in the dilution of the product. However, they also require more careful measuring on the part of the consumer if they are to reap the full value of the product. As will be seen in the section on all-purpose cleaners, the range of concentration of active ingredients in recent all-purpose cleaner patents is sufficient for these products to be formulated either as normal strength products or as ultras. These concentrated formulas have largely been rejected by North American consumers and the "regular" concentration is what is seen on store shelves.

Nevertheless, all-purpose cleaners are generally the beginning points for entry and for specialization in a given market. The niche products are the fastest growing part of household cleaning in mature markets, and yet they are starting to appear in developing markets as well. Strangely, all-purpose cleaners (or APCs) can be

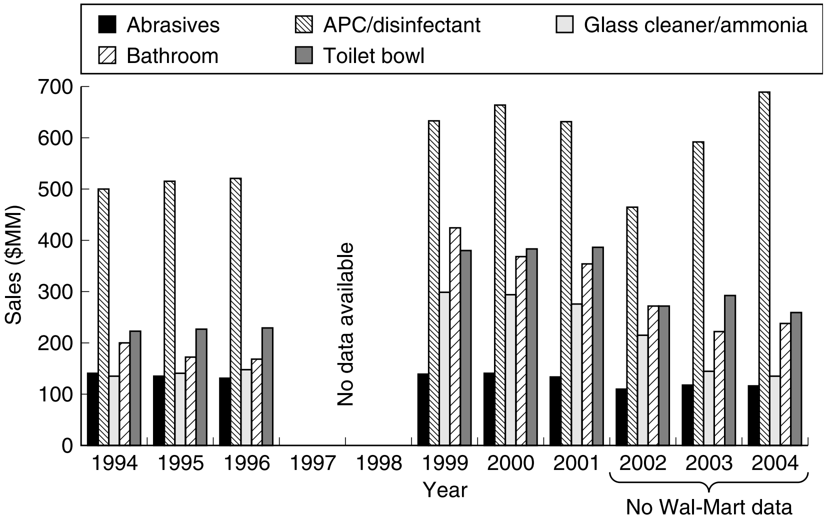


FIG. 13.1 Sales amounts for household cleaners in North America. Wal-Mart data are not included after 2001, which accounts for the apparent decrease in volume in 2002. (Source data all from *Household and Personal Products Industry*, November 1994–1996; December 1999–2001; April 2002–2004.)

considered specialty products themselves, growing out of the real all-purpose cleaner of the past — a heavy-duty cleaning powder. This can still be true in less mature cleaning markets.

II. ALL-PURPOSE CLEANERS

A. Historical Background

1. Powder Cleaners

The evolution of household cleaners begins with all-purpose cleaners. Specialization to handle the multiple problems of household cleaning has arisen relatively recently. Before the 1930s [12], consumers had only soap powders with which to do all their household cleaning, which included not only kitchen and bath surfaces but also laundry and dishes. Glass windows were nearly the only surface that could not be effectively cleaned with this product. This multiple use of a basic cleaning product continues in many developing regions of the world.

In the 1920s powdered products began to appear in the U.S. market that were formulated especially for general household cleaning. These were generally highly built, very alkaline formulations designed to be dissolved in warm or hot water for tasks such as floor mopping, grease removal, and bathroom cleaning.

TABLE 13.1 Powdered All-Purpose Cleaner Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Soap, alkylbenzene sulfonate (usually one only)	1–10
Builder	Phosphates, carbonates, silicates (usually a mixture)	50–60
Sodium sulfate	Processing and delivery aid	30–50
Perfume, color, etc.		0.5–1.0

Built formulas refer to the use of phosphates, silicates, carbonates, etc. These ingredients mitigate the effects of hard water by chelating hard water ions, supply alkalinity, and also buffer the system to high pH values. At first powdered products still used soap but later began to use the modern anionic surfactants (such as alkylbenzene sulfonates). A typical example of this kind of formula is given in Table 13.1.

These cleaners were more effective than their predecessors, but they also required a large amount of rinsing. The builders, which boosted cleaning efficacy, also increased the amount of residue left behind when the cleaning solution dried on a surface. Depending on water temperature and hardness, these cleaners could also be difficult to dissolve completely in a bucket of water. Being somewhat hygroscopic powders, they also tended to cake and solidify once their container, usually a cardboard box, was opened.

2. Cleansers

As far back as the 1880s a product was sold as a pressed cake of soap with abrasive [13]. However, modern powder cleansers also started to appear at roughly the same time as powder all-purpose cleaners (approximately 1930 to 1935). The addition of abrasives to the basic cleaning product helped use mechanical as well as chemical energy to do cleaning, but obviously made these products unsuitable for general use. In this sense, cleansers can be thought of as some of the first "specialty" cleaners because the presence of abrasive made them appropriate for very tough cleaning jobs, but also limited their usefulness because they could scratch softer surfaces. (Typical cleanser formula amounts are shown in Table 13.2.)

This tends to be the continuing theme of specialty cleaners — the formulation delivers more directed power at a particular cleaning problem, and then disqualifies itself from other tasks due to this adaptation. Consumers often comment that they want a truly "all-purpose" cleaner, but tend to buy targeted products [14].

Both powder all-purpose cleaner and powder cleansers are still in the U.S. market and maintain large shares of the market in developing areas of the world. Powder cleansers are still a major part of the abrasive cleaning subcategory, but

TABLE 13.2 Powdered Cleanser Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Soap, alkylbenzene sulfonate (usually one only)	1–5
Builder	Phosphates, carbonates, silicates (usually a mixture)	5–30
Abrasive	Silica, feldspar, calcite	60–90
Disinfectant	Usually hypochlorite-generating compound (e.g., trichlorocyanuric acid)	0–2
Perfume, color, etc.		0.25–0.5

powder all-purpose cleaners in the U.S. were represented recently only by one major brand (Spic and Span®).

The formulas have had to react to modern pressures, the largest of which were the limitations and bans of phosphates and on branched alkyl aryl sulfonates. Phosphate builders are usually not used, or used in very small quantities, in most household cleaners outside of automatic dishwashing detergents. Usually carbonates, bicarbonates, and silicates are used along with more modern ingredients such as EDTA (ethylenediamine tetraacetic acid) and its various derivatives, NTA (nitrilotriacetate), citrates, and polyacrylates. (Many of these compounds were under toxicity and environmental investigations.) [15]. Some small amount of nonionic surfactants may also be used, although alkylbenzene sulfonates now dominate as the surfactant of choice. Hydrotropes such as sodium cumene sulfonate and sodium xylene sulfonate may also be added to help aid the dissolution and cleaning of the main surfactant. In these choices, household surface cleaner formulation has mirrored the developments in fabric care.

Cleansers have also undergone some formulation changes that are specific to their group. One major change was the addition of bleach to major cleanser brands in the 1950s. Cleansers had been used in the past to "sand out" stains, with some degree of surface damage. With the introduction of ingredients such as the isocyanurates (like trichlorocyanuric acid, TCCA), usually in the range of 0.5% available chlorine, stains could be removed due to hypochlorite bleaching rather than muscle. This addition also opens the possibility of disinfectant claims for the product. However, this addition also brings with it more demands on the formulator, as the formula is harder to stabilize. Compounds such as TCCA decompose with water to form hypochlorite bleach. This is good for the usual use conditions but confers water sensitivity on the formula. Usually small amounts ($<5\%$) of water-adsorbing compounds are added to prevent premature activation of the bleach. However, two factors work against the formulator. The normal packaging of cleansers is cardboard cylinders that are not able to be resealed tightly, and the

TABLE 13.3 Mohs Hardness of Some Abrasives and Household Surfaces

Surface	Mohs hardness
Corundum (alumina)	9
Quartz (sand or fused silica)	7
Glass	5–7
Feldspar	6
Steel	5–6
Aluminum	3
Calcite (marble, limestone)	3
Plastics	2–5

product is usually stored under a sink. Under these conditions prolonged storage of the product usually results in loss of bleaching ability.

The largest recent change in cleansers has come in abrasives. These have generally become softer as time goes on, going from sand originally to calcium carbonate (calcite) now in the major brands. (Some smaller brands continue to use feldspar or similar compounds as abrasives, which rate on the Mohs scale around 5.) This constitutes a change on the Mohs hardness scale from about 7 to 3 [16]. (Table 13.3 lists the Mohs scale hardness of some abrasives and household surfaces. Mohs hardness is not always diagnostic of surfaces with elasticity where impact hardness tests are usually used. However, with respect to scratching, the Mohs scale can give some indications.) This is also a reaction to changing times — many household surfaces are now plastics of various kinds and are easily scratched by silica. For instance, where glazed ceramics in the bathroom could be scrubbed for years without seeing signs of wear, today's methyl methacrylate shower enclosures would show damage after a single vigorous use of a silica cleanser. The major exception to this trend is the increasing use of solid polymer countertop, such as Corian®, which encourages the use of strong abrasives to eliminate nicks and stains in the surface.

Mention should also be made here of the low market share products that are acidic cleansers. Some make a claim for rust stain removal. This is based on the inclusion in the formula of oxalic acid that is particularly good at chelating iron ions [17]. However, this also brings a particular problem: oxalic acid is moderately toxic (evidently due to upset of the ion balance in the body) which might mean warnings on the label. Naturally, the low pH is supplied by the acid content of the product. It would be expected, given the low surfactant concentration (similar to other cleansers) and the low pH, that grease cleaning by this type of cleanser would be less than that of the alkaline cleansers due to the effect of alkalinity on grease cleaning.

B. Cream Cleansers

Both cleansers and all-purpose cleaners are now also available in liquid forms, which were the next stage of their evolution. The liquid form has two main advantages. Liquids can be formulated in a concentrated form that can be diluted by the consumer before use to the desired strength. This dilution operation is easier for the consumer because the liquid form mixes easier and dissolves better than the powder form that preceded it. The liquids can also be used straight from the container on heavily soiled areas; the powder cleaners had to be made into a paste before they could be applied.

From the formulator's point of view, there is a mixture of advantages and disadvantages. Water is an even less expensive diluent to use than the sodium sulfate or abrasives that were used in powder forms. However, because all the ingredients are dissolved or dispersed, this makes possible more interactions between the ingredients than in a powder. Fortunately the liquid form broadens the choice of surfactant available because they do not have to be available in powder form.

Liquid cleaners with suspended abrasives — cream cleansers — first started to appear in the U.S. and Europe in the 1980s. This chapter does not go into detail on the formulation of these products because although they are fluid household surface cleaners, they should be properly considered as suspensions and not as true liquid formulas. Their arrival on the market so recently is due to the difficulty of producing stable suspensions of abrasive particles; the advancement of polymer science and clay technology during the last 30 years has played a large role in the successful formulation of these products.

Unlike their parent product, powder cleansers, the cream cleansers usually use the gentler calcite abrasive. This, combined with their liquid form, helps to convey the image of less harsh cleaning to the consumer. This is especially important to consumers who have softer, plastic surfaces in their bathrooms such as the fiberglass (polymethyl methacrylate) shower enclosures which are much more easily marred than the traditional vitreous materials [18].

The patent art for this kind of cleaner begins in the mid-1960s [19–21], but there continues to be abundant patents written up to the present time [22]. The main point of most art is the stable suspension of the abrasive particles and this is achieved largely by raising the viscosity of the system. Imanura [23] uses crosslinked polyacrylic acid as an aid to suspending the abrasive. Two patents give examples of two polymers mixed together, one of which is a polysaccharide [24,25]. Brierly and Scott's patent [26] gives an example of the use of clays to thicken the formula, their aim being the stabilization of the formula during high shear processing steps. Another patent gives the alternative of either clay or fumed silica as the thickening agent [27], as well as combinations of polymer with clay [28]. Alternatively, the same inventors also give a method for stabilizing the cleanser at high shear using monoalkylolamides [29]. Other recent art uses colloidal alumina associated with a surfactant to suspend the abrasive [30–32]. Another approach is to use stearate soap to thicken a formula in which the aluminum oxide is used as the abrasive [33]. A somewhat novel approach by two groups of inventors [34,35] uses neither of the usual approaches, but instead generates a liquid crystal phase to suspend the abrasive. There are also examples of nonthickener viscous systems, a mixture of surfactant, nonpolar solvent, and electrolyte [36] or a mixture of surfactants [37,38]. In all cases the viscosity of the product is quite high, of the order of 500 to 5000 cP.

The most challenging formulations also contain hypochlorite bleach as well as trying to suspend an abrasive. As many suspending or thickening agents are sensitive to oxidation, it becomes difficult to put together a product lacking syneresis. For cream cleansers, the most successful approach for bleach-containing formulas seems to be alumina/surfactant thickening systems [39,40]. The alumina particle size is very small and calcium carbonate is used as the abrasive. However, in recent years the art of using polymer thickeners such as polyacrylates with bleach has improved with more patent art appearing on this [41,42]. One of the approaches is to limit the ionic strength of the formulation [43].

There is also an example using oxalic acid and suspended abrasive to give iron stain removal, more aimed at bathroom soils [44].

Sometimes the abrasive is given as an optional ingredient in an otherwise completely liquid cleaning formula. In one example of this type, the abrasive is combined into a terpene/limonene solvent-based cleaner while remaining stable [45]. In another example, the surfactant instead of the abrasive is largely eliminated [46].

A generalized formula for liquid cleansers is given in Table 13.4. Most of the recent patent art concerns the thickening system, while another significant part deals with “soluble abrasive” [47–52], including one that uses a soluble form of borax [53,54]. The solubility of the abrasive is probably intended to defeat the largest consumer complaint about cleansers, either powder or liquid: the difficulty of completely rinsing away the abrasive after use. However, one unusual example uses plastic particles as the abrasive, suitable for scrubbing plastic surfaces (like methacrylate shower enclosures) but are still bleach stable [55].

Cream cleansers can be even more difficult to rinse away because of the agents used to keep the abrasive suspended, such as clays. One unusual example uses silicone compounds to make the residue less visible and make the surface more glossy and to feel smoother [56].

Another example of silicon compound use is in the very specialized area of glass-topped stove cleaner/conditioners [57]. These can be thought of as a special kind of cream cleanser with an added benefit. The strength of an abrasive cleaner is needed to remove the baked-on soil encountered on a stove top, and as long as the abrasive is less than Mohs hardness 6 the glass top will not be scratched.

TABLE 13.4 Cream Cleanser Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Soap (stearate), alkylbenzene sulfonate	1–15
Nonionic surfactant	Ethoxylated alcohols, amine oxides	0–10
Builder	Phosphates, carbonates, silicates (usually mixture)	1–20
Solvent	Alcohol, glycol ether, limonene	0–7
Thickening agent	Polyacrylate polymer, clay, alumina	0–10
Abrasive (soluble compounds used at levels beyond their solubility)	Usually calcite ($CaCO_3$), but also sodium carbonate or bicarbonate, potassium sulfate, sodium citrate, borax	10–90
Bleach	usually hypochlorite but can be peroxide	0–1
Hydrotrope	sodium cumene sulfonate, sodium xylene sulfonate	0–5
Perfume, color, etc.		0–1
Water		40–80

However, polysiloxanes will react with the glass surface to give a treatment that reduces the tenacity of new soils ("conditioning").

C. Gel Cleaners

A natural development of thickening systems is to develop transparent or translucent thickened systems. Such a form is generally called a "gel" although it may or may not conform to the technical rheological definition of a gel. Because such products are thickened, they lend themselves to the addition of abrasive because the structure of the gel can suspend the solid. However, some cleaners are formulated as gels to achieve benefits like cling on a surface. One of the ways of achieving thickening in the gel is through the surfactant system [58], especially a liquid crystal system [59]. There are largely aesthetic advantages to this type of approach. In ordinary cream cleansers, the appearance is white and opaque — the abrasive is largely invisible. In a gel cleaner, the abrasive could be made to stand out from the background because the medium is clear. In one case, the abrasive is made a different color than the medium [60].

D. Liquid All-Purpose Cleaners

1. Historical Background

Simple all-purpose cleaners were introduced in liquid form starting in the 1930s. Liquid all-purpose cleaners were for many years differentiated mainly by the specific active ingredient that they contained. The simplest liquid cleaner was ammonia with some added soap which has been used for nearly a hundred years [61]. This is an effective grease cleaner, but is very unpleasant and harsh to use. Simple household bleach solutions date back to the early 1900s [62]. These are effective stain removers, and have some effect on proteinaceous soils, but are not particularly good for tough oily soils. Liquid disinfectant solutions date back to the 1870s [63], but these were more targeted to the elimination of germs than to soil removal. The closest products to modern formulations begin with pine oil formulas, dating back to 1929 [64]. This would have given good grease cleaning with a more pleasant (and safer) odor. However, there are consumers who dislike pine odor and would prefer a different cleaner. Modern formulas without pine oil were introduced between 1955 and 1965 in the U.S.

Liquid all-purpose cleaners at that time still incorporated many of the characteristics of their dry predecessors. They still used the popular anionic surfactants such as alkylbenzene sulfonate and builders with high alkalinity to achieve their goals. However, they had three important differences. First, liquids dissolve (or disperse) more quickly than powders. This means the cleaning solution can be prepared by the consumer quickly at ambient water temperatures. Second, they are not as limited by their solubility. Higher amounts can be added to the cleaning solution without the precipitation that could be encountered with the older powder cleaners. Third, they are neater to dispense and store. The development of plastic bottles has been a huge boon for this product form. Liquid household cleaners originally came in glass bottles, which are heavier and easier to break than plastic bottles. The cardboard boxes of powder cleaners would have been an advantage for that product form until the commercialization of plastic bottles. The availability of higher density polyethylene combined with blow molding technology (developed for glass) resulted in the widespread use of plastic bottles in the late 1950s [65]. This accelerated in the mid-1960s when household bleach led the conversion in the household area by converting from glass to high-density polyethylene (HDPE) [66]. The development of polyethylene terephthalate (PET) in the 1980s for carbonated beverages expanded the choice for rigid plastic bottles [67]. With these developments the advantages for liquid formulations now dominate: plastic bottles are light, durable, and easily reclosable.

However, despite these advantages there are some drawbacks as well. Although they might have had a weakness on greasy soil, powder all-purpose cleaners were not particularly deficient in cleaning; they were deficient in convenience. In general, this tends to be the biggest component in the evolution of household cleaners. A major change in form or formulation is not motivated by claims of superior cleaning; these claims tend to be made among cleaners of the same form. The major motivation seems to be increasing the convenience for consumers while maintaining the cleaning efficacy. This may be achieved by more convenient dispensing, or shortening the number of steps in the cleaning process. It may be the transfer from muscular effort on the part of the consumer to chemical energy supplied by the cleaner. These trends will be seen in all the various types of cleaners discussed here.

Part of the high efficacy of powder detergents was their high concentration of builder salts. To formulate the same level of builders into liquid detergents required even higher levels of surfactant. This usually results in higher foaming. Although high foam may be preferred in applications like shampoos and dishwashing detergents, such sustained foam is undesirable in household cleaning. Many surfaces that are washed with all-purpose cleaners are large and horizontal, e.g., floors and countertops. If a cleaner has a slowly collapsing foam, the consumer must laboriously rinse the surface. Even in areas where rinsing is relatively easy, such as a bath or shower enclosure, the extra effort and time spent rinsing a high-foaming product is undesirable to a consumer. The immediate "flash" foam produced when the cleaner is first used serves as a signal of its efficacy. Once this message is communicated, the foam should collapse to give easier rinsing and some formulations are made to optimize this, usually involving the use of soap/fatty acids [68,69].

Continuing to use the high levels of builders used in powders would also have meant continuing another rinsing problem: residue if the cleaning solution is left to dry on surfaces. A consumer will not consider a surface clean unless it shines. Residue from the cleaner left on the surface, even if all the soil has been removed, will diminish a consumer's evaluation of the cleanliness of the surface. Residues from crystalline compounds like builder salts tend to dull the native shine of a smooth surface. The degree of shine left on the surface is an important indicator to the consumer of the degree of cleanliness of the surface. In an effort to counteract the foaming and residue effects, formulators began decreasing builders, using solvents, and putting more effort into finding surfactant synergies.

2. Solvents

Solvents became useful when the product form changed to liquids. Their main role is to penetrate and soften grease to facilitate its removal by the surfactant. Their fluid form made them attractive to use in liquid formulations, although the solubility of good grease cutting solvents in water is very low. Some examples of these are pine oil and D-limonene (see Figure 13.2). These are still very popular today as grease cutting solvents, not only for their efficacy, but also more recently due to their "natural" origins. This reflects on the current marketing ploy of playing on some consumers' opinion that vegetable-extracted chemicals are intrinsically safer or more ecologically sound than petroleum-based ones. Although the first pine cleaners appeared in the early part of the twentieth century, formulations built around pine oil still occur in the patent art, most recently as an alternative to more volatile organic solvents [70]. Pine oil content in cleaners has dropped significantly, from 70 to 90% originally to 10 to 30% currently [71].

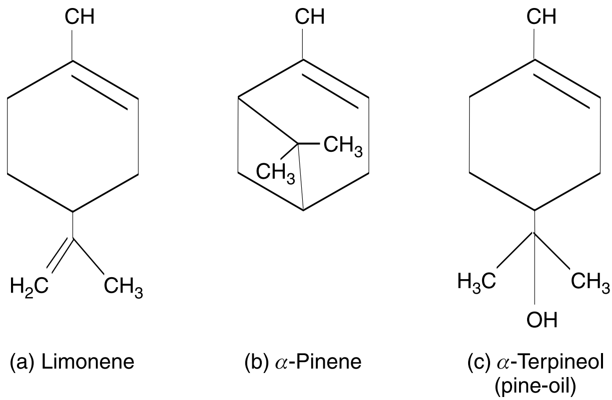


FIG. 13.2 Structure of naturally derived grease cutting solvents (terpenes).

A recent trend has developed around "orange oil" cleaners [72]. In this case, most sellers of these cleaners mean D-limonene, as limonene is indeed obtained by extraction from the rinds of oranges (and to a lesser extent other citrus fruits) used in the juice industry. This is a very effective grease cutting solvent, similar to α-pinene of pine oil. "Natural" cleaner companies have spent some time and energy educating consumers to the efficacy of this ingredient as an alternative to other cleaning additives. The solvent power of limonene is similar to pinene, and to some consumers the orangey or lemony odor of the orange oil is preferable to the smell of pine oil. Used in sufficient amount the orange oil can indeed contribute to the cleaning efficacy of a formulation. However, in many cases the amount of actual orange oil present in the cleaner is below 0.5% and it contributes mainly to the fragrance of the product rather than its efficacy. One can find a number of examples in the patent art where limonene is highlighted as a significant ingredient [73–75]. The orange oil trend has been most strong in all-purpose cleaning products in several forms (dilutable cleaner, spray cleaner, wipes) as well as some polishing products that wish to imply more cleaning power.

Much more common and more easily formulated because of their higher water solubility are the glycol ether solvents. This approach dates back as far as the early 1970s [76,77]. Earlier formulations made use of the simpler ethylene glycol monoalkyl ethers (Cellosolves®), but this use has been largely discontinued because of health hazards [78]. The diethylene glycol monobutyl ether is most favored, although the use of the propylene glycols is increasing. As the chain length increases the health hazards decrease [79], but the solubility in water also decreases. This increases the difficulty of formulating stable products.

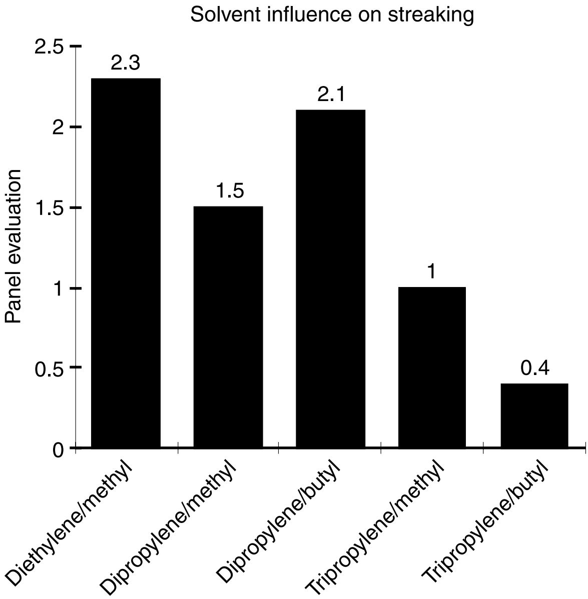


FIG. 13.3 Streaking/filming as a function of glycol ether. (Source: Michael, D.W., U.S. Patent 5290472, 1994.)

However, stable products are made, as evidenced by recent patent art which mentions the use of tripropylene glycols and their ethers for concentrated floor cleaning products [80,81]. In this case, the glycol ether is claimed not only as part of the cleaning system, but also as a way of enhancing the shine on a vinyl flooring surface. In Figure 13.3, a comparison is made of the streaking/filming characteristics based on solvent changes alone. There is also mention in other art of longer chain lengths in the ether portion of the glycol ethers also being used [82].

Other solvents can also be found in the literature. In particular, when the surface to be cleaned is painted or vanished (and therefore susceptible to solvent damage) the solvent must be chosen with care [83].

It can be seen from the structure of the glycol ethers (Figure 13.4) that if the alkyl chain is extended sufficiently then it begins to approximate the structure of simple nonionic surfactants, those of the ethoxylated alcohol family. This has led some chemical producers in recent times to introduce compounds meant to be hybrid chemicals with the properties of both solvent and surfactant. They are not at present used to any great extent in household cleaners, but remain a possibility for future formulations.

Monoglycol monoether:

$$HO-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-O-[CH_2]_n-CH_3$$

Ethylene glycol monobutyl ether: R = H, $n = 3$
Propylene glycol monobutyl ether: R = CH_3, $n = 3$
Propylene glycol monoethyl ether: R = CH_3, $n = 1$

Diglycol monoether:

$$H[-O-CH-\underset{\displaystyle R}{\underset{|}{CH_2}}]_m-O-[CH_2]_n-CH_3$$

Diethylene glycol monobutyl ether: $m = 2$, R = H, $n = 3$
Dipropylene glycol monobutyl ether: $m = 2$, R = CH_3, $n = 3$
Tripropylene glycol monobutyl ether: $m = 3$, R = CH_3, $n = 3$

Monoglycol diether:

$$CH_3-[CH_2]_m-O-CH_2-CH_2-O-[CH_2]_n-CH_3$$

Ethylene glycol dimethyl ether: $m = 0$, $n = 0$
Ethylene glycol dipropyl ether: $m = 2$, $n = 2$

FIG. 13.4 Generalized structures of glycol ether solvents.

Alcohols are sometimes used in dilutable all-purpose cleaners, but they are usually tertiary or benzyl alcohols [84,85]. The grease cutting ability of the lower alcohols is inferior to these and to the glycol ethers. Lower carbon alcohols (especially ethanol and isopropanol) find their main use in glass and light-duty cleaners. In these products the greasy soil load is lighter and the volatility of the short-chain alcohols has advantages.

One other restriction on the formulator with regard to solvents is the passage of environmental regulations in some localities on restrictions on amounts of volatile organic compounds (VOCs) in household products. The limitations vary from government to government, as well as the definition of what is volatile. In the U.S. several individual states as well as the federal government have restrictions on VOCs. Formulators intending their product for pan-North American sale would do well to abide by the most restrictive set of rules in their formulating. Similar considerations apply for pan-European sales and rules in individual European countries.

The aim in modern formulation is to minimize builder concentration due to the problems in rinsing and residue cited above, as well as the environmental restrictions on phosphates. Part of this is done with the choice of solvent and part with the surfactant synergies.

3. Surfactant Innovations

One important area is actually that of surfactants working in negative synergy so as to give quick-breaking foams even with high total surfactant concentrations. This is most commonly done by including a small amount of soap in the formulation. Interest has also been shown in the counterion, a potassium soap combined with paraffin solvent claimed to give a much reduced tendency for stable foam [86].

This brings up the important point that the choice of counterion is also key for efficacy of the main anionic surfactants used in the cleaning formula. It has been known for some time that divalent metal salts of alkylbenzene sulfonate, paraffin sulfonates, and the like are better grease cleaners than the analogous sodium salts [87,88]. These are more difficult to use due to their lower water stability, but they can be formulated with some of the more effective grease cutting solvents [89–90]. It has also been claimed that if ammonium salts of the anionic surfactants are used less residue is left on the surface [91].

Many formulations continue to depend mainly on anionic surfactants for detergency. The major change in the last 50 years has been the change from branched alkyl sulfonates to linear ones, based on concerns about biodegradability [92]. (This was essentially complete in the U.S., Europe, and Japan by the late 1960s, but has taken place more slowly in the developing world.) However, there is a growing trend toward the use of other surfactants beyond the workhorse anionics that have served for so long [93]. There are, for example, all-purpose cleaners that depend more on nonionic surfactants [94,95]. Nonionics are less sensitive to water hardness, can be synthesized to target hydrophilic/lipophilic balances (HLBs) [96], and lead to less foaming. Much of the pioneering work in this area was and is done by the primary suppliers of the materials, such as the work of Shell on primary alcohol ethoxylates [97] and the more recent work by Henkel and Kao on alkylpolyglycosides [98–100]. The sugar-derived polyglucosides [101] show good surfactant qualities and are becoming favored because of the environmental claims that can be made for vegetable rather than petroleum feedstock material. They also show mildness to the skin. In contrast, ethoxylated alkyl phenols are falling out of favor due to their low biodegradability and resulting health concerns [102,103].

Some formulators claim that it is possible to achieve effective cleaning with nonionics while completely excluding anionic materials [104–108]. It is now also claimed that some short-chain nonionics can give superior cleaning [109]. The claim for all nonionic formulas is that they are less sensitive to water hardness. There are also cases where longer chain, block copolymer nonionics are used. In one particular case [110] the nonionic is used not only for its cleaning, but also for its residual spotting/filming characteristics. The general practice, however, is to use a combination of both anionic and nonionic components [111]. In part, this may be because nonionic surfactants have a lower tendency to foam, and foam is expected by consumers as a sign that the "active" is working. Therefore, including a certain amount of anionic surfactant helps to signal the consumer that the detergent is present [112].

It can also be argued that anionic surfactants give the best grease cutting efficacy/price ratio [113]; linear alkylbenzene sulfonate is a commodity chemical, for all intents and purposes, being the highest tonnage surfactant (estimated 3 million metric tons) in the world, due in large part to its use in laundry detergents as well as in household cleaners. Nonionic surfactants are more expensive and of lower tonnage than anionics but are growing in popularity. The alkoxylated alcohols are generally lower foaming than the anionics which can be either an advantage or a disadvantage. Nonionics are usually significantly milder to skin than most anionics, but this is not usually high on the list of preferred benefits for household cleaners. Fortunately, a mixture of nonionic surfactant with anionic surfactant increases the mildness of the formulation over the anionic alone. In general, due to the synergy between surfactants, particularly those of different charge groups, it is advantageous to use mixtures of types rather than all one kind.

As noted above, grease cutting solvents are included in nearly every all-purpose cleaning formula. These solvents are generally kept to low levels because of volatility and general safety considerations. It is interesting to note, therefore, that recent claims are being made for surfactants to also have solvent-like cleaning functions [114,115].

A new subclass of formulations in this area is the microemulsions. These special phases were used in areas such as oil recovery as early as the 1970s, and have been exploited more recently in secondary oil recovery, organic synthesis, and analytical extractions [116]. However, microemulsions have come much more slowly to the household cleaning area, although there are anecdotes of Australians making what is essentially a microemulsion cleaner in the early 1900s to wash wool. (This was reported to be a mixture of white spirit, soap (surfactant), and eucalyptus oil (oil) in water [117].) Much has been written recently on microemulsions [118,119], their advantages over regular emulsions being increased stability, spontaneous formation, and oil solubilizing potential. They are also transparent (unlike emulsions which are generally milky), therefore giving the aesthetics of a true solution. There are examples in the literature that are formulas intended for industrial cleaning of computer components or metal parts [120,121]. In these formulas, the highly hydrophobic solvent (usually a chlorinated hydrocarbon) is delivered to the surface in an aqueous media. Microemulsions, when used neat, also exhibit ultralow interfacial tensions; this increased contact should give them an advantage in the first step of cleaning. The clear advantage of the microemulsion in most cases is the ability to stabilize the solvent in a mixture with other hydrophilic components. The cleaner is used neat only in certain cases, whereas it should be used dilute more often where the interfacial advantages would be lost on dilution but the solvent would contribute more strongly to the cleaning.

The usual approach in consumer products (as opposed to industrial cleaners) is to deliver high amounts of a hydrophobic, but more consumer-friendly, grease cutting solvent such as pine oil or D-limonene. It should be expected that almost any water-based cleaning formulation that contains over 15% hydrophobic solvent and yet comes as a clear transparent liquid is a microemulsion. (This can easily be determined with quasielastic light scattering experiments or other such techniques to determine if droplets of the proper size distribution exist in the liquid [122].) Examples may be found that use these insoluble grease removal solvents as the essential oily material in microemulsions, sometimes with glycol ether solvents added as the cosurfactant [123,124], although more water-insoluble solvents have also been used [125]. All microemulsions formulated for household cleaning so far have far more hydrophilic components than hydrophobic, opposite to the industrial examples. Surfactant types vary, with one of these examples using an anionic/nonionic mixture while the other is all nonionic. Still another example uses a anionic/nonionic surfactant mix with glycol ether cosurfactant but uses the perfume as the oily material essential for forming the microemulsion [126–128]. Another uses a nonionic surfactant as the oil component of the microemulsion [129,130].

4. Added Benefits and Disinfectancy

The addition of any added benefits tends to narrow the scope of a cleaner, and so there are a few general types included in all-purpose cleaners. The most popular is the presence of disinfecting or antimicrobial action. An excellent overview of disinfectants in general and a more detailed treatment is given in Block [131,132]. Biguanides, alcohols, aldehydes, and phenols as well as quaternary ammonium surfactants ("quats") and oxidizing agents (bleaches, largely hypochlorite bleach) are used [133]. Phenols, the basis of original household disinfecting cleaners (e.g., the original Lysol disinfectant, a mixture of cresols with soap to solubilize them in a water solution), have fallen out of common use in household cleaners as disinfecting agents due to toxicity concerns [134–136], although the original Lysol formula may still be sold in Europe. (This Lysol disinfectant should not be confused with the plethora of other Lysol brand products, many of which are disinfectant *and* cleaning products.) Phenol derivatives such as *o*-benzyl-*p*-chlorophenol or *o*-phenylphenol are still somewhat used in household cleaners, but not very widely [137]. They are more widely used in very low concentrations as preservatives. Similarly, aldyhydes (such as gluteraldehyde and formaldehyde) are not generally used because of the difficulty of making such reactive organic compounds stable for long periods in water-based cleaners. However, compounds that break down to produce formaldehyde are used in low levels as preservatives in liquid cleaners.

In view of the recent popularity of "natural" products it is unsurprising that there is also patent art on using essential oils with antimicrobial properties [138,139], of which pine oil is a very old example.

The most commonly used of the disinfectants are quats and alkali metal hypochlorites (rather than oxygen bleaches which are weaker disinfectants). Sometimes they can be combined, as in the case of quats and alcohols [140,141] or pine oil and acid [142]. In fact, pine oil, which was long used as a disinfecting agent, requires high concentrations and is a fairly narrow-spectrum compound. (Spectrum denotes the variety of organisms a disinfectant can kill.) In practice nowadays pine oil is almost never used by itself; the most common combination is pine oil and quats where they compensate for each other's weakness. Acids are also gaining popularity as disinfecting agents [143,144]. Biguanides are used more often in personal care products and are seldom used in household cleaners because of their relatively lower efficacy, but patent art does exist [145]. There is even an example based completely on solvents [146]. Ethanol and isopropanol have long been used as disinfecting agents but have to be formulated at relatively high concentrations [147]. Pine oil gives the most freedom of formulation, bleach the least.

The effective concentration of the disinfecting agent varies widely with the type, and depends on the anticipated use conditions — contact time, soil load, and the amount the consumer is likely to use. The conditions for testing the effectiveness of the disinfectant dictate the label use instructions. If the test was run for 10 minutes, then the consumer is directed on the label to contact the surface to be disinfected for 10 minutes before wiping or rinsing. Table 13.5 gives a brief summary of some of the characteristics of common disinfecting compounds.

The main restriction on using quats is that association of the quats in solution with most anionic surfactants inactivates the disinfecting action of this cationic compound. The action of quats [148] is well known to be boosted by the addition of common chelating agents [149,150], with the sodium salts of EDTA most commonly used [151]. It is also claimed that their effectiveness can be increased through the choice of cleaning surfactant used with them [152,153]. Ethoxylated quats are also starting to appear in the patent art [154–156]. Quats are usually formulated at high pH values, although they seem to have activity down to pH 3 [157]. However, acid pH formulations do exist [158]. Most of the quat-containing disinfectant cleaners on the market tend to be formulated in the pH range 8 to 9. Pine oil can have a narrow spectrum of antimicrobial effectiveness which can be broadened by adjunct compounds such as quats or some organic acids [159].

The broadest spectrum disinfection, at a low price, is delivered by bleach, which is often a compensating factor for the difficulty of formulation. Formulation with bleach usually prevents the use of most common nonionics, paraffin sulfonates, alkylbenzene sulfonates, betaines, long-chain unsaturated quats, etc. The surfactants most often used with hypochlorite bleach are amine oxides, soaps,

TABLE 13.5 Characteristics of Commonly Used Disinfecting Agents

Compound (example)	Spectrum of disinfection (types of organisms killed)	pH range for effective kill	Typical concentration needed	Typical formulation concentration (%)	Chemical incompatibilities/ comments
Alcohol (ethanol, isopropanol)	Many types of bacteria and fungi; not spores		50–80%	60–80	Not used neat as evaporates too quickly to kill effectively
Hypochlorite bleach (sodium hypochlorite)	Bacteria, fungi, viruses, protozoa, and spores	6–8	50–500 ppm	1–5	Catalyzed decomposition by heavy metals like iron and copper; unstable at effective pH; active form is hypochlorous acid (HOCl)
Peroxide (hydrogen peroxide, peracetic acid)	Bacteria, fungi, viruses, and spores	3–7.5	50–500 ppm	0.5–5.5	Catalyzed decomposition by heavy metals like iron
Pine oil (α-terpeneol)	Gram-negative bacteria	>7	~5000 ppm[a]	30–80	Usually not used alone; most often combined with quats or alcohol
Quats (benzalkonium chloride)	Bacteria (less effective on gram-negative bacteria), yeasts, and mold	3–10.5	200–1000 ppm	0.2–3.0	Inactivated by anionics and hard water salts
Phenolics (2-phenylphenol)	Bacteria, fungi, viruses, and protozoa	3–9	400–1500 ppm	3–20	Not compatible with quats; inactivated by nonionics
Organic acids (citric, lactic, acetic)	Bacteria (both gram negative and gram positive)	2–3	70–1500 ppm	1–5	Often need mineral acid to lower pH; active agent is nonionized form

[a] Lee, W.H. and Rieman, H., The inhibition and destruction of enterobacteriaceae of pathogenic and public health significance, in *Inhibition and Destruction of the Microbial Cell*, Hugo, W.B., Ed., Academic Press, New York, p. 411.

Source: Data taken from Block, S.S., Disinfectants, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Vol. 8, Kroschwitz, J.I. and Howe-Grant, M., Eds., Wiley, New York, 1993, p. 237; Richter, F.L. and Cords, B.R., Formulation of sanitizers and disinfectants, in *Disinfection, Sterilization and Preservation,* Block, S.S., Ed., Lippincott Williams & Wilkins, New York, 2001, pp. 477, 480.

and sodium alkyl sulfates, although there is one example using a nonionic [160]. It has been known for some time that amine oxides interact with anionic surfactants at certain ionic strengths to generate liquids with dynamic viscosities from 10 to about 5000 cP [161–164], or, in one case, the interaction of an amine oxide with a polycarboxylate polymer [165]. In this way, bleach-containing formulas can be thickened by the use of the surfactants alone [166]. Therefore, bleach all-purpose cleaners can have three benefits in addition to the primary cleaning: removal of oxidizable stains, disinfection, and increased cling or residence on vertical surfaces.

Most bleach cleaners, however, are simple, water-thin solutions. The most common formulations are a simple combination of hypochlorite bleach, sodium hydroxide (to achieve a pH of 10 to 12), amine oxide surfactant, and a low quantity of perfume. However, despite their simplicity, these types of products are very effective stain removers and disinfectants.

There is an interest in nonhypochlorite disinfection, as evidenced by patent art for institutional use. Examples can be found that use peroxyacids to achieve antimicrobial effects [167–169]. The advantage of these formulas would be lack of odor and corrosion that can be encountered in hypochlorite formulas.

As disinfectant cleaners are being used throughout the home (as all-purpose cleaners), the inclusion of characteristics such as low streaking (important for cleaning shiny surfaces) is also being claimed in antimicrobial formulations [170,171].

Although disinfectant cleaners are still very popular in North America, there are questions about the need for these types of cleaners in Europe where there is more awareness of "good" versus "bad" bacteria, and therefore more question about the wisdom of wholesale killing of bacteria. Disinfectant cleaners were first promoted and sold in times when a household might actually have a member infected with a serious infectious disease. This serious need for disinfection in the household seldom occurs in the developed world now. This is not true, of course, in some developing nations where serious epidemics can justify a need for broad-spectrum disinfection. However, several events of the past two decades have fostered an ever increasing interest among consumers in disinfection or germ-killing cleaning:

- The AIDS epidemic of the 1980s.
- Information campaigns about salmonella and *E. coli* food-borne infections.
- Information about the "germiness" of sponges and kitchen cleaning implements.
- Outbreaks/epidemics of contagious diseases (severe acute respiratory syndrome (SARS), Ebola virus, hantavirus).
- The anthrax scares of 2001 (mistakenly). (Household disinfectants are generally ineffective on spores.)

However, disinfectant household cleaners are also more likely now to be mentioned in newspaper and magazine articles as contributing to the problems of antibiotic-resistant bacteria; these tend to be reports in the popular press where all antimicrobial products tend to be mentioned, despite no demonstrated scientific link between the household cleaner disinfectants and the problem [172–174]. As noted, disinfectant cleaners continue to have popularity, but given some of the trends in microbial control issues, they may be either more heavily regulated or limited in the future.

Bleach can be added to an all-purpose cleaner simply for the stain removal properties as well, with no disinfectant claims made. (In fact, bleach is one of those ingredients, like aloe, that carry its own strong associations; many consumers would assume a bleach cleaner was a disinfectant whether it was claimed on the label or not.) Consumers often make “witches’ brews” of household chemicals to make their own cleaning solutions. Most consumers are well aware of the “don’t mix ammonia with bleach” rule, although they are generally unaware of other chemical interactions that can take place. Certainly if a regular household cleaner is mixed with household hypochlorite bleach, the bleach will start degrading most surfactants. As noted before, only a limited subset of surfactants are compatible with bleach. A commercially formulated product gives the stain-removing property that consumers are looking for in their homemade versions with considerably more safety and effectiveness.

This is another recent trend in “ingredient stories” — the rise of oxygen bleach cleaners. This is another fad in ingredients that is too recent to know if it has staying power or not. Oxygen bleaches are demonstrably less effective on destaining, but they are also safer to surfaces. It is this last trait that is most mentioned — destaining with surface safety. This started because of the sale of tubs of sodium sulfate/hydrotropes with sodium percarbonate [175]. This was meant to be used as a laundry additive and as a household stain remover when dissolved in a recommended amount of water. Consumers use this powder product largely as a laundry additive but it evidently ignited an appetite for oxygen bleach products. Most of the products have come in spray cleaner form rather than dilutable, and so the particulars of their formulation are detailed in the spray cleaner section.

Besides disinfection and stain removal, there are few other added benefits of major market importance. The next most important is the special class in which a polymer film is left behind on the surface. The most common example of this is not all-purpose cleaners, but are the “mop and shine” products for floor cleaning. This subset is intended solely for floor cleaning and leave behind a film intended to mimic the shine and soil resistance of waxing a floor. Unlike waxes, however, these polymer films do not need to be buffed to make them glossy [176]. The only drawback to this kind of formula is the possible buildup of polymer on the surface. These polymer films tend to be slightly colored, and so repeated layers can yellow the surface. The aim of inventions in the field is therefore to give polymers that deposit on the surface readily in formulations that avoid buildup [177].

Another benefit that also seems to have the benefit aimed at floor cleaning (because it may be about the only cleaning job still done with a bucket in developed markets) is the idea of coagulating the soil in the bottom of the bucket. This should mean that the wash water remains cleaner (if the mop is not put all the way to the bottom of the bucket) and soil removed from the floor is not redeposited. Although the patent art goes back to the late 1980s [178], only recently has a cleaner been marketed in the U.S. making exactly this claim.

This concept of polymer adsorption for greater shine and soil resistance has since been extended to other household surfaces, going from specialized floor products back to all-purpose cleaners. These generally use nonionic polymers such as polyethylene glycol, polyvinyl pyrrolidone, or other film formers [179,180]. One very interesting invention states that by the use of a polyalkoxylated alkylolalkane and vegetable oil surfactant a formula may be made that shines shiny surfaces but which imparts no gloss to matte surfaces [181] and a similar one that also uses a vegetable oil surfactant [182]. The concept of preventing soiling can also be extended to preventing subsequent microbial growth and so combine antisoiling with germ prevention claims [183,184].

Another recent interesting invention is the formulation of an insect repellent into an all-purpose cleaner [185–187]. The key here is that the active ingredient is not an insecticide but simply a repellent which makes it possible to leave it behind routinely in the cleaning process without concerns for repeated human contact.

There are also examples of formulations that include a dye so that soil can be visualized so as to signal to the consumer when "complete" cleaning has taken place by the absence of the color [188]. Admittedly, some soils, like soap scum and grease, are apparent on light-colored household surfaces mainly by their dulling of the natural shine of a surface. In this case, the dye is sensitive to the presence of protein, so if the soil was a pure grease soil (like many kitchen soils) it would fail to react, whereas it would probably be highly indicative of bathroom soils.

5. Formulation Technology

Table 13.6 gives ranges for common ingredients for all-purpose cleaner formulation. Although it is not explicit from the previous discussion, "regular" all-purpose cleaners are intended to be dilutable. The consumer may use them full strength from the bottle for cleaning a very heavily soiled small area, or may dilute them in the range of 1:32 to 1:128, with a dilution rate of 1 part cleaner to 64 parts solution being most common. There are all-purpose cleaners launched in North America and Europe that operate at the top of the dilution range; these are the "ultra" or concentrated products, similar in concept to the ultra laundry detergents. These have largely disappeared from the North American market. There are also some patents appearing for household surface cleaners that are mentioning

TABLE 13.6 Liquid Dilutable All-Purpose Cleaner Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, ethoxylated alcohol sulfate, soap	0–35
Nonionic surfactant	Ethoxylated alcohol, amine oxide, alkanolamide fatty acid	1–35
Hydrotropes	Sodium cumene sulfonate, sodium xylene sulfonate	0–10
Builder	Carbonates (more rarely phosphates), silicates, citrates, EDTA salts, polyacrylates	0–10
pH adjuster	Ammonia, sodium hydroxide, magnesium hydroxide, alkanolamines	0–10
Solvent	alcohol (pine oil, benzyl alcohol, or lower carbon number alcohols), glycol ether (Carbitol®, Dowanol®, etc.), D-limonene	0.5–50
Disinfectant	Hypochlorite bleach, pine oil, other low carbon number alcohols, quaternary ammonium compounds	0–15
"Shine" polymers and other benefits	Polyacrylate, polyethylene glycol, polyvinyl pyrrolidone, organosilanes	0–25
Perfume, color, etc.		0.1–3
Water		QS

the concentration of the formula [189–191]. The largest difficulty in formulating such products is usually keeping high concentrations of surfactant from creaming or separating. The use of hydrotropes and solvents, and the minimization of electrolytes, is especially important in achieving this goal. If such concentrated formulas can be made stable, the manufacturer gains the advantages of less packaging, smaller shipping weights, and less storage space. The consumer gains advantages in more easily stored containers and less packaging to recycle while the absolute cleaning potential in its delivered form increases. The difficulty for consumers is in changing their habit of dosing so as not to waste the concentration of the new formulations. These types of concentrated all-purpose cleaners should be considered as existing toward the top of the surfactant concentrations listed in Table 13.6.

With higher concentrations of surfactant, the formulas also tend to become thicker. In most cases, the increase in viscosity will be minor, but in some cases it can become significant. If the product is meant to be dilutable by the consumer, then the perception of pouring and dispersability of the product cannot be adversely affected by the viscosity. The ways to decrease the viscosity in these cases is to decrease the surfactant association that is responsible. Many of the commonly used solvents can affect the solubility of the surfactant and therefore redistribute the relative amount of monomer versus associated forms. Changes due to ionic strength can have the same effect and so the addition of simple salts to the formula can also remedy the problem. Of course, if it is desirable to thicken the product, this can be done most easily through the addition of various polymers such as polyacrylates, polyethylene oxides, cellulose gums, polyglycols, etc., depending on which is most compatible with the surfactant system.

The pH of most all-purpose cleaners is between 8 and 12. Generally this is the best range for grease cleaning in that the alkalinity can (to a small degree) saponify some portions of a grease, thereby assisting the surfactant/solvent system in removing soil. However, high pH can also damage some sensitive surfaces, such as aluminum, as well as being irritating to skin. In the interest of giving consumers more advantages, formulators strive to work at pH values as close to neutral as possible to reduce these negative effects. This means that more care has to go into optimizing the surfactant system and sometimes more reliance on the grease cutting solvents. For instance, pine cleaners tend to be acidic, but the pine oil, more than the pH, contributes to the grease cleaning. This approach also has its dangers, as some surfaces such as paint and wall coverings can be sensitive to solvents.

As can be seen from the preceding discussion, all-purpose cleaners started with the oldest surfactant, soap, and have progressed to more powerful surfactants and then further developed sophisticated surfactant synergies. As these developments are made, there is less and less reliance on the old inorganic builders and more interest in solvents, particularly those with grease cutting ability. Only concerns about human toxicity and environmental regulations limit the choice of solvent.

6. Aesthetic Ingredients

Fragrance is a very important part of household cleaners, often overlooked in the technological drive for formula performance. However, fragrance can often be the driving attribute in a consumer's evaluation of a product. Fragrance can sometimes be difficult to incorporate stably into a product, due to its low solubility (oily nature) and chemical reactivity (presence of aldehydes, esters, ketones, etc.). One of the ways of easing the addition of a perfume oil into a formula is to premix the fragrance with either surfactant (a lower HLB component) or with the solvent. Higher concentration formulas, rich in surfactant, often have enough solubilization power to make the addition of the fragrance less difficult than in more dilute products like glass cleaners.

Colors can also sometimes be difficult to stabilize in a cleaner. Obviously, this is particularly a problem in bleach-containing cleaners. The strategy in coloring bleach products, if they are thickened, is to color them with pigments that can then be stably suspended by the thickening system of the product.

(Powder cleansers may also use pigments, but this is significantly less of a problem in nonliquid systems.) Most liquid cleaners use dyes as their coloring system, and, as with fragrances, the primary chemical compatibilities must be considered when picking a color system.

7. Minor Ingredients

In the course of formulating all-purpose cleaners there may be a need for other minor ingredients in addition to the main cleaners (the surfactant, solvent, or builder). These ingredients include hydrotropes, hard water control, and buffers. These ingredients do not include any that are added for special benefits such as shine enhancement, disinfection, soil release, etc.

When builders are used in a formula, they also fill the function of hard water controls and buffering agents. However, the high electrolyte concentration imparted by the use of these builders may make it necessary to use a hydrotrope (see Chapter 2). In general, hydrotropes are organic compounds that enhance the solubility of other species. In cleaning formulations they facilitate the dissolution and continued solubility of the main detergent surfactant in a liquid formula. Many times the solubility of the surfactant is limited by high salt content or other factors. Examples of hydrotropes are given in Table 13.6. As the use of inorganic builders decreases over time, the use of hydrotropes is also decreasing. However, hypochlorite bleaches also increase the electrolyte concentration, as can the inorganic thickeners in cream cleansers. In these cases, the use of a hydrotrope may also be required.

When, as in many modern formulas, builders are excluded or limited to decrease visible cleaner residue, other means are necessary to control water hardness and buffer the formula. In some areas where the water hardness is very high (above 250 ppm as $CaCO_3$), even modern anionic surfactants can be partially precipitated. Soap is very easily precipitated. The most common remedy is to add one of the salts of EDTA or NTA to chelate the water hardness ions and therefore maintain the anionic surfactant efficacy. (Although these compounds may be classed as builders because they control water hardness ions, they usually do not supply significant alkalinity to the formula.) These components can still contribute to residue and need to be limited. In recent times these compounds have come under scrutiny for toxicity concerns, with some governments considering legal limitations. These environmental and toxicological concerns are anticipated in the literature [192]. Of course, this problem of divalent cation precipitation does not occur with nonionic or cationic surfactants, which is an advantage when formulating.

The other problem when builders are eliminated is stabilizing the pH of the formula. Many anionic surfactants can impart a slightly acid pH to the solution when dissolved. If the aim of the formula is largely grease cleaning, this is most efficiently done at basic pH. Therefore, the pH can be adjusted using common bases such as ammonia or sodium hydroxide. Ammonia is useful in that it is volatile and therefore leaves no residue, but it also imparts a distinctive odor that is not pleasing to some consumers. However, neither of these choices is a good buffering agent. If the pH of the formula is to be maintained in a lower range (pH 8 to 9) or if the formula pH tends to drift over time, then alkaline buffering agents, usually one of the alkanolamines, are used.

E. Floor Cleaners

All-purpose dilutable cleaners are often used for floor cleaning. This results in a laborious task: mixing of the solution in a bucket, washing of the floor with a mop (which must then be cleaned), rinsing of the cleaned surface (difficult on a large horizontal surface), and then cleaning the solution bucket in which the removed soil resides.

In an effect to shorten this task, one of the recent developments was the "ready to use" floor cleaners. These are even more dilute than spray cleaners, formulated at the high dilution that conventional cleaners are used for floor cleaning (Table 13.6, diluted 1:32 or 1:64). They are usually packaged in plastic bottles with push/pull or flip-top caps. This means that the solution making and bucket cleaning steps are eliminated. In addition, it is contended that these low-dilution cleaners do not need rinsing, also eliminating that step. (The most recent development, that of the Swiffer® type floor cleaning systems, is discussed in the section on wipes.)

Wood floor cleaning also seems to be a special case for some consumers with cleaners formulated for this particular use [193]. Certainly, wood floors have a higher sensitivity to water-based cleaners than almost any other type of flooring. This is one of the few types of dilutable cleaner in which soap is seen as the main surfactant [194].

F. Test Methods

There are several key performance areas to test for all-purpose cleaners. As may be deduced from the previous discussion, these are cleaning, ability to foam, and residue/shine. Unfortunately, very few published standardized methods exist in this area, especially residue/shine. Although foam height and soil removal are easily quantified, the impact of various amounts of residue and its distribution on a surface are not. Most residue/shine tests are based on the evaluation on scales from 1 to 10 by panels of observers of prepared samples. Usually the method used is described in the corresponding patent. A usual general method is to apply the cleaning solution, either by wiping or by pipetting, onto a clean glossy surface, usually of a dark color. Black ceramic wall tiles are convenient for this purpose. The solution is left to dry on the surface, and a panel of observers rates their impression of residue on the resulting pattern.

1. Cleaning Tests

For cleaning tests, the methods for applying soil, simulating the cleaning process, and judging the result are well established [195,196]. What is not well established is the precise identity of the soil used. For all-purpose cleaning, the target soil usually investigated is grease. This is meant to replicate the soil left on kitchen surfaces due to normal household cooking practices. Of course, the type of oil or fat used in cooking can vary widely around the world, from vegetable oils and margarine to beef fat, lard, and butter. Even among the vegetable oils, there can be differences between olive and corn oils, due to the distribution of chain lengths and unsaturation. These factors affect how the grease is changed by heating and exposure to the air in thin films [197].

In many cases, a pure grease soil is not used. Sometimes the soil is colored with carbon black to make it more visible. However, this also has the effect of introducing a solid particulate into the soil mix [198,199]. Other particulates have also been introduced such as humus, clay, ferrous oxide, soot, and filtered vacuum cleaner dust [200,201]. However, the grease component of the soil usually predominates. If the grease soil is liquid (such as vegetable oil), then it can be sprayed on the surface neat. Mixtures of particulates with oils are also spread on surfaces using paint rollers. However, liquid soils usually require longer aging periods before they can be used. Soils can also be prepared by dissolving solid greases (tallow) in various solvents (naphthenic hydrocarbons, chloroform, etc.) and then spraying the solution or dispersion. The solvent flashes off, leaving a solid grease layer (usually without particulate). These soils need shorter aging times because their solid form makes them more difficult to clean than oily soils. However, there are two concerns with this type of procedure: (1) the proper protection of laboratory workers from these hazardous solvents and (2) the contamination of the greasy soil with any residual solvent that might influence the cleaning process.

The soil is applied to typical kitchen surfaces: vinyl floor tile, sections of Formica, ceramic tile, pieces of enamel, aluminum, stainless steel, painted wall sections, etc. The local point of sale is the determiner of the choice of surface, so knowledge of local materials of construction is necessary. It is sometimes necessary to alter the surface in order to make the soil tenacious. This is sometimes done with a light sanding of the surface to roughen it, or with chemical etching such as strong acid or strong base treatments of susceptible surfaces. It is preferred to alter the composition or aging of the soil to increase tenacity only where necessary, although surface roughening is sometimes considered accelerated "aging" of a surface. It is, indeed, the daily wear and tear of living with the surfaces that results in their alteration, and any changes in the surface should be done with a view to mimicking the natural aging changes that take place in the surface.

Once the soil has been aged, either at ambient temperature or by heating and drying in an oven, cleaning experiments can be carried out. The usual apparatus for this testing is a Gardener abrader (Figure 13.5). This consists of a testing platform

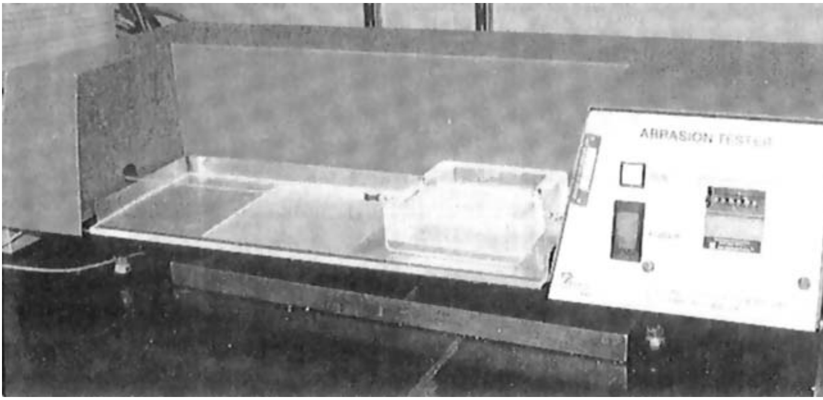


FIG. 13.5 Gardener straight line abrader machine.

and a carrier for holding cleaning utensils that is driven by a motor back and forth along the platform. Cleaning utensils fitted in the machine are also chosen according to local habits and practices. They can be sponges, mohair, folded cloth, folded paper towel, or scrub brushes. Small pieces of sponge wrapped around solid blocks are the usual choice. The utensil holder is usually made to hold two separate sponges so that the cleaners can be tested side by side. Often, variations in the individual quality of a surface and its applied soil make it necessary to do direct comparisons of cleaners on the identical item. Also, a standard amount of weight is applied to the utensil holder to simulate the force a person employs in the wiping process. This force is usually in the range of 200 to 500 g per sponge including the weight of the carrier and the loaded sponges.

In some cases, such as spray cleaners, the test product can be applied directly to the surface and a wetted utensil used for cleaning, but for most general or more concentrated all-purpose cleaners the solution is loaded onto the utensil. The utensil is usually wetted so that it is wet but not dripping water. The cleaning solution can be used neat or dilute depending on the intention of use. If floor cleaning is simulated, the cleaner is diluted according to label instructions usually in the range of 1:64. If tough soil spot cleaning is simulated, then the cleaner is used neat. It can be applied to the utensil in two ways. Either a specified amount of cleaner is poured or pipetted onto the sponge, or the utensil mounted in its holder is soaked in a shallow pool of the cleaner for a specified time. The utensil is then fixed in the holder on the abrader.

The abrader is then set in motion, making reciprocal sweeps back and forth over the soiled surface which is fixed on the testing platform. Cleaning can be done in two ways: a fixed number of strokes can be used, or the process continued until one or both sides of the testing surface is completely clean. The first method can be used to compare cleaners at different number of strokes to generate data on the "kinetics" of cleaning. The second method mimics the practice of the consumer, which is to wipe until the surface is clean. In this case, the number of stokes needed to give 100% cleaning is tallied for at least one cleaner. The slower cleaner can then be continued until it is completely clean and its higher number of strokes recorded, or its amount of lesser soil removal tallied when the superior side reaches 100%.

Soil removal can be judged by eye, but the more common methods use a reflectometer. First, the "new" surface is measured before soiling. Most conveniently this is done on a white surface. The surface is soiled, usually with a colored soil. As mentioned before, the soil may be colored with carbon black or other particulates giving a gray or brown appearance. It may also be colored with oil soluble dyes. After soiling, another reflectometer reading is made. The cleaning is done, and the surface is then usually rinsed to eliminate cleaner residues or loosely held soil. Then the final "cleaned" measurement is made. The percentage soil removal is calculated as:

$$\%\ \text{Soil removal} = \frac{R_\text{c} - R_\text{s}}{R_\text{n} - R_\text{s}} \times 100$$

where R_c is the reflectance of the cleaned surface, R_s is the reflectance of the soiled surface, and R_n is the reflectance of the surface before soiling.

Another way of doing grease testing was shown by a consumer organization [202]. Although the choice of ingredients for the grease soil in this test is not the most consumer relevant, depending on mineral oil and petroleum jelly rather than household kitchen grease, the method by which the grease was removed is interesting. (This soil also included a fair proportion of particulates in the soil.) In this test, the greasy soil was applied in a narrow strip perpendicular to the travel of the sponges in the abrader apparatus. There were clean areas on both sides of the soiled strip. In this way, these experimenters measured not only the soil removal from the greasy area, but also the tendency of the cleaner to smear the soil onto previously clean areas. So a cleaner that performs poorly on soil redeposition or one that adsorbs the soil poorly into the cleaning implement will be judged inferior by this test.

Other, special, soils may also be tested. A "sticky" kitchen soil has been cited in the patent literature [203], consisting of vegetable shortening and all-purpose flour. This soil was baked on. Heating grease tends to oxidize and, to some extent, polymerize it into a resin-like coating. This can also happen over long periods at room temperature, resulting in a very tenacious soil. (Even dust soils can become more tenacious with time where it can no longer be simply vacuumed but must be removed by wiping.) A variety of soils was used by a consumer organization to test sprays and dilutable cleaners, meant to show a variety of cleaning problems (grape juice, ketchup, vegetable grease, and baked lard) [204]. In the case of cleaners containing bleach it is desirable to test the stain removal ability of the cleaner. Relevant household stains should be researched and chosen as the test soil. Only oxidizable stains, of course, will react to the bleach. One common widely used test uses tea stain on an enamel surface. Plates made of enamel on steel are boiled in a concentrated tea solution. They are air dried, rinsed with deionized water, and this is then repeated until the uniformity and degree of staining desired is reached [205]. This soil is cleaned and evaluated in the same manner as the grease soil.

Static soaking tests can also be done which eliminate the contribution of the mechanical action of the abrader test. The surface has a volume of the cleaning solution trapped within a ring (like a rubber washer), and covered to stop evaporation. After a set time the cleaning solution is poured off, the surface rinsed, and the area evaluated (either by eye or by reflectometer) to determine degree of stain removal. This can also be used as a test for damage to the surface by the cleaner if done on an unsoiled surface.

Although grease is the main soil target, followed by particulate soil, for all-purpose cleaners they may also be tested against other nonkitchen problems such as soap scum. Soap scum testing is described in the section on bathroom cleaners.

2. Foam Level Testing

Foam tests of all-purpose cleaners are done similarly to other fields. One of the most common tests is the cylinder test. The cleaner may be placed, neat or diluted, in a glass graduated cylinder. The cylinder is then inverted a specified number of times, and the resulting foam height noted. This immediate reading is referred to as “flash foam.” The cylinder then may sit undisturbed for various lengths of time, and the gradual collapse of the foam recorded in decreasing foam heights. Another test is the Ross Miles foam test [206]. In this method the solution is dropped over a specified distance into a receiver. The foam produced by this fall is measured immediately and after 5 minutes. Different foam aesthetics are preferred around the world, although generally it is preferable that the foam does collapse, as this is perceived to decrease the effort of rinsing.

3. Surface Safety

Another area of investigation is surface safety. Households contain many different surfaces that may be soiled. If a consumer uses these products as true all-purpose cleaners, they will be carried from room to room, encountering many of these surfaces. It is wise to test the effect of a cleaning formulation on various items, depending on local materials. This is done most simply by immersing a solid block of material in the cleaner, or by letting a pool of the cleaner contact a representative surface. The length of time for the test is left to the experimenter’s discretion. The compatibility of a cleaner with a variety of surfaces is part of the designation of an all-purpose cleaner. Evaluating surface safety becomes even more important when aggressive substances such as strong solvents or bleach are included in the formula. Inclusion of these types of ingredients tends to limit the formulation's use, relegating it to the category of a specialty cleaner in some consumers' minds. This is especially true of bleach cleaners, whose aggressiveness to many colored surfaces is well known. Cleaners containing high concentrations or more efficacious solvents may be aggressive to coated, plastic, or paper surfaces such as paint, shellac (used on wicker and some metal surfaces), or various types of wallpaper. It is also important to test low or high pH cleaners on metal surfaces such as aluminum.

4. Disinfectancy

Disinfectancy tests are usually regulated by local government. For example, in the U.S. the rules and procedures for disinfectancy are set out by the Environmental Protection Agency, and in France they are given by AFNOR (Association Française de Normalisation). (However, since the formation of the European Committee for Standardization (CEN), CEN-TC216, the Technical Committee for Disinfectants and Antiseptics, has issued methods for all of the European Union.) The usual test for disinfectancy in the U.S., for both disinfectant compounds and cleaning formulations, is the use dilution test [207,208]. These tests usually consist of challenging a use dilution of the cleaner with specified microorganisms, followed by incubation. The disinfectancy of the formula is determined by the number of surviving cultures at the end of the incubation period. For the use dilution test, for example, the usual score for successful disinfection is lack of subsequent growth in 59 out of 60 tubes. U.S. regulations specify three different levels of disinfection claim, depending on the organism(s) used in the test [209]. "Sanitization" (in the U.S.) is usually defined as a lower level of kill than disinfection. Similar tests are laid out in the European tests [210]. As disinfection is very dependent on how the solution is applied and the contact time, these are usually carefully designated in the test method. The method has to be modified for spray cleaners as they are delivered ready to use (needing no dilution), and are sprayed on the surface in a thin coating of droplets [211]. Regulatory agencies usually require preview and negotiation of the test method if any changes are made to their standard procedure.

5. Miscellaneous Testing

If the product is not a disinfectant formula, it may be advisable to conduct adequacy of preservation tests. In these tests, the formula, as made for sale, is challenged with various microorganisms. This test sample is incubated for a time, and the amount of growth measured. Aging tests for the shelf life of the formula are also advisable, usually run for up to 12 to 18 weeks at both room temperature and elevated temperatures.

Other tests may also be required by various governments. Eye irritancy warnings on the product, for example, may be required depending on the outcome of standard irritancy tests. There are also many regulations or labeling procedures regarding the biodegradability of cleaning formulas and their ingredients. In these ecologically aware days, many primary suppliers of surfactants and other active ingredients do their own biodegradation tests. An excellent overview of the field of biodegradability and various testing methods is given by Swisher [212]. It is wise for the formulator to inquire about these tests, especially if the product is intended for use in Western Europe or other ecologically conscious areas. There may also be regulations relating to the shipping and handling of large amounts of the cleaner and so some tests may have to be done regarding, for instance, the flammability of the cleaner. The closed or open cup flash point test is a standard for this [213].

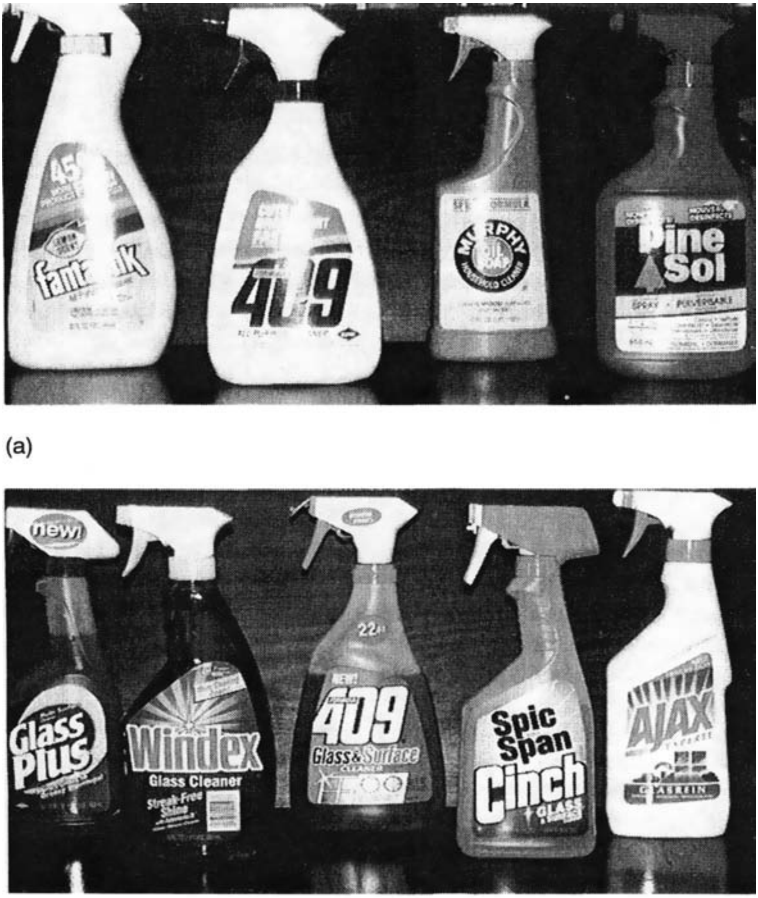
These are standard tests, used for standard attributes of the cleaner. If special new added benefits, such as shine enhancement, are invented for a cleaner, then new testing methods must also be invented to measure them.

III. SPRAY ALL-PURPOSE CLEANERS

A. Historical Background

Spray all-purpose cleaners began to emerge on the U.S. markets in the 1950s. In the beginning they were pump sprayers, but the late 1970s saw the development of the more ergonomic trigger sprayers. These are now coupled with shaped bottles to give convenient gripping (Figure 13.6). These formulations extend the convenience of the liquid form by marrying it to a very convenient dispensing container. The trigger sprayers deliver more product to the surface than the older pump forms and with reduced hand fatigue [214]. The formula in the spray bottle is generally in ready-to-use concentration as opposed to the formula in the regular bottle which is meant to be diluted by the consumer. These spray cleaners are used predominately for spot cleaning and special needs rather than for larger area cleaning (e.g., floors). They are also generally used for lighter soil loads (finger prints, thin films of oil) than for tougher soils (thick layers of aged grease on range hoods) which are reserved for more concentrated products, the regular dilutable cleaners. This marriage of cleaning formula to specific package form, tailoring the action of the cleaner to the way it is dispensed, is an important trend in household surface cleaning.

All-purpose cleaners, as powders, were dispensed from boxes or bags. This could be a messy operation, and spills are difficult to clean up. Liquid all-purpose cleaners are dispensed from bottles, usually equipped with screw off or flip-top caps. Therefore, these were not only less messy to dispense, but they were easier to close tightly to eliminate spills. The caps could also be used to measure the product



(a)

(b)

FIG. 13.6 Modern spray trigger packaging: (a) glass and surface cleaners, (b) mold and mildew and bathroom cleaners.

so that the appropriate amount of cleaner could be specified by the formulator without the need of a measuring device separate from the container. As noted before, plastic bottles, of light weight, inexpensive, and nearly unbreakable, were another packaging innovation that made use and dispensing of the cleaner easier and more convenient. The more convenient formula is accompanied by the more convenient dispensing system.

Spray cleaners are also of this type. The formula is already at the concentration appropriate for use, and the dispenser easily spreads a small amount of cleaner.

Aerosol packaging has played a smaller role in this area than in others like furniture polishes, air fresheners, and hair care. It has survived most often when a thick foam meant to stick to vertical surfaces is needed as in the case of oven cleaning or bathtub enclosures. In future it can be expected that as packaging innovation continues, specialized formulas will be matched to them to create more convenient and targeted cleaning systems for consumers to use.

In theory, almost any dilutable cleaning formula, including pine, disinfectant, grease cleaning, bleach, etc., can be "watered down" to give an effective spray cleaner. The trigger sprayers used with these formulas tend to exaggerate the foaming qualities of the cleaner, so the surfactant levels are generally at the lower end of the ranges given in Table 13.6. (Even at these concentrations, a spray cleaner is much more concentrated than the solutions generally used for floor cleaning where the cleaner has been diluted 30 to 60 times.) Also, these convenience cleaners are generally used without rinsing, so minimum ingredients have to be used to minimize residue. Any crystalline ingredients also have to be minimized to reduce buildup on the trigger itself when residual cleaner dries on the nozzle.

These are general restrictions on spray cleaners. About the same time that all-purpose cleaners were developing into sprays, formulas were also becoming less "all purpose." One of the first specialties to appear was glass cleaners. At the present time there are also formulas adapted for bathroom cleaning, stain removal, carpet cleaning, oven cleaning, etc. These types of specialization also impose their own special restrictions. One of the largest areas of specialization is grease cleaning, which in very developed markets can be subdivided into three different soil loads.

B. All-Purpose Spray Cleaners

Most closely related to the dilutable cleaners packaged in bottles are the all-purpose spray cleaners. These are used for the heaviest soil in spot cleaning — small greasy areas like stove tops, small spills, sticky spots like drops of jelly on countertops, etc. The small, quick nature of the job does not justify getting out a bottle and a bucket; the difficulty of the soil load calls for something close to the concentration of the dilutable all-purpose cleaner. As a general trend, these spray formulations are richer in solvent and poorer in surfactant than their dilutable counterparts. Also in common with the dilutable cleaners, the main trends in formulation are a greater emphasis on safer solvents, increasing use of nonionic surfactants, and decreasing use of builders and other salts. Typical formula ranges for this type of cleaner are given in Table 13.7. One unusual example provides for formulation of the cleaner at either acid or alkaline pH [215]. It would be useful therefore, as either a typical all-purpose spray cleaner or as a "vinegar" glass cleaner, depending on the pH. The compositions of these formulations fall between those of Table 13.7 and Table 13.8 (due to the possible inclusion of acetic acid, not included in Table 13.7).

TABLE 13.7 Spray All-Purpose Cleaner Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, ethoxylated alcohol sulfate	0–10
Nonionic surfactant	Ethoxylated alcohol, alkanolamide fatty acid, amine oxide	1–10
Builder	Carbonates (more rarely phosphates), silicates, citrates, EDTA salts, NTA	0–10
pH adjuster	Ammonia, sodium hydroxide, magnesium hydroxide, alkanolamines or citric acid	0.1–10
Solvent	Alcohol (pine oil, benzyl alcohol, or lower carbon number alcohols), glycol ether (Carbitol®, Dowanol®, etc.), D-limonene	0.5–0
Disinfectant	Pine oil, C2–C3 alcohol, quaternary ammonium compounds	0–5
Bleach	Hydrogen peroxide	0–10
Antistreak polymers	Polystyrene/maleic anhydride, polyethylene glycol, etc.	0–5
Perfume, color, etc.		0.1–2
Water		QS

TABLE 13.8 Spray Glass Cleaner Formulas

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, ethoxylated alcohol sulfate	0–1
Nonionic surfactant	Ethoxylated alcohol, alkanolamide fatty acid, carbamates, amine oxide	0.01–3
Amphoteric surfactant	Betaines, sulfobetaines	0–10
Builder	Carbonates, silicates, citrates	0–2
pH adjuster	Ammonia, sodium hydroxide, alkanolamines or acetic acid	0–5
Solvent	Lower carbon number alcohols, glycol ether (Carbitol®, Dowanol®, etc.)	0.5–40
Antistreak, antifog polymers	Silanes, ethoxylated silicones, polyethylene glycol, polyvinyl alcohols	0–1
Perfume, color, etc.		0.001–0.5
Water		QS

A survey of the literature reveals a preoccupation with streak-free cleaning when the all-purpose cleaners are in spray form [216–219]. The last citation is unusual for its inclusion of soap as a component that, in combination with a nonionic surfactant, gives better streaking properties. Usually soap is formulated into the cleaner, if at all, as a foam breaker [220]. One of the drawbacks of these spray cleaners is that even a low level of builders, chelators, buffers, etc., still leaves a residue which is perceptible on very shiny or transparent surfaces. The traditional answer to this problem was to then go back and clean these types of surfaces with a glass or window cleaner to remove the all-purpose cleaner residue. Work on these formulations concentrates on optimizing surfactants [221–223] especially if it helps to minimize the solvents [224,225]. Minimizing all ingredients helps to minimize residue and streaking, but minimizing the solvent also has the attributes of avoiding VOCs and reducing the odor of the cleaner. Odor can be more of an issue in cleaners that are sprayed because of the aerosolization of the cleaner.

One unusual example of a hard surface cleaner of this type claims a residual effect on the surface that reducing the cleaning effort needed on subsequent cleanings. The surprising part of this invention is that the claim is based, in part, on the presence of lipase in the formula [226]. This is a rare example of the use of an enzyme in a consumer-intended hard surface cleaning formula. The use of enzymes in hand dishwashing, automatic dishwashing, and laundry is quite common.

Disinfectant cleaning had largely been limited to bathroom cleaners and dilutable all-purpose cleaners, but made a breakthrough with the introduction of an "antibacterial" spray cleaner for kitchens in 1994 [227]. At this time disinfectant was the usual term used in the product name of bathroom cleaners and dilutable all-purpose cleaners making germ-killing claims. The ones that have "antibacterial" in the name of the product usually have the term "disinfectant" somewhere else on the label. These are largely marketing distinctions in the U.S.; some localities may have laws about the exact wording that can be used. In practice, household cleaners with both names (at least in the U.S.) use the same ingredients and make the same label claims. Consumers seem to have slightly different views of the two terms and so it is a marketing, and not a formulating, choice [228].

C. Glass Cleaners

Glass cleaners are made to have the least possible residue. (Formulas of this kind go back to the late 1960s [229].) However, this low residue is usually accomplished by ultralow levels of ingredients which results in very light-duty cleaning. Glass cleaners have sufficient ingredients to remove common window soils such as fingerprints, dust, water spots, etc. They are not intended for heavy-duty soil loads like kitchen grease or sticky food spots. The main consideration for glass cleaners is that they deliver the minimum cleaning while leaving no streaks or residues that would be readily apparent on transparent surfaces. For this reason, volatile ingredients are desired in glass cleaners. This will be limited due to VOC legislation.

The trend previously noted for grease or all-purpose sprays continues for glass cleaners. Glass cleaners depend even more on solvent content and less on surfactants than the all-purpose sprays, which depend more on solvent and less on surfactant than the dilutable all-purpose cleaners. This is readily apparent if Table 13.8 is compared to Table 13.6 and Table 13.7. Two other differences are also apparent. One is that the more powerful grease cutting solvents (pine oil, D-limonene, etc.) tend not to be used in glass cleaners because of their lower volatility and oily character. Volatility is an important consideration in glass cleaners. The solvents that are used in glass cleaners, especially the low carbon number alcohols, may not be the best grease cutting solvents, but they give very quick drying of the cleaner. Also, given the ultralow concentration of surfactant, it would be very difficult to solubilize more nonpolar solvents. Ethanol or isopropanol used in glass cleaners are water miscible as well as being very volatile which makes them ideal glass cleaning solvents. However, much of the recent patent art devotes itself to the use of other solvents to improve cleaning without contributing to streaking [230,231]. If the cleaner does not dry quickly, the cleaner film may not be evenly rubbed out by the user, resulting in streaking. The streaks will not be apparent until the cleaner completely dries, and so it is desirable that this happen while the consumer is engaged in the cleaning task, not later.

The other difference noticeable from comparison of the tables is the use of different groups of surfactants: amphoterics [232–235] and amido nonionics, although the use of the more mundane anionics is more common. There seems to be advantages to these types of surfactants for less streaking, which is of special concern in glass cleaning. In the first example cited, it is claimed that because of the way the formula is constructed, it does not lose its performance (cleaning and lack of streaking) when perfume is added. It should be commented that perfume can be a source of streaking/residue problems in glass cleaners, and in most glass cleaners the perfume is kept to a minimum.

A signal in hard surface cleaning that is often highlighted in commercials (especially those for glass cleaners) is the "squeak." Greasy or dirty surfaces will not squeak when the surface is rubbed due to the lubrication of the surface; consumers assume that a surface that squeaks is very clean. In one patent, it is claimed that the surfactant and buffer can be chosen to foster this effect in the cleaned surface [236,237].

The ultralow amount of surfactant and the weak degreasing character of the solvents used generally results in significantly less cleaning power than in the other spray all-purpose cleaners. Of course, most of the soil levels encountered in glass cleaning are low, so this does not usually constitute a problem. However, another ingredient can help the cleaning. Many glass cleaners are also alkaline, to aid in cleaning the most common window soil — greasy fingerprints. The alkalinity is usually produced by “fugitive” compounds such as ammonia, which minimizes residue, obviously an important consideration in glass cleaning. However, the formula sometimes needs better buffering than ammonia can provide so the use of alkanolamines and carbamates is also well established. The key is to avoid crystalline compounds (traditional builders) to avoid noticeable residue on the transparent glass surface. The only acid glass cleaners are those that contain acetic acid. These depend on the reputation for good window cleaning developed by the home remedy of vinegar and newspaper for cleaning windows. (This is still a widely popular way to clean glass, although there is speculation as to whether or not the modern vegetable-based newsprint inks are more or less effective than the old petroleum-based inks.)

Streaking is caused by the drying of the residual product on glass in droplets larger than 0.25 μm, which can scatter visible light [238]. Only if there is no residue, or the residue breaks up into droplets smaller than this size, can streaking be avoided. Lubricity is also a factor in window cleaning. Unlike other cleaners, window cleaners are formulated to evaporate quite rapidly. This can cause some difficulty in wiping the cleaner in its final stages. Ammonia salts of surfactants and builders tend to be favored in window cleaners. Not only is ammonia a volatile compound that can conveniently be used to adjust the pH, it also seems that these ammonia salts increase the lubricity of the formula during wiping [239,240].

These cleaners are also trying to deliver added benefits. They usually fall in the category of antifogging, of which there is voluminous patent art [241,242]. Antifogging consists in preventing the formation of water droplets that scatter visible light and result in the “fog” on the glass. There are two mutually opposite approaches: either to make the surface so hydrophobic that all the water is repelled and drains off the surface or to make the surface very hydrophilic so that the water wets the surfaces very well in a continuous film and avoids the formation of droplets. There are examples of both approaches in the patent literature. Some of these claim that in addition to the antifogging effects, usually achieved through the deposition of a polymer film, there are also antisoiling benefits. Antisoiling benefits alone can be achieved with silanes [243] which can react with siliceous surfaces. Another patent claims the use of polyglycols as both adjuncts to the surfactant system as well as giving the antifogging/ antisoiling benefits [244,245] or amine oxide polymers [246]. Antifogging can also evidently be achieved by synergistic mixtures of surfactants [247]. Another benefit that is claimed is the uniform draining of water from the glass surface [248] which tends to decrease water spotting. This was also achieved with a film using polyvinyl alcohol and/or cationic polymers. There is also an example using polycarboxylate polymer to impart a lasting sheeting action to glass [249]. This is a major benefit when the cleaner is also intended to be used on automobile windshields or to clean outside windows.

Another glass cleaning variation that was launched as a product is a no-drip application. Glass cleaners, of their nature, have the viscosity and flow properties of water. This gives them a tendency to drip if the spray is concentrated in one area. Glass surfaces are most often vertical, and so thickening the cleaner to give it more cling might be attractive to some consumers. Most of the formulations use polymers to thicken the glass cleaner [250,251]. The problem cited in these patents is that the presence of thickening polymers usually makes the cleaner harder to rub out, which could cause streaks, undesirable in glass cleaning.

These cleaners, in common with the all-purpose sprays, are also delivered in trigger spray packages. They were at one time packaged as aerosol sprays, but protest against aerosol packaging has largely eliminated them. The major recent change in window cleaners has been the development of wipe products, which is discussed in its own section.

D. Glass and Surface Cleaners

Another relatively recent development in the marketplace is the introduction of glass and surface cleaners. These are cleaners that are presented as being able to clean greasy soil, and yet leave no residue. This gives the advantage to the consumer of having to only buy one product to do both the jobs of glass cleaner and all-purpose cleaner. In practice, they cut grease less than all-purpose cleaners and streak more than window cleaners. However, they also streak less than the all-purpose sprays and cut grease better than do window cleaners. In general their formulations are between the all-purpose cleaners and window cleaners. They share with the window cleaners high solvent levels and minimal builder concentrations. However, they also have surfactant levels closer to those of the all-purpose cleaners. There are some advantages claimed for betaines in the literature of these cleaners [252–254]. These inventions are usually synergistic mixtures of betaines and other surfactants that are claimed to give good grease cleaning while minimizing streaking or residue. Modified sulfobetaines have also been claimed in glass/general cleaning formulations [255] where it is pointed out that the solvent/buffering system of the product also has a role with the surfactant in keeping filming and streaking to a minimum. More exotic surfactants have also been used, for the benefits of good cleaning with less streaking, such as amido-substituted soaps [256]. Like the glass cleaners, glass and surface cleaners also may contain polymeric ingredients to decrease streaking [257]. They are also delivered in bottles equipped with trigger sprayers. These have also been recently formulated as wipe products as with glass cleaners and all-purpose cleaners. These are discussed in their own section.

E. Test Methods

1. Cleaning Methods

The test methods for these spray cleaners are similar to those described for dilutable all-purpose cleaners. Grease cleaning is tested the same way with surfaces.

Amounts of soil are sometimes adjusted to lower levels, especially for glass or glass and surface cleaners. Another adjustment that can be made is that the product may be sprayed directly on the soiled test surface rather than applied to the sponge. The cleaning tests may also use paper towels or mohair cloth (to stand in for cleaning cloths) instead of sponges, depending on the local consumer habit.

For window or glass and surface cleaners, the test substrate is often glass. This allows not only for testing soil removal on the surface of interest, but then the same surface may be evaluated for residue [258]. The soil tested may also be changed for glass cleaners. In this case, the main task is not cooking grease, but the grease of fingerprints. Therefore, the soil is changed from animal/vegetable fat to synthetic sebum [259], sometimes mixed with dust [260]. For glass and surface cleaners, either soil may be used because it is used for both glass and general-purpose cleaning.

2. Streak/Residue Testing

The major difference in this area, especially for any cleaner promoted for use on glass, is the emphasis on residue/streak testing. The most challenging surface is that of glass mirrors because of their reflectivity. Streaking or residue is readily apparent. A given amount of cleaner is wiped on the surface in a specified number of strokes, sometimes as few as one. If more than one stroke is used, all the strokes are done in the same direction — no perpendicular or circular wiping is done. The usual applicator is a soft, lintless cloth or paper towel [261]. The area is left to dry. A panel of observers rates the prepared surfaces, taking care to view the surface from several angles. Streaks or residue are not always apparent from a single lighting condition, and the surface should be tipped several ways for proper observation. Many of the methods outlined in the patent literature also specify the humidity under which the evaluation takes place as this and the room temperature are said to influence the evaluation. Alternatively, streaking can also be evaluated using the product on black ceramic tiles and using a glossmeter to measure the residue on the surface [262].

3. Other Testing

Foam level becomes a question of the interaction of the formulation with the spray trigger. The inherent foaming character of the formulation can be tested by the methods used for other household cleaners. However, this foam profile may be changed by the trigger used. The degree of foaming should also be evaluated by spraying the product out of the trigger.

There are other characteristics that are also due entirely to being a sprayed product. Although some of these attributes are part of the testing of the actual packaging itself, they should also be done with the formulation. It is desirable to test the area covered by a single spray, and the volume of product delivered.

One could also measure the amount of time it takes the product to run down the surface or its cling.

Surface safety is evaluated in the same manner as for the dilutable cleaners, by letting the product sit on a surface for a predetermined amount of time. Safety profiles for spray cleaners can be quite different from dilutable cleaners due to the different proportions of solvent/surfactant generally used.

The antifogging qualities of glass or glass and surface cleaners can be tested by exposing them to steam and noting whether a fog forms on the surface.

Some of the usual product testing becomes even more important with these dilute spray cleaners. For instance, higher concentrations of solvents could change the flammability of the product, and therefore the shipping of the product. The abundance of water and the low concentration of surfactant might make the product more susceptible to microbial degradation and therefore adequacy of preservation is more important.

F. Household Cleaning Wipes

The biggest change around the turn of the millennium in household cleaners (largely in the developed markets of Europe and North America) was the rise of wipes as a product form. These take the theme of convenience even further, presenting the cleaner at its use concentration (like spray cleaners) but already impregnated in the cleaning implement. Wipes constitute yet another delivery system for liquid cleaners.

The major uses for nonwovens traditionally are areas where a significantly less expensive fabric is needed, such as linings for footwear, linings on upholstered furniture, and barrier layers in road building. They have also been very useful in the filtration industry and in surgical drapes/apparel where disposability is important. Nonwovens in consumer products have a longer history of use in personal care products. Baby wipes have been a significant consumer product in developed markets for over two decades. (Nonwovens also figure prominently in the fabrication of feminine hygiene and incontinence products.) More recently, the innovation in personal care use of nonwovens has been as facial cleanser wipes.

By contrast the use of nonwovens in household cleaning products is much more recent (compared to baby wipes) although there were a few introductions of this product form as long as 15 years ago [263]. The literature gives examples of formulation going back 20 years [264]. These product entries, as glass cleaning wipes, silver polishing cloths, and toilet wipes were largely unsuccessful at the time. However, wipes as a household cleaning form have experienced unprecedented growth and success recently, particularly in Europe. As the field of wipes is relatively new, a short discussion of the nonwoven substrate is given here. As might be expected, dry wipes, used predominately for dusting, are not discussed here as they lack a significant liquid cleaning component in use, although they might have been treated with surfactants, polymers, etc., during manufacture.

1. Nonwoven Substrates

A nonwoven is exactly what the name implies: a fabric or substrate made by bonding or interlocking fibers (by mechanical, chemical, or solvent means, or combinations of these [265]) rather than by weaving them. Additionally it is usually made from individual cut fibers or continuous filaments rather than from a continuous yarn [266]. Depending on one's definitions, nonwovens could be considered ancient as both paper and felt can be considered nonwovens. (For more complete coverage of the topic of nonwovens and their uses, the reader is referred to the publications of INDA, the association of the nonwovens industry [267].) There is extensive art and science in the construction of nonwoven materials that will not be discussed here. Key considerations in the design of a nonwoven are the length, denier (diameter), surface roughness, and cross-section of fibers, and their chemical composition. Suffice to say that the common synthetics used in nonwovens, polyethylene terepthalate and polypropylene, are well known to household cleaner formulators as packaging materials. (Polyethylene is usually not used because of its comparative brittleness.) The challenge can begin when the wipes contain a certain level of cellulose fibers, which are often added for either absorbency or biodegradability. The chemical interactions between the cleaner formulation and cellulose can be significant especially as the cleaner (being largely water) will be absorbed into the cellulose fibers.

Nonwovens, due to their high surface area, cellulose content, and some of the manufacturing processes (such as hydroentangling), can carry a bio-burden that could tax the preservative in the cleaning solution of the ensuing wipe product. If the product needs to be preserved, attention should be paid to the nonwoven substrate as well as the solution.

2. Cleaning Solution

The substrate is one half of the "formulation" of a wiping product. The other half is the cleaning solution on the nonwoven. In general these are very dilute systems, but some can contain large amounts of solvents. Wipes are usually fully saturated with the cleaning solution, and the packaging usually tries to maintain this. The coating level is usually of the order of 150 to 500% of the weight of the nonwoven substrate being coated, depending on its absorbency. Therefore wipes are usually packaged in plastic tubs, canisters, or laminated film flow wrap to maintain the high level of liquid on the wipe.

As the cleaning solutions are largely water it is reasonably easy to impregnate the nonwoven substrate with the solution. This can be done in two different ways. In the first method, the nonwoven is unreeled from numerous rolls, each separate length of substrate being wetted with the solution. The separate lengths are brought together, one on top of the other in the number needed for final product. This continuous stream of stacked, wetted substrates is then cut to the length desired to yield the individual stacks to be inserted into packages. In the other method, the nonwoven is unreeled, and collated as dry fabric. Then, either before or after it is cut into individual stacks it is soaked with the cleaning solution. This can happen on the manufacturing line or in the package.

3. All-Purpose and Glass Cleaning Wipes

Table 13.9 gives typical ingredients for the cleaning solution of wipes in general. These are supplied at use dilution, and this concentration is similar to that supplied

TABLE 13.9 Generalized Formula for Impregnating a Wipe

Ingredient	Examples	Amount for APC, glass, disinfecting wipes (wt%)	Amount for floor cleaner wipes (wt%)
Anionic surfactant	Alkyl sulfate, alkylbenzene sulfonate, ethoxylated alkyl sulfate, soap	0–10	0–0.3
Nonionic surfactant	APG, ethoxylated alcohol, amine oxide	0–14	0–0.07
Amphoteric surfactant	Betaine, sultaine	0–10	0–0.01
pH adjuster	Citric acid, triethanolamine, morpholine, ammonia, sodium hydroxide	0–2	QS
Hard water chelator	EDTA	0	0–0.4
Solvent	Ethanol, isopropanol, limonene, glycol ether	0–30	0–4
Disinfectant	Quat, biguanides, organic acid	0–5	0–0.03
Biocide (quat) release agent	Potassium citrate, magnesium sulfate, ammonium chloride	0–5 (disinfecting)	0
Suds control	Soap, silicone	0–0.1	0–0.5
Specialty polymers	Polyacrylic acid, polyethylene glycol	0–2	0–0.04
Perfume, color, etc.		0.001–0.5	0.001–0.5
Distilled or deionized water		QS	QS

in a spray bottle product [268–271]. The typical array of surfactants and solvents is used in these types of products as in their bottled predecessors. (The trend noted before continues here: the innovation is not so much in chemical formulation as in the delivery/packaging of the product.) Much of the patent literature is concerned with streak-free cleaning. In general, wipes are not used for heavy-duty cleaning but more for routine cleaning or touch ups where either the soil level is low or the soil is easily moved (like dust). It is assumed in the use of wipes that the surface will not have to be rinsed (as with dilutable cleaners) nor will it be wiped to dryness with a separate implement (as with spray cleaners used with sponges/paper towels). Therefore the expectation on the wipe to do streak-free cleaning that dries quickly is high. Volatile solvents are an easy way to do effective cleaning with no residue, but they contribute significantly to the odor of the product and can be limited by VOC considerations. Therefore, some inventions are concerned with lower levels of solvent [272].

The all-purpose wipe products cover the gamut of general household cleaning, being positioned as all-purpose cleaner, glass and surface cleaner, and glass cleaner despite little change in the formulations. The biggest change tends to be that the glass cleaners contain significantly higher solvent concentrations and lower surfactant levels, as in the bottled products. There is a distinct advantage with these types of products, since the formulator supplies the implement, to give the consumer better residue profile because the implement can be essentially lintless. Therefore, wipes are often aimed at shiny surfaces, glass being the ultimate example of the shiny surface [273–275].

One recent entry in the wipes category leverages the packaging of the wipe to contribute to its efficacy. A wipe is impregnated with a typical dilute cleaning solution, but it is individually packed in a thin flow wrap bag. In use, the single packaged wipe is put into a microwave oven and heated according to the directions. The vaporizing solution inflates the bag and eventually pops it, releasing the hot water and solvent vapors into the microwave. This is intended to soften and loosen any baked on soils in the microwave. The user can then take the heated wipe and clean the microwave surfaces. The idea of microwave-heated cleaners does appear in the patent literature [276].

4. Floor Cleaning Systems

The area in which these types of nonwoven products have made the biggest impact is, surprisingly, floor cleaning. The main advantage to these systems is that they represent essentially “bucketless” floor cleaning, which started almost 10 years ago in the literature [277]. There are two different styles of product: wet and dry wipes. Both are used in conjunction with a “mop:” a resilient slightly spongy pad on the end of a long handle that supplies reach for floor cleaning.

In the wet system, wipes are supplied saturated with the cleaning solution. The wet wipe is secured to the bottom of the pad to clean the floor [278,279].

In the “dry” system, dry nonwoven pads are supplied separately from the cleaning solution, which is bottled. The dry nonwoven is attached to the bottom of the pad on the mop, and the cleaning solution is fixed in some way to the mop, either in a holder for the bottle or in a reservoir. In the cleaning process, the consumer sprays the cleaning solution by activating a device on the mop and then wipes the mop over the wetted area [280]. In either case, the consumer uses the wipe until no more soil can be picked up from the floor.

This type of system has undoubtedly been one of the largest changes in consumer cleaning habit and practice in the last ten years. First, the system makes floor cleaning immediately available, cutting out the setup phase of getting out a bucket, cleaner, and mop and then making a solution. Second, it also eliminates the cleanup of the mop and bucket. Third, because minimal solution is used on the floor and the wipe is highly absorbent, the claim is that the cleaned floor does not need rinsing, so that time consuming and laborious step also is eliminated. For many consumers this has completely changed the way they clean floors.

The formulations of both the liquid impregnated on the wipes and the liquid supplied in a bottle are similar. They are more similar to glass cleaning formulas in their surfactant concentrations, although they tend to have lower solvent content than do glass cleaners. They are likely to contain suds suppressors (such as silicones) because excess foam would leave the impression that the surface needed to be rinsed.

True to their use as floor cleaners, similar trends are seen in the formulation of floor cleaning wipes. There are wipes where soap is the main cleaning surfactant [281], and ones where there are formula ingredients to entrain the particulate soils [282].

5. Disinfectant Wipes

Another popular class of wipes is one used simultaneously to both clean and disinfect surfaces. The advantage is that the solution in the wipe is applied to the surface without rinsing or wiping to dryness. The disinfectant solution is therefore applied at its proper strength directly to the surface and left there. A variety of antibacterial agents and solvents are used [283–285], especially the typical quats used in other household disinfectant cleaners. They are used to both spot clean and disinfect small household areas such as countertops and tables. These also make spot disinfection very convenient, available instantly as the wipe is pulled from its container. Again, a disposable implement is supplied with the cleaner, which means that the “germy” soil that has been cleaned up can be thrown away on the implement. This is not much of an advantage for a consumer that uses paper towels, but for those that use sponges or woven cloths that would have to be cleaned after use the wipes are a significant increase in convenience.

The same features that make a wipe a good delivery system for disinfection would also make it appropriate for delivering other treatments for surfaces such as decreasing soiling or decreasing dust deposition [286]. The advantage once again is that the treatment is applied to the surface at its intended concentration and is left to dry without wiping to dryness. This antisoiling benefit is now present in toilet wipes that have been commercialized.

6. Test Methods

Wipe cleaners can be tested in one of two ways: either just the cleaning solution can be tested (using the methods outlined above for spray or dilutable cleaners) or the final wipe itself with cleaning solution on the nonwoven substrate can be tested. The testing of the wipe for cleaning performance would have to be, because of the form, abrader testing. In this case, however, there would be no question of how to apply the cleaner, or how much, if wet wipes are used.

In a similar way, the wipe can be used on a glossy surface (such as black ceramic tiles) or on a mirror surface to test for streaking. The testing would be done in the manner previously outlined.

G. Bleach Spray Cleaners

Bleach spray cleaners for general household use have emerged with the bleach containing all-purpose dilutable cleaners. These constitute a yet even more specialized niche than the glass or glass/surface cleaners due to the sensitivity of many household surfaces to bleach. The majority of such sprays on the market are hypochlorite bleach based and are close or identical in formula to the dilutable bleach all-purpose cleaners. That is, they contain about 1 to 2% hypochlorite bleach, a low level of bleach-compatible surfactant (usually amine oxide), an alkalinity agent like sodium hydroxide, and possibly some builder salt such as phosphate or silicate. These cleaners combine a medium level of grease cleaning with the obvious stain-removing properties of the bleach. The trigger sprayer used with the product can deliver either the usual aerosol or, more usually, a loose foam. Bearing in mind that the ingredients have to be hypochlorite stable, the formulations would have most in common with those in Table 13.7.

The other group, of recent entry, is the "oxygen" spray cleaners, as noted in the dilutable cleaner section. These are very similar in formulation to glass and surface spray cleaners, but with the addition of a quantity of a peroxide-producing species ($<7\%$) and a lower pH to stabilize the peroxide [287]. (The surfactant used, of course, has to be oxygen bleach stable.) The cleaning solutions are actually colorless themselves probably owing to the difficulty of stabilizing a low level of dye in a bleach-containing solution, and the impossibility of suspending a pigment in such low-viscosity formula. However, they are sold in colored bottles to give consumers the familiar look of a colored cleaning solution. The performance capabilities of the formulas should be similar to those of the all-purpose cleaners with the addition of destaining ability owing to the peroxide. Although they do not have the stain removal potential of the hypochlorite formulas, they do have significantly greater surface safety and so are better for general household cleaning. As noted above, these products are formulated at low pH in order to stabilize the peroxide as the more traditional bleach cleaners are formulated at high pH in order to stabilize the hypochlorite.

These cleaners are tested in a similar manner to other spray all-purpose cleaners with the addition of tests for destaining ability.

IV. BATHROOM CLEANERS

Bathroom cleaners, along with bleach cleaners, are the largest category of specialty liquid cleaners. These products are formulated and packaged with the specific soil and cleaning problems associated with modern bathrooms. All-purpose cleaners are also used to clean bathroom surfaces, but they are not targeted at soils such as soap scum and so suffer some deficiency when compared with the specialty products. As already mentioned, this specialization is a two-edged sword. Although these cleaners are very efficient on targeted soils, the ingredients to accomplish this often limit their use in other circumstances. Most often, as will be seen, the concern is with surface safety. Also, there are psychological barriers. There is no reason why an acid toilet bowl cleaner could not be used to clean hard water stains from a kitchen sink, but very few consumers would be willing to do this.

Three categories of bathroom cleaner are discussed here: general bathroom cleaners, mildew removers (with some cross-over to bleach cleaners), and toilet bowl cleaners. "Automatic" toilet bowl cleaners are not discussed due to the dominance of solid, and not liquid, forms in this group.

A. General Bathroom Cleaners

There seems to be a worldwide consensus that the main problem in bathroom cleaning is soap scum, followed by the related problem of hard water deposits [288]. All-purpose cleaners have some effect on soap scum, but tend to have difficulty with hard water spots. General bathroom cleaners tend to target these problems and tailor their chemistry accordingly. These types of cleaners are usually moderately alkaline or strongly acidic. Some make disinfectant claims and others do not. Although bathroom cleaners are commonly packaged similarly to dilutable all-purpose cleaners in squared or handled bottles, in North America (and increasingly in Europe) this particular subset of specialty cleaners is dominated by trigger spray packaging.

Bathroom cleaners are the predominant area where soil prevention treatments are important. There are very few kitchen or general-purpose cleaners that make claims to make general household surfaces easier to clean, although there is patent literature to that effect. However, this is a growing and increasingly important benefit in bathroom cleaning. Are bathroom surfaces that much harder to clean than kitchen surfaces? Are bathroom soils more difficult? Are consumers more accepting of surface treatments in the bathroom than in other rooms of the house? Whatever the answers are, there seems to be a perception that bathroom cleaning is difficult and laborious, and any tool that can decrease this factor is welcome.

It should be noted that bathroom cleaners, while predominately trigger spray cleaners in the U.S., and either trigger sprays or in pour out bottles in Europe, still appear as aerosol sprays in some parts of the U.S. These generally use the typical aerosol propellants [289] appropriate to the types of cleaner (alkaline, acid, or neutral).

1. Alkaline Bathroom Cleaners

Alkaline bathroom cleaners are direct descendants of the all-purpose cleaners. They tend to have somewhat higher builder levels than modern all-purpose cleaners, presumably to try to chelate some of the hard water ions that contribute so significantly to tough bathroom soils. One example attributes the cleaning to the form of EDTA used in the cleaner [290,291]. Many of these types of cleaners also have disinfectant claims. Bleach bathroom cleaners fit this general description, but due to their destaining ability they are discussed in a later section. This category includes general bathroom cleaners that use alkyl dimethylbenzylammonium chlorides as their disinfecting agent. Use of this quat to achieve disinfectant places the constraint of nonanionic surfactants on the formulation. Generally nonionic surfactants are used. One cleaner formulation claims the use of polymers to retain the disinfectant on the surface and so prolong the action [292]. These cleaners, like their disinfectant and nondisinfectant all-purpose cleaning forerunners, have moderate soap scum removal abilities and poor water stain cleaning. Still, there are claims in the literature for effective soap scum cleaning with alkaline systems [293]; in a thickened system such as this, the added cling time on the vertical surface would be an advantage. However, they do find application in areas where many surfaces are acid sensitive [294], such as countries where many bathroom surfaces are marble. Still, the most activity in bathroom cleaners has been in acidic bathroom cleaners [295].

2. Bathroom Shower Treatments

An exception will be made here to discuss a product that is largely a surface treatment rather than a cleaner *per se* as it illuminates the surface protection trend evident in bathroom cleaning. These were first introduced in the mid-1990s.

Shower treatment products are liquids intended to be used immediately after showering to *prevent* soils from occurring and “setting” on the shower surfaces. Therefore these products are intended to be used while the surfaces are still wet from showering. Before they are used the first time, the consumer is often directed to first clean the surface, and then apply the shower rinse. Although the patent art for these products says that the product can also be used to clean the shower surfaces, this shows that they do not have the power to clean a significantly soiled surface, and are intended more as daily applications to work as preventatives.

The formulations are clear, essentially colorless, water-thin liquids supplied in trigger spray bottles. The formulas are reasonably similar, being based on chelation, soil softening, and water film formation on the surface [296,297]. The mechanism seems to be to chelate the hard water ions in the water left on the surfaces to prevent soap scum formation. The surfactant used is specified to be nonionic (both of the typical ethoxylated alcohols and of the sugar-based surfactants [298,299]) so that it can interact (in a solubilizing not precipitating way) with both anionic and cationic surfactant residues. Also, the small amount of surfactant and/or solvent helps to make whatever water is left on surfaces spread and wet the surfaces, thereby forming a film that conducts the potentially soiling components down the wall and then to the drain as well as preventing water droplets. Water droplets result in more concentrated areas of residue after they dry where a uniform film of water will leave behind a thinner, more uniform, and less noticeable coating, even if the soiling components were not moved to the drain. The surface can therefore appear cleaner when in fact the same amount of residue can be present on the surface. (This is similar to the approach used in automatic dishwasher products to prevent water spotting.)

An interesting specification in the original patent art is the use of distilled or deionized water, where the water makes up over 90% of the formulation. In practice the hardness of formulation water must usually be controlled, but that would be much more critical in a product of this type since the main aim is to rinse hard water residues off the shower surface. Table 13.10 gives some examples of typical ingredients and ranges.

The formula is also usually formulated to be slightly acid/neutral (pH 6 to 7). Depending on the acidity of the other ingredients added (such as the chelant) the agents used to adjust the pH are volatile (fugitive) compounds and, unlike

TABLE 13.10 Shower Treatments

Ingredient	Examples	Amount (wt%)
Nonionic surfactant	Ethoxylated alcohol, APG, amine oxide	0.5–3
Additional surfactant	Betaine, alkyl sulfate, octyl pyrrolidone	0–10
pH adjuster	Ammonium hydroxide, morpholine, citric acid	QS
Hard water chelator	EDTA, NTA	0.1–3
Solvent	Lower carbon number alcohols, glycol ether (Carbitol®, Dowanol®, etc.)	1–8
Disinfectant	Quaternary ammonium	0–0.5
Perfume, color, etc.		0.0005–0.001
Distilled or deionized water		QS

sodium hydroxide, would not tend to contribute to residues on the surface. In some ways these formulations owe as much to glass cleaner as to bathroom cleaner formulations.

Another interesting aspect is that shower enclosures are usually either ceramic (grouted tiles) or plastic (methacrylate, or Plexiglas®). One patent emphasizes the choice of surfactant and its effect on plastic. Nonionic surfactants have been said to cause "crazing" in plastic surfaces [300], and one shower rinse formulation claims the use of amphoteric surfactants for superior soil removal and greater safety to plastic surfaces [301].

3. Acidic Bathroom Cleaners

Acidic bathroom cleaners have some distinct advantages on common bathroom soils. First, the main matrix for the soil referred to as soap scum is soap that has been precipitated by water hardness ions. Imbedded in this matrix may be skin flakes, lint, dirt, etc. (see Figure 13.7), but the waxy precipitated soap serves to hold the mass together and make it adhere to surfaces. Acids can work to reverse this chemical reaction, turning some part of the soap fatty acids into liquid components (notably oleic acid). This serves to soften the soil overall and thereby make it more easily removed. Second, if there were any ion bridging of the soil to a receptive

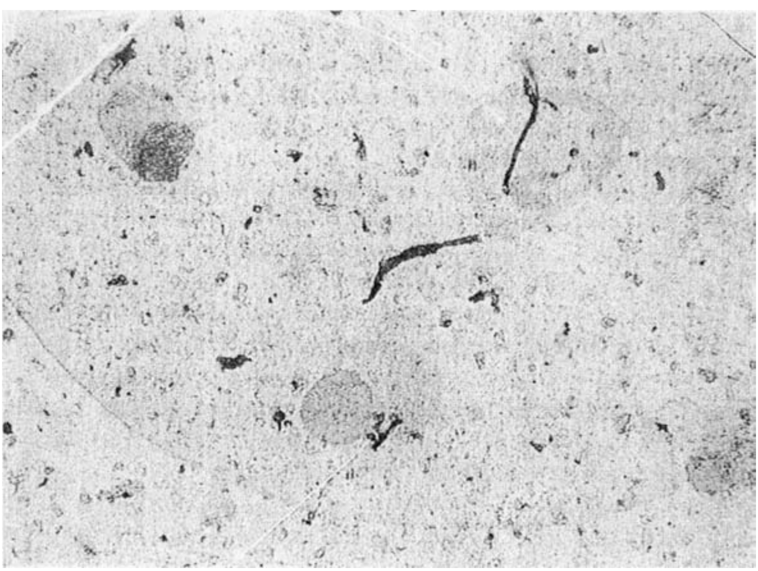


FIG. 13.7 Photomicrograph of home-generated soap scum. Visible are water spots (large circles), skin flakes (dark speckling), and fabric fibers within the soap scum matrix (magnification ×50).

surface (ceramic), similar to the bridging effects found in ore flotation, then strong acid could be used to disrupt this bonding, freeing the soil from the surface. Acid is also effective at dissolving hard water spots, stains, and encrustations, these being mostly $CaCO_3$, $MgCO_3$, and similar salts.

There are also some minor advantages to acid cleaners. Although an acid cleaner can sting any open wound, in general moderate acid pH is kinder to skin than alkaline pH. Acids are generally more effective at removing rust or copper stains than alkaline products. The most effective of these acids, such as oxalic acid, have chelating effects that also aid in the cleaning action similar to EDTA salts at high pH. Disinfectant quaternary ammonium surfactants are also compatible with acids, although the same restriction as to choice of cleaning surfactant holds at low pH as well as at high [302]. It was long thought that the most effective pH for quaternary disinfectant action was high pH, hence its common use in alkaline bathroom and all-purpose cleaners. However, disinfection has been documented at a variety of pH values depending on the organism and the formula [303].

More examples arise that give the acid as the disinfecting agent itself, therefore getting double duty out of the acid: low pH for soap scum and hard water stain cleaning, and disinfection [304].

However, acid also has one main disadvantage: many bathroom surfaces may be acid sensitive. Certainly marble fixtures top the list; the beautiful shine of a well-polished marble surface is easily destroyed in even one application of an acid cleaner. The cement grout between wall tiles is another sensitive surface. The modern addition of latex to the grout mixture helps resist acid attack, but cannot stop it completely. In Europe many ceramic tiles and enamel surfaces are also acid sensitive, prone to accelerated wear if an acid cleaner is used. As seen in the examples cited below, the use of more moderate pH (in the range 2.5 to 5) will slow the damage, but it will not stop it completely.

There is also a minor disadvantage to acids if used in trigger spray products. In these cases, the respirable mist produced by the sprayer may irritate the nose and throat of the consumer. This can be mediated to some extent by the delivery of the product, discussed below.

The beginnings of this field are, predictably, centered around the kind of acid used. Very strong mineral acids are generally avoided in favor of better buffering organic acids. Indeed, several patents give claims that the performance of a higher pK_a acid is superior to that of a strong acid at comparable pH levels [305]. A synergy between different acid mixtures [306], or the advantages of a particular acid are usually claimed [307–309]. The patent literature also gives examples where this fundamental weakness of acids, their attack on certain surfaces, is claimed to be circumvented. Usually this includes the use of phosphoric acid or derivatives [310–313]. Some patents claim the use of microemulsions. One recent invention cites the use of an esterase to generate acid under mild pH conditions to enhance cleaning performance [314].

Interestingly, many of these bathroom cleaning formulas were first developed using zwitterionic, amido nonionic, and ethoxylated alkyl sulfates just about the time that such surfactants were becoming popular in spray all-purpose/glass and surface cleaners [315–317]. They also use similar solvents to the all-purpose sprays, leaning heavily on the glycol ethers. Table 13.11 gives a comparison of alkaline and acid general bathroom cleaners. Figure 13.8 shows a general comparison of the soap scum cleaning abilities of the two types of formulas.

TABLE 13.11 Spray Bathroom Cleaner Formulas

Ingredient	Examples	Acid cleaner amount (wt%)	Alkaline cleaner amount (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, alkyl sulfate, ethoxylated alcohol sulfate	0–6	0
Nonionic surfactant	Ethoxylated alcohol, alkanolamide fatty acid, carbamates, amine oxide	0–3	1–5
Amphoteric surfactant	Betaines, sulfobetaines	0–2	0–2
Builder	Carbonates, citrates	0	0–2
Chelator	EDTA	0	0–15
Alkalinity	Sodium hydroxide, alkanolamines, sodium carbonate	0	0.25–5
Acid	Phosphoric, dicarboxylic (like glutaric), citric, sulfamic, acetic	0.5–10	0
Solvent	Lower carbon number alcohols, glycol ether (Carbitol®, Dowanol®, etc.)	0–10	0–10
Disinfectant	Quaternary ammonium surfactants	0.1–3	0.1–3
Bleach (may also disinfect)	Acid: peroxide; alkaline: hypochlorite bleach	0–3	0–3
Polymers for thickening, water sheeting, etc.	Xanthan gum, polyacrylate, polyvinylpyrrolidone	0–0.1	0–0.1
Perfume, color, etc.		0.05–1	0.05–1
Water		QS	QS

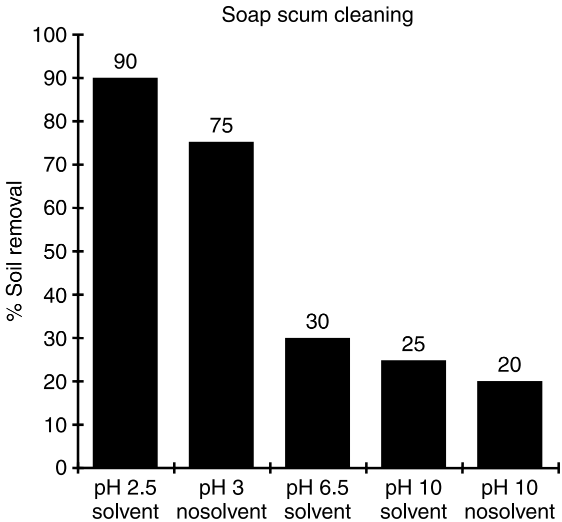


FIG. 13.8 Relative soap scum cleaning; experiments done with formulas at different pH with and without glycol ether solvents.

Both kinds of bathroom cleaner also usually use solvents as part of the formulation. This also helps to soften and loosen the soil, particularly in the case of the alkaline cleaners that do not have the acid conversion of the calcium salts to the acid form. One unusual example in the patent literature uses a silicone surfactant and solvent to lift soap scum; there are essentially no other examples of this type of formulation for this use [318].

One of the other problems of bathroom cleaning is that many of the surfaces with tenacious soil are vertical. There should be an advantage to increasing the residence time of the cleaner on such surfaces. One way to do this is to produce a thick foam with the cleaner by combining the formulation with the right delivery system, usually a trigger spray or aerosol. The cleaner is formulated to stabilize the foam formed [319]. However, the foam cannot be too persistent or it becomes a rinsing problem [320]. Another way to increase the residence time is to thicken the product, usually with surfactants [321–323], although the use of polymers is not unknown [324]. Once again, care must be taken to make sure that the thickened product rinses easily. One very interesting alternative approach gives a thixotropic gel that forms a water-impermeable skin in use, preventing the cleaner from drying out and thereby increasing the time of action on the soil [325].

There are also cleaners that are formulated with polymer thickeners to reduce misting [326]. In this case, the object is to increase the particle size of the droplets formed upon spraying so as to decrease the number of droplets that will continue to float in the air. The longer a particle floats, the more likely that a consumer will breathe it. Considering the aggressive chemistry used in many bathroom cleaners, this can be irritating and unpleasant. Thickening the product increases the resistance of the liquid to moving through the spray head therefore increasing the energy needed to divide the liquid into droplets and so producing fewer, larger droplets. Any cling given to the product on the surface then becomes a side benefit to reducing the irritation. However, thickening can also slow the diffusion of active ingredients to the soil or stain, thus counteracting the effect of increasing residence time. Therefore, the benefits of reduced misting and increased residence must be balanced with ease of rinsing and slowed diffusion. These properties can also be important for bleach sprays, as discussed below.

Added benefits are also arriving in this field paralleling their arrival in all-purpose cleaning. Disinfectancy, the oldest added benefit, is found less in the acidic formulations than in the alkaline ones. However, as previously noted, quaternary ammonium surfactants are active as disinfecting agents at low pH as well as at alkaline pH [327,328]. The newest of added benefits, as in all-purpose cleaning, is the inhibition of soiling [329–331]. One entry into the North American market in the early 1990s claims to waterproof surfaces "to keep dirt from sticking and building up" [332]. This would be a desirable trait in bathroom cleaning: many soils are tenacious, the surface area to be cleaned is large, and the opportunity to resoil intrinsic to the use of the room. This trend was noted above with the introduction and growth of a whole class of shower enclosure treatments. The trend continues with the recent entry of a bathroom cleaner that claims the inclusion of Teflon® to make the surface more resistant to soiling. This combines two trends in one: the antisoiling treatment and the use of a name recognition ingredient. The same brand in the U.S. has also launched a toilet bowl cleaner making similar claims. However, as noted in a *Chemical and Engineering News* article of January 2005, the technology used in this product is not fluoropolymer, despite the use of the Teflon® name which is strongly associated with fluoropolymers. The patent art contains numerous examples using a variety of surface treatments including siloxanes [333], anionic polymers [334], fluorosurfactants [335], and zwitterionics [336] in which the antisoiling effect is presumably the change in the surface due to deposition of active ingredient. There is one example where it is claimed that even an anionic hydrotrope can change the surface energy and prevent soiling [337]. Another claims that the polymer in the formula chelates the hard water ions to prevent subsequent soiling [338]. There is even one example intended to be used at alkaline pH, remarking on the good cleaning achieved, since it is noted that the acid cleaners generally give better cleaning [339]. Some examples use polymers, but only claim better wetting and lack of streaking without claiming antisoiling [340].

B. Mildew Removers

Bleach-free cleaners generally show little effectiveness against the black stains caused by mold/mildew. Bleach cleaners are effective at removing this stain, and usually have the added benefit that they tend to kill the offending organism at the same time. Oxygen bleach products are not apparent in this category, as they often lack the speed and effectiveness of hypochlorite bleach that the consumer is accustomed to using. Mildew removers are actually a subset of the general bleach cleaners described before, although they usually predate the bleach cleaners intended for general household use. The advantages of bleach cleaning specifically in the bathroom are that most of the major surfaces tend to be bleach resistant, the disinfectancy supplied by the bleach is highly desirable, and there is a prevalent, highly colored stain to be removed.

Mildew removers are very closely related to the spray bleach cleaners discussed above. The main distinction between general household bleach cleaners and mildew removers is the concentration of bleach. While in the household cleaners the bleach level rarely exceeds 2% available chlorine, in mildew cleaners the level may reach as high as 3%. This is testament to the tenacity of the melanin stain that molds and mildews are able to produce, particularly in porous substrates like grout. Beyond this difference, the types and amounts of surfactants tend to be similar, as are the choice of alkalinity agent and the presence of any builders.

These cleaners should not only be tested for their stain-removing ability, but also for their soap scum cleaning. Although such alkaline products generally show poor soap scum cleaning compared to the acid bathroom cleaners, many consumers use them for general bathroom/tile cleaning.

One of the main problems with these types of cleaners has been the mist produced by the trigger sprayer. The situation is similar to the irritation described above for general bathroom cleaners. Although this mode of delivery contributes much to the convenience of the product, it also makes the product very unpleasant to use. The respirable particles produced with their high alkalinity and bleach can be very irritating to the consumer. One way to combat this is to thicken the product, and there is literature to show that this can be done with polymers [341] or with surfactants [342–346], or a combination of both [347]. The important aspects to balance are reducing the mist produced by the product while still achieving a consumer-acceptable spray pattern. If the product becomes very thick, the spray pattern often collapses to a narrow stream. For some uses, this kind of pinpoint application may be preferable, but for other consumers, a broader spray pattern is expected.

Newer products are also claiming to not only remove mildew stain or kill mildew, but also to keep it from recurring. Once again, this is another incidence of the trend in household cleaners to give added benefits. Many products are so efficient at removing the mildew stain that a further step to ease the cleaning problem must be taken to differentiate new products. A commercial entry made using this claim also uses a packaging innovation relatively new to household cleaning: a dual bottle with a single trigger sprayer (Figure 13.6b). Evidently the chemistries used in this product are not compatible on storage. One bottle contains the solution used to remove the mildew stain (bleach) and the other contains the ingredients used to keep the mildew from recurring [348]. Both solutions are delivered simultaneously when the single trigger, with dual dip tubes, is pulled. Once again, packaging works with chemistry to give a new product benefit. This approach to bathroom cleaning evidently proved too bulky or not effective enough to justify the cost of this packaging.

Another place where dual packaging also comes into play is the use of peroxide for mold cleaning. Peroxide has a higher oxidation potential than hypochlorite (−1.36 eV for sodium hypochlorite and −1.8 eV for hydrogen peroxide), but paradoxically does not work with the speed of hypochlorite on bathroom mildew. However, peroxide has essentially no odor, in contrast to hypochlorite that has a distinctive and unpleasant odor. Without activation, peroxide bleach would take longer to do the job that hypochlorite does more quickly. One patent, therefore, incorporates an activator into a peroxide mold cleaner, but puts the formulation into a dual-chamber package so as to ease the job of stabilizing the formula on the shelf [349].

Another recent change is a product that claims to penetrate and remove mildew "from the root." It is claimed on the package that foaming action is what allows the product to penetrate.

It is likely that new claims are on the horizon for bleach mold cleaner as a study has found that (hypochlorite) bleach solutions neutralize indoor mold allergens [350]. Hypochlorite bleach would also inactivate many types of protein residues (like those from dust mites) by denaturing the protein. Indoor allergen cleaners were launched and on the market briefly in 1999 to 2000, which were nonbleach formulas (depending instead on benzyl benzoate, an acaricide). These products were recalled and discontinued due to consumer complaints.

The "holy grail" of bathroom cleaning would be to be able to clean effectively soap scum and to remove mildew stains. As stated above, generally the best soap scum/hard water stain cleaning is found at low pH where hypochlorite bleach, the most effective mildew decolorizer, is unstable. Formulators continue to try to combine the two and there is an example of a formulation with bleach for destaining that claims to also give good soap scum removal by ion exchange [351]. There is another example where the acidic and hypochlorite portions of the cleaner are kept in separate parts of a dual-chamber package until dispensed onto the surface [352].

There are not a large number of examples of bathroom surface cleaning wipes, although an example in the patent literature stresses mold and mildew inhibition [353]. This is a natural extension of wipe usage as it is meant to be used without rinsing.

C. Test Methods

1. Soap Scum and Hard Water Cleaning Methods

The test methods for evaluating bathroom cleaners are very similar to those for evaluating all-purpose cleaners, and the ASTM published a soap scum cleaning method first in 1993, revised in 1997 [354]. The Gardener straight line abrader is still used, with sponges or other appropriate utensils for cleaning tests. The substrate usually used for evaluation is a ceramic tile, this surface being generally representative of ceramic, porcelain, and enamel. The same equation is used to measure the percentage soil removed after measurements with either a reflectometer or with a glossmeter. In this case, as in the case of all-purpose cleaning, the main discrepancy among cleaning methods is the choice of soil composition and application. The soil in many methods is applied by being dissolved or dispersed in a solvent, isopropanol, chloroform, etc., and then sprayed on the surface. However, the method in the new ASTM procedure is for the soil to be "painted" on the surface while hot and melted. The soap scum is usually calcium stearate, calcium oleate, or calcium palmitate, or a mixture of all three. It may or may not be mixed with other soil components. The most common is carbon black or charcoal that also colors the soil so that it can be seen on a white tile [355]. The ASTM soil is a very complex mix using synthetic sebum, carbon black, potting soil, and two separate mixtures of stearate. One of the stearate mixtures uses all the common hardness ions found in household water, the usual calcium and magnesium plus the less usual inclusion of iron. Another test uses soil made entirely of calcium stearate, artificial body soil (including sebum), and carbon lamp black [356]. Conversely the pure white calcium fatty acid can be used on glossy black tiles. This last choice has the added advantage that glossy black tiles are often used for residue/shine tests.

Hard water spotting is usually a much easier soil to clean than soap scum or mildew. It is related to soap scum in that it has the same root cause: hard water. Water spots may be produced by applying hard water (150 ppm as $CaCO_3$, either all calcium salts or with a set Ca to Mg ratio) to a glossy tile surface. This should be allowed to air dry. Multiple applications of the hard water may be necessary to build a tenacious, visible soil. The ease of removal of the spots gives the strength of the cleaner. For more difficult hard water problems, such as lime buildup around water faucets, a quick test can be done. If a cleaner can dissolve a piece of chalk, it is a good indication that it can remove these kinds of scale. Therefore one way of estimating the cleaning performance on hard water deposits is to measure the weight loss of cubic marble chips soaked in the cleaner. (In the reverse sense this can also be a test of the cleaner's safety when used on an acid-sensitive bathroom surface.)

Ease of rinsing is another test that can be performed. In one case, this is described as scrubbing a sink with a set amount of product to generate foam. This is then rinsed with moderately hard water, collecting the rinse water under the sink to quantify the amount needed until no foam is visible in the sink [357].

2. Mold and Mildew Cleaning

An important bathroom soil is mold/mildew stain. A distinction has to be made with regard to this soil. Cleaning tests are a measure of the cleaner's ability to remove the melanin stain produced by the organism. This is not necessarily a measure of the cleaner's ability to kill or retard the organism causing the stain. To do that, formal disinfection or mildicide tests have to be performed. The usual place for mold growth is the grout between wall tiles, so it is important that grout, or some other such porous surface, as well as tiles are included as the cleaning surface. A nutrient medium is applied to the test surface and this is inoculated with the organisms of interest (usually *Aspergillus niger*). The culture is incubated for several weeks, and then the surfaces are inspected for mildew growth. Cleaning tests may then be performed, with special attention going to the cleaning on the grout surfaces [358]. Alternatively, cleaners can also be tested for mold inhibition. In this case, the cleaners are applied to the surface before the introduction of the medium and microorganisms. The tiles are allowed to incubate, with periodic checks on the growth (or nongrowth) of the mold.

For claims pertaining to killing mildew, controlling its growth, or general disinfecting action, local government regulations should be consulted. In the U.S. this means following the tests set out by the Environmental Protection Agency (EPA) [359]. The tests usually require production samples of cleaner to be used against test organisms grown according to specified methods. The application of the cleaner and the time of contact are usually also described.

3. Other Tests

Residue/shine, foam, disinfectancy, and surface safety tests are done as described in the section under all-purpose cleaning. Grease cleaning tests may also be performed with bathroom cleaners, as bathroom soils such as lipstick and bath oils have an oily component. The other nonperformance tests (eye irritancy, biodegradability, etc.) are also outlined in the section on all-purpose cleaners.

A test of resoiling tendency should also be done for products claiming this. The simplest approach would be to clean a surface with the formulation and then try to generate the usual bathroom soil on the surface afterwards. This can also be done as a combined cleaning/resoiling test if the test is done as a conventional cleaning test followed by the new application of the soil.

D. Toilet Bowl Cleaners

Toilet bowl cleaners are also a product where great specialization has taken place in the form of the dispenser. The most modern of the toilet bowl packages feature shaped necks that allow the product to be squirted directly under the rim of the toilet (Figure 13.9). This allows users to keep themselves, and their hands, out of the toilet bowl. With more traditional packaging, the user would have to reach down into the toilet in order to squirt the product under the rim and try to maneuver the bottle inside the confines of the bowl space.

Toilet bowl cleaners also include products placed in the toilet tank to be released on flushing into the toilet bowl. Many of these products are solid "pucks" or

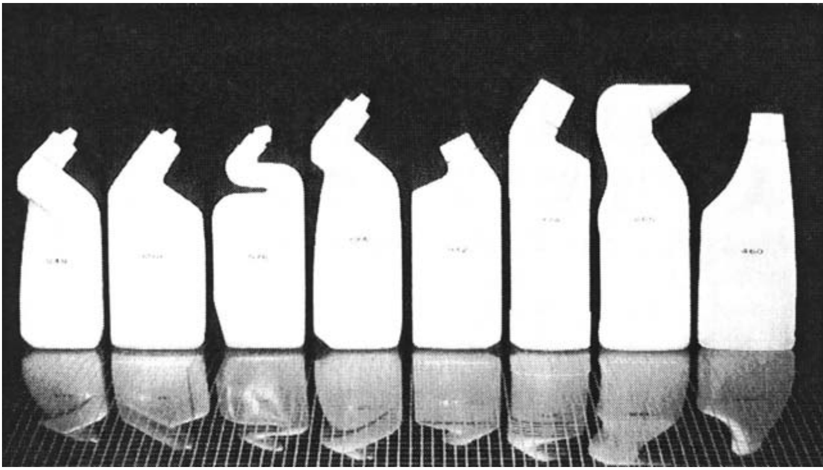


FIG. 13.9 Modern toilet bowl cleaner packaging.

blocks and are beyond the scope of this review. Others are liquid formulas with very elaborate dispensing devices. The device can be built to release the cleaning liquid at the beginning or end of the flushing cycle. If delivered at the end of the flush, it usually is held with the water in the tank, thereby imparting its benefits to the tank as well as the bowl. The cleaning liquids contained in the devices are generally very simple low-viscosity formulas. Their compositions are given in patents mainly devoted to the intricacies of the mechanical devices [360,361]. Typically they contain traditional anionic or nonionic surfactants (0.5 to 10%), perfume (0.01 to 1%), and large amounts of dye (1 to 10%). The concentrations are higher than might be expected because they will be significantly diluted in use, either in the bowl or in the tank. The color of the water is used as a signal to the consumer that the cleaner is present (and is aesthetically pleasing to some) and so the level of coloring agent is much higher than generally found in household cleaners. Sometimes disinfectant quaternary ammonium surfactants (0 to 5%) are used. Often, these kinds of products will also make extended benefit claims (by virtue of their residence in the bowl) for inhibiting bacteria growth [362] or inhibiting stains [363].

Originally, toilet bowl cleaners, like all-purpose cleaners, were powders based largely on sodium bisulfate [364]. They were packaged in dispensers very much like powder abrasive cleansers. In fact, many products that have been mentioned in this review are used to clean the toilet. General bathroom cleaners, liquid and powder abrasive scourers, all-purpose cleaners, and even simple household bleach are used by consumers for this task. Modern cleaners specialized for toilet bowl cleaning, however, have one factor in common that these other formulas generally lack: high viscosity. The viscosity of toilet bowl cleaners is generally between 300 and 1000 cP. Only cream cleansers have higher viscosities. When applied to the rim of the bowl they gradually flow down the sides. The high viscosity also increases the contact time of the cleaner with the surface aiding in soil removal. The consumer does not have to spread the cleaner over the surface and scrubbing should be decreased. Other than this common denominator, toilet bowl cleaners, like general bathroom cleaners, are either acid or alkaline, although there is an unusual example formulated at neutral pH [365].

1. Acidic Toilet Bowl Cleaners

Acidic toilet bowl cleaners are by far the largest group. The greatest cleaning problem, outside of the obvious organic soils, is hard water buildup. Toilets function most of the time as water storage tanks and therefore suffer the same evaporation/scale problem as other tanks. Acids are especially efficacious against this type of problem. The usual array of acids are used in this field (similar to those used in general bathroom cleaners) although lower pH values are targeted. The use of oxalic acid, which is particularly good at removing rust, can be especially beneficial in this type of cleaner [366] if rust stains are a local problem, although other acids can also be recommended [367]. More attention has been given recently to the choice of acid used in these cleaners, citing environmental, or surface safety issues [368,369]. One set of researchers are adding enzymes to their acidic cleaners, to fight biofilm formation [370,371]. (This is one of the few examples of enzymes in household cleaners, only the second cited in this review.) An outline of the formulas used for acidic toilet bowl cleaners is given in Table 13.12.

Newer toilet bowl cleaner formulations are moving to the newer classes of surfactants with the rest of household cleaning [372]. More nonionic surfactants than anionic surfactants are used. These acid formulas are generally self-thickening,

TABLE 13.12 Acid Toilet Bowl Cleaners

Ingredient	Examples	Amount (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, ethoxylated alcohol sulfate	0–3
Nonionic surfactant	Ethoxylated alcohol	2–20
Cationic surfactant	Quaternary ammonium	0–2
pH adjuster	Phosphoric, hydrochloric, oxalic, citric acids	0.5–20
Electrolyte	Nitrate, chloride	0–10
Bleach	Persulfate salts, hydrogen peroxide	0–10
Thickening agents	Polyoxyethylene, cellulose gums	0–1
Abrasive	Calcite, silica	0–15
Perfume, color, etc.		0.01–0.5
Water		QS

using a high concentration of electrolytes combined with the surfactant to produce the high viscosity. It is also important that toilet bowl cleaners give lower foam than do all-purpose cleaners. It is desirable to have all the foam disappear quickly. Nonionic surfactants are preferred over anionics for both these purposes. Thickeners, such as polyacrylates, are sometimes used to supplement the natural viscosity of the surfactant system. As noted at the beginning of this section, cling to the vertical surfaces of the bowl is important and is usually achieved through thickening of the formula, although foaming can foster cling. In one application, the clinging foam is produced through the reaction of acid and base, but the invention is also careful to have the foam collapse as well [373]. This is also one area in which peroxide compounds are widely used. Persulfate salts have long been used in powder toilet bowl cleaners so that bleaching and acidic cleaning were combined in a single formula. Persulfate salts are now also making appearances in liquid formulas. In one formula, it is claimed that the dilution on adding to the toilet bowl helps the cleaning because the pH rises rapidly destabilizing the bleach [374].

Disinfection is also a benefit desired by consumers in toilet bowl cleaning. This can be achieved with quaternary ammonium surfactants, as in bathroom and all-purpose cleaners. Quats are effective bactericides at both low (1 to 4) and high (8 to 12) pH and so are compatible with very acidic toilet bowl cleaners. One of the problems with disinfection is knowing whether the product has been used at the proper dilution, and one toilet bowl cleaner formula gives the signal via a pH-dependent dye [375].

Similar to the technology used to produce cream cleansers, there are also formulas that can produce liquid toilet bowl cleaners with suspended abrasives [376,377]. The main difference between the cream cleansers and this type of product is that the suspending system should be acid stable instead of alkaline and/or bleach stable. Suspended particles are appearing in more and more of the toilet bowl cleaners. This has been commercialized in a gel form, which shows the suspended particles.

As noted in the bathroom cleaning section, antisoiling claims are also coming to toilet bowl cleaning. The commercialized formula is labeled to contain Teflon® (but does not use fluoropolymer as mentioned above), and a patent uses a fluorosurfactant [378].

In a similar vein (although not precisely soil prevention) is a toilet bowl cleaner meant to be used daily and allowed to sit for as long as overnight [379]. In some senses this is similar to the shower rinse products, meant to be used daily to prevent the buildup of soil. The examples in patents are given both as acid and alkaline.

2. Bleach Toilet Bowl Cleaners

The other category of popular toilet bowl cleaners is that containing bleach. The chemistry to produce these formulas is very similar to that for thickened bleach all-purpose cleaners. The most common example uses amine oxide/anionic surfactant combinations to thicken the formula, sometimes supplemented by a polymer [380]. The formula can also be self-thickened, as in the case of acid systems, by the interaction of surfactant and electrolyte [381]. The same surfactants are used in these formulas as with other bleach formulas, and similar alkalinity agents. One formula claims the use of the chelator to help remove the hard water salts that are a problem in toilet bowl cleaning [382]; the high pH necessary to stabilize hypochlorite would be a drawback in the cleaning of hard water scale. The bleach level tends to be in the range 0.5 to 5% available chlorine.

New formulas have appeared in the patent art using oxygen bleaches instead of hypochlorite. These formulas would have the advantage of low pH, and therefore be more useful for the typical toilet bowl problems such as minerals, as well as having bleaching ability that consumers find attractive. One of these formulas uses persulfate salts, long known as powerful oxidizing agents, but difficult to stabilize as liquid systems [383,384]. Another approach is to use peroxyacids, such as peracetic acid, where the bleaching agent and the limescale remover are combined in the same compound, thereby combating the two most common toilet cleaning problems [385].

As mentioned in the section on bathroom cleaning, there has been a recent entry in toilet bowl cleaners that claims the inclusion of Teflon® to prevent soil formation on the cleaned surfaces. This is the first cleaning formulation to claim this, having only been claimed before in the slow-release products (that do minimal cleaning).

3. Toilet Cleaning Wipes

Toilet cleaning wipes, as opposed to the toilet bowl cleaners, seem to be intended more for the toilet surfaces outside of the bowl, as using a thin wipe with a dilute solution would not seem to be the best product for under the water line inside the bowl. In the case of toilet wipes, the substrate can vary from that of the usual, largely synthetic fiber nonwoven used in other household wipes. It is desirable to be able to flush the toilet cleaning wipe, which means it should break up (so as not to clog pipes) and be biodegradable (so as to not damage septic systems). This is often accomplished through the extensive use of cellulosic material [386]. If the point is only to be flushable (and not necessarily biodegradable) then fibers other than cellulose can be used [387]. Most recent entries in this area have claimed that they are flushable, but this is something of a hot topic in the nonwovens industry [388]. This eliminates the toilet-soiled wipe from the bathroom. Another recent wipe, a companion to the liquid in-bowl cleaner and bathroom cleaner, is a wipe that contains Teflon® to make surfaces soilless.

4. Test Methods

Not much has been published on the subject of testing the efficacy of toilet bowl cleaners. References to “toilet soil” are made in some patent literature, but the details of the ingredients of the soil are not made clear. The efficacy testing is done by soil solubilization efficiency, and if bleach is present, soil discoloration. Tests can be made against hard water stains, as described in the bathroom cleaning section. As with other household cleaners, the normal disinfectancy tests for a locality can be used.

One test that has more relevance for toilet bowls, especially in high mineral areas, is a test for iron or manganese staining. Either ferric chloride or manganese(II) solution is spread on a light etched ceramic tile. The toilet cleaners were tested as static soaking tests with no mechanical action [389].

For in-tank automatic cleaners, the most important test is usually lifetime of the product. In the most brute force method, the product is installed in a real toilet. The toilet is then repeatedly flushed to determine how long the product will last, measuring either the persistence of some ingredient such as color or bleach in the bowl water.

V. CONCLUSION AND FUTURE TRENDS

The area of household hard surface cleaning has advanced at a rapid rate in 70 years. From its beginnings in simple soap powders, it has branched out into many types of specialized cleaners (see Figure 13.10). It is at present a dynamic field, full of both formulation and packaging innovation. These advances tend to work in synergism, as in the development of trigger sprayers and spray all-purpose cleaners. The following summarizes some of the highlights and future trends.

(1) In well-developed markets, the drive is to supply the consumer with greater convenience through added benefits such as two-in-one products and the recent boom in wipes. Included in this trend is the combination of bleach with various all-purpose cleaners and cleansers that has now evolved into an interest in peroxygen compounds. Bleach cleaners give the consumer more effective stain removal combined with traditional cleaning (solid soil removal). Although cleaning is always the main requirement, the household surface cleaners of the future will do more: prevent tenacious soil adhesion, reduce fogging, give more shine, prolong disinfection, etc. These kinds of added benefits are just making their appearance in household hard surface cleaning but are gaining more acceptance in the market as shown by the shower treatment sprays.

(2) Giving more benefits is at times at odds with the concomitant trend to give easier cleaning through greater chemical targeting of soils (grease or mildew) or special needs, e.g., streak-free window cleaners. The chemistry needed to target these problems often limits the scope of their use in the household. An example is the inadequacy of window cleaners for overall grease cleaning in the household. Another example is the compromise of bleach cleaners: greater stain removal, but limited to use on bleach-resistant surfaces.

(3) The overall direction is, however, to let the chemistry do more work and relieve consumers of their mechanical contribution to the cleaning process. This is

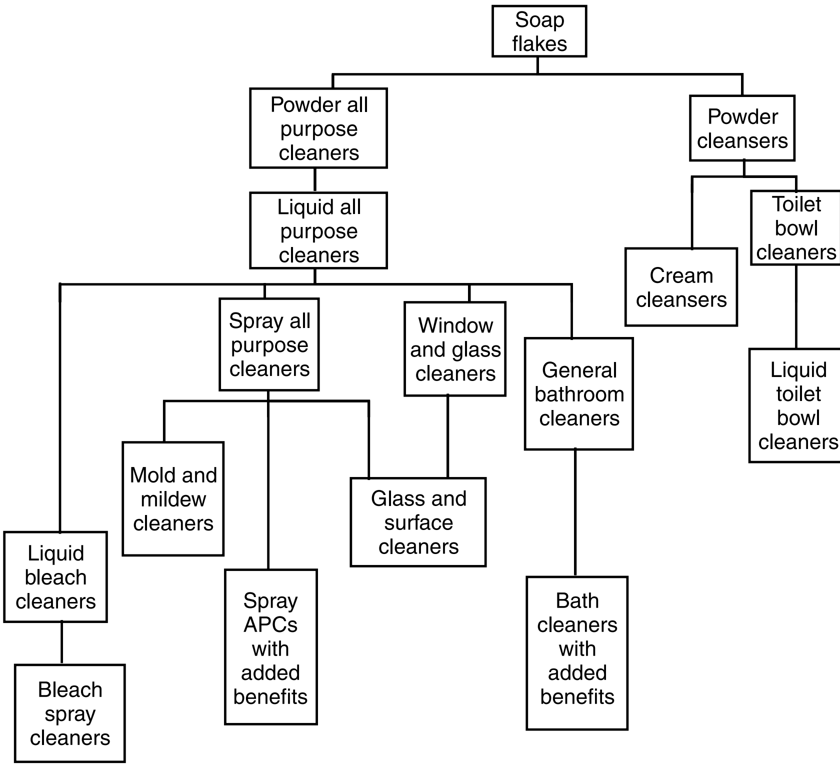


FIG. 13.10 Lineage of specialty household cleaners.

being achieved through continuing invention of chelants and solvents, studies of ingredient synergies, and the increasing use of polymeric ingredients for various added benefits. This is coupled with the invention of new household surfaces that are increasingly more difficult to soil and/or easier to clean. This would account for the decrease in consumers' use of abrasive cleaners. Liquid cleaners are now sufficient for nearly every cleaning job, leaving only special "tough" jobs for cleansers such as very worn surfaces or baked-on soils. Abrasive cleaners will probably never completely disappear but represent an increasingly smaller portion of the market.

(4) For a while dilutable all-purpose cleaners were tending to become more concentrated, giving the consumer use and storage advantages. However, the consumer seems to have rejected these attempts at concentration, perhaps not seeing the value of these formulas through a failure to adapt their use methods to take advantage of them. At the same time there has been a proliferation of very

dilute cleaners that exist as convenience spray products, largely as targeted cleaners mentioned above. This goes to the extreme with the ready-to-use bottled floor cleaners and the liquids in wipes where the concentration of the active ingredients (excluding solvents) is less than 2%.

(5) Powder products for household cleaners are now in the minority of products, and are decreasing every year. The household cleaning category in developed countries is dominated by the ease and convenience of liquid products. It is expected that the same trend will eventually emerge in developing countries.

(6) Packaging continues to evolve in this area in synergy with changing chemistries. Redesigns of toilet bowl cleaner bottles and the invention of the trigger sprayer have already greatly changed the array of products in the hard surface category. New dual-chamber packages offer the most exciting possibilities. Mixtures that have limited shelf life can be stored separately and dispensed simultaneously. These are prime examples of how new containers can augment the convenience, safety, or delivery of a cleaner to its target. In some ways nonwoven substrates used in wipes can be considered as “packages” to deliver the cleaner, continuing the innovation in packaging trends. The importance of packaging innovations to the field of household cleaners cannot be underestimated and seems to continue primarily in the direction of delivering convenience.

(7) Packaging continues to be a more innovative area rather than the actual ingredients in cleaning formulations. To a large extent, the surfactants used 20 years ago are still used, supplemented by the recent addition of betaines and amine oxides. It remains to be seen if surfactants like alpha olefin sulfonates (AOS) will eventually be used in this area in preference to the benzene sulfonates used today. Gemini surfactants, so prevalent in the academic literature, are almost entirely absent from the commercial literature (with the exception of Dowfaxes®). Enzymes are rarely used as ingredients in hard surface cleaners, although they appear extensively in laundry detergents and to some degree in dishwashing products. They tend to appear more often in powder products, thus the higher use in laundry detergents and automatic dishwashing products. Enzymes are relatively expensive and unstable (in liquids) whose real value to the efficacy of a formula must be carefully evaluated. “Natural” ingredients are likely to become more important in formulations, particularly as ingredients flagged on labeling to consumers. As more is learned about them and the production techniques (consistent supply, harvesting, analytical qualification) become more advanced it is anticipated that targeted uses will be developed for these ingredients.

(8) One of the biggest current questions is whether the recent boom in wipe products will continue in the future. Wipe products are very expensive per use compared to even the combination of a spray cleaner combined with a paper towel, never mind the comparison to a dilutable bottled cleaner and a wash cloth (which can be washed and reused). However, products with higher per use price but much improved convenience, such as trigger spray cleaners, have survived

and thrived. As long as consumers are willing to pay the mark-up for convenience at least some of the wipes will survive in household cleaning, as baby wipes have succeeded in personal care.

(9) More cleaners will be targeted in the future at controlling environmental health situations like allergens. This is a natural development of the ever increasing disinfection cleaner trend. It is also extremely topical given the subliminal concern over bio-warfare threats such as the anthrax scare of 2001 to 2002 in the U.S. and the global outbreak of SARS in 2003.

(10) More attention is being paid to the safety of household surface cleaners. There are at least three aspects of safety: less irritating to the consumer, less aggressive to household surfaces, and more environmentally acceptable.

(11) One of the biggest changes in surfaces in the home in developing nations over the past 15 years has been the increasing presence of electronic gadgetry: sound equipment, more elaborate televisions, faxes, and computers and their associated printers and monitors. Currently there is a very limited selection of products targeted at cleaning these electronics, but their maintenance will probably become more important in the future.

(12) Other than this, most surface types in the home — finished woods, stone, concrete, plastics like acrylates and terepthalates, steel, and ceramics (porcelain and glass) — seem to have stabilized in the developed world, although the relative amounts of these surfaces vary according to fashion trends. Some of the newer surfaces still are not well distributed throughout the developing world but will become increasingly so.

The sheer volume and variety of chemistry in this field is challenging, and only promises to continue. Likewise, the increase in the number of products and their overlapping claims should also continue.

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