The Changing Science of Cleaning Up

Top Formulation Trends in the World Detergent Industry Franco Pala, Principal Research Scientist, Battelle

The detergent in stores today is not your mother's laundry soap. Changing market pressures have led to new formulations for laundry, automatic dishwasher and other detergents. Detergent manufacturers are continually tweaking formulations to make them more sustainable, effective and suitable for today's technologies.

What are the biggest trends in the industry, what is driving them, and where might the detergent market be going in the future? The Battelle World Detergent Program was started in the early 1990s to answer these questions for manufacturers and raw material suppliers. This report summarizes some of the biggest trends we've seen over the last decade.

The Decline and Fall of Polyphosphates

Perhaps the biggest change in detergent formulation over the last ten years—and the one most noticed by consumers has been the removal of polyphosphates. Phosphates and polyphosphates were commonly used as builders in both laundry and automatic dishwasher detergent. They act as water softeners in order to improve the performance of active agents such as surfactants.

However, phosphates and polyphosphates are difficult for municipal water treatment plants to remove from wastewater streams. When they make their way into the environment, they can lead to overgrowth of algae in waterways, lakes, ponds and marine environments. Severe algal blooms lead to eutrophication, creating "dead zones" that are uninhabitable for other marine life. Some types of algae also release toxins.

These environmental concerns have driven the gradual removal of phosphates and polyphosphates from both laundry and automatic dishwashing detergent. Regulations requiring phosphate-free laundry detergents date back to 1992 in the U.S. and 1998 in the European Union. Regulatory requirements for automatic dishwashing detergent didn't take effect until 2010 in the U.S. and will not be fully enacted in the EU until January 2017. Other parts of the world have lagged behind in regulation but are starting to take notice. While polyphosphates are still widely used in Asia and Latin America, some major brands are beginning to phase out phosphate-based builders worldwide regardless of local regulations.

These changes have required manufacturers to develop new builder systems to take the place of phosphates and polyphosphates in their detergent formulations. Laundry detergents have moved to builder systems based on silicate, carbonate, zeolite and alternative builder polymers. These chemicals are perceived as safer than phosphates and polyphosphates. Replacing phosphates in automatic dishwashing detergents has proven to be more problematic due to high amounts of dried or baked-on soil and limitations in the types of surfactants that can be used in the machines. Initial formulations depended on higher concentrations of silicates, citrates and carbonates. Formulations also used new complexing agents such as the sodium salts of methylglycindiacetic acid (MGDA) and N,N-bis(carboxymethyl) glutamic acid (GLDA). Also known as chelating agents, these chemicals neutralize the effects of calcium, magnesium, iron and other ions found in hard water that interfere with the action of the active cleaners. In addition, there has been a rise in more complex building systems with increased dependence on copolymers in automatic dishwasher detergents.

When the regulations went into effect, many brands saw negative consumer reaction to the phosphate-free detergents; fairly or unfairly, many consumers felt that their trusted brands no longer worked as well as they used to. This reaction was especially pronounced for automatic dishwasher detergents. Areas with harder water, such as the northern central and Rocky Mountain regions of the U.S. and much of Europe, present the greatest challenges for phosphate-free detergents.

Builder system formulations are likely to continue to evolve in order to better meet consumer expectations, especially as the new phosphate-free automatic dishwashing detergents hit European markets. New complexing agents and water softeners



are likely to be needed to improve performance in areas with hard water or very hard water. In general, the trend seems to be towards more complex building agents with many different chemicals working together to fill the roles once filled by polyphosphates.

The Rise of the Enzyme

Another major trend observed in recent years has been the increase in the use of enzymes. Until 2008, there was a steady rise in the amount of surfactants used in both laundry and automatic dishwashing detergents. Since 2008, analysis has shown a decrease in the reliance on surfactants and an associated increase in the activity and complexity of the enzyme systems.

Enzymes and surfactants work entirely differently. Surfactants work by lowering the surface tension between two liquids or between a liquid and a solid. In detergent, surfactants help to lift soil from the surface and keep it suspended in water so it can be easily rinsed away. Surfactants are dirt-agnostic; they work on any type of organic or inorganic soil. In contrast, enzymes work by breaking down organic compounds. Their action is very specific; different kinds of organic compounds require different enzymes to break them down.

Enzymes and surfactants can complement each other in a detergent formulation. Because enzymes do not break down all kinds of dirt—in particular inorganic stains and soils—detergents are likely to always need some type of surfactant. However, the use of enzymes can allow detergent manufacturers to reduce the amount of surfactant required for effective cleaning. This trend has been seen across many major brands starting in 2009.

One major driver in this trend is consumer and regulatory pressure towards "greener," more sustainable detergent products. Enzymes are protein-based, and thus break down faster in the environment than chemical surfactants.

Traditional enzymes used in detergents include protease, which breaks down other proteins, and amylase, which breaks down starch. These enzymes work much the same as enzymes found in saliva and work well for many types of food stains. More recently, there has been an increase in types of enzymes used in detergent products. A typical detergent may now contain four or five different enzymes. These may include:

- lipase, which acts on lipids (fats)
- mannanase, which breaks down compounds commonly used in processed foods such as polysaccharides
- cellulase, a special enzyme that breaks down natural fibers and is used to reduce pilling on clothing
- pectinase, to break down pectins found in fruits

In the future, detergents may add even more enzymes, each with their own specific action. Adding additional enzymes will increase the range of stains that detergents are able to handle.

The industry is also likely to see changes in detergent chemistry to increase the efficacy of the enzymes. Enzyme activity is highly dependent on the chemistry of the solution they are contained in as well as factors such as water temperature. New formulations that provide increased enzyme activity in cold water, for example, would provide better stain-fighting activity in cold-water washes.

From Powders to Liquids to Capsules—and Back Again?

Over the years, the detergent market has moved from powders to liquids to single-dose tablets, compact powders and concentrated liquids and, more recently, water-soluble capsules or gel packs. Today there is more consumer choice available than ever, with major brands offering dozens of potential product options including dye-free, high efficiency (HE) and superconcentrated formulations.

Concentrated laundry liquid entered the market in the early 1990s in Europe and North America. During their first decade, they gradually took market share from compact powders (originally introduced in Japan in the 1980s) in most parts of the world. In the decade 2000-2010, the market decisively shifted in favor of liquid over powders in Europe and especially North America. Emerging markets such China and Latin America have seen a similar trend in the most recent years.

Over the last decade, some brands started putting out "superconcentrated" formulas to save on packaging and inventory. However, these have not been universally embraced by consumers around the world. Some producers have withdrawn super-concentrated formulas from some regions and moved back to more diluted liquids. However, the market for superconcentrated formulations is still highly dynamic, with different producers taking different approaches. We can expect the market for concentrated and super-concentrated formulas to continue to evolve in response to consumer preferences.

Since their introduction to mainstream markets in 2012, gel packs have been growing in popularity for both laundry and automatic dishwashing detergent. These single-dose products encase liquid detergents in a water-soluble pouch. They provide ease and convenience for consumers, who can skip measuring messy powders or liquids and simply toss the dissolvable capsules into the washing machine or dishwasher. Some of the capsules have multiple products contained in separate sections of the gel pack. The products are released together when the pouches dissolve. This allows softeners, activators and other boosters that are not shelf stable when mixed together to be integrated into a single system.

However, concerns about child safety have cut into the gel pack's popularity. Since the arrival of the gel packs on the market, there have been several reports of accidental poisonings involving young children. *Consumer Reports* no longer endorses the use of laundry gel packs because children may mistake the colorful pouches for candy. The detergents contained in the pouches tend to be highly concentrated, making them especially toxic. Some manufacturers are now adding bitter-tasting agents to their formulations to make them less appealing.

The chemistry in gel pack products can also be more complex, leading to higher formulation and manufacturing costs. Standard liquid detergents use water as a solvent; some detergents may be up to 70% water by mass. However, because the pouches are made to dissolve in water, detergents contained in gel packs have to use other types of solvents. These are both more expensive and potentially more toxic or less environmentally friendly. Of course, the manufacturing process for the pouches themselves also adds to the cost of the product.

So far, it is unclear whether cost and safety concerns will trump convenience for consumers. Gel packs are not the first attempt at single-dose products; tablets (essentially compressed powders) arose in the 1990s and quickly achieved popularity, especially in parts of Europe. However, popularity peaked in the early 2000s. While still available for both laundry and dishwasher detergent markets, they did not achieve the promise that early indicators predicted. It is too early to tell whether gel packs will follow the same declining trajectory or if they will be able to overcome consumer concerns.

A Bleach is a Bleach is a Bleach?

Bleaching systems tend to remain fairly stable over time; compared to other aspects of detergent formulation such as builders and surfactants, there have been relatively few changes in bleaching systems over the last several decades. The biggest change is the disappearance of sodium perboratebased bleaches from the world market since 2008. Sodium perborate was commonly used as a source of active oxygen in bleaching systems until 1998, when the Environmental Health Criteria 204, published by the International Program on Chemical Safety, indicated that boron demonstrated developmental and reproductive effects in animals. Since then, it has gradually been replaced by sodium percarbonate in detergent formulations in most parts of the world.

Bleaching activators have likewise remained very stable.

However, this does not mean that there is no room in the market for new bleaching systems or activators. Companies creating bleaches and activators that are less toxic, more environmentally sustainable, or more appropriate for colors and cold-water washing would be likely to find a market.

Where Do We Go From Here?

Where does the market go from here? New options for consumers may be just around the corner. For example, innovative technologies such as microencapsulation allow manufacturers to combine incompatible products, such as bleaches and activators, into a single shelf-stable product. Other advances in materials science and detergent formulation may give rise to as-yet-unimagined new product options for laundry, dishwashing and household cleaning.

While there are many unknowns, there are several critical drivers that are likely to influence further changes in product formulation.

• The "green" movement: Consumer preference is driving increased interest in products that are more sustainable to manufacture and safer for the environment when released in wastewater, such as surfactants derived from natural oils instead of petroleum.

- Raw materials costs: Many detergent precursors are derived from petroleum, making their costs highly dependent on a volatile oil industry. The speed of movement to alternative naturally derived or synthetic raw materials will depend heavily on the relative costs of each of these alternatives in the future.
- Appliance technologies: Detergent formulations will continue to be driven by changes in the machines consumers are using. The move to high-efficiency washing machines, which use relatively little water, has already resulted in the formulation of new HE detergents. As more consumers make the change to newer energy-saving machines they are likely to drive continued improvement in detergents designed for low-water and cold-water washing.

Want to Know More?

The Battelle World Detergent Program gives you cost-effective, accurate and timely data to document emerging trends in the quickly changing detergent, household chemical and personal care markets. We give detergent and household product manufacturers, raw materials suppliers and appliance manufacturers the information they need to make strategic product decisions. Subscribers receive:

- Regular analysis of the composition of major brands in North America, Latin America, Europe and Asia/Pacific
- Annual reports and client meetings to document industry trends
- Access to technical expertise developed over 20+ years of experience in the detergent, household chemical and personal care product fields

Battelle's multidisciplinary team of chemical engineers, chemists and market research experts analyze more than 260 individual products annually to provide the most comprehensive picture of industry trends available. • Regulatory trends: Regulatory agencies are putting increased scrutiny on the various chemicals that make up detergents and personal care products. One area to watch may be in preservatives. These are biocidal agents added to prevent the growth of molds and bacteria in products. Recently, there is growing concern about their environmental impact when preservatives are released in wastewater. Proactive companies are already making changes in their formulations to meet anticipated regulatory changes, especially in the personal care product market.

These and other market forces will continue to drive innovation in the detergent industry for many years to come. Savvy manufacturers and raw materials suppliers will want to keep a close eye on these trends so they can stay on the leading edge of the market.

Laundry

- Heavy-duty powders (regular, compact; standard and color)
- Heavy-duty detergent tablets
- Heavy-duty liquids (regular, concentrated) and capsules (standard and color)
- Fine fabric detergents (powders, liquids)
- Hand wash (soap bars, syndet bars, pastes)
- Fabric softeners (liquids, sheets)

Dishwashing

- Hand dishwashing (liquids, paste, gels)
- Automatic dishwashing (liquids, paste, gels, powders, tablets)

Cleaning

- Hard-surface cleaners (all purpose, special purpose)
- Lavatory care (toilet bowl cleaner, bowl- or cisterncleaning blocks)
- Stain and odor removers
- Bleaches (liquids, solids)
- Dry-cleaning kits

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