The Safety of Household Products

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ABSTRACT

When detergents were essentially soap, it was easy to assume that they were perfectly innocuous in use. Even later, when synthetic actives and phosphate builders appeared, it wasn't necessary to carry out extensive testing to confirm their safety. However, nowadays one has to say with certainty that a detergent product is not only safe to use but also to manufacture and release into the environment. This is a big, often long and expensive, job. A battery of tests have had to be developed and every likelihood covered as far as possible. The kinds of tests used will be briefly discussed and examples given of the lengths to which manufacturers go to ensure the safety of our products.

Soap, the first detergent, was made and used with no safety testing for over 2,000 years. If only soaps were still used, considerable time and money would not have to be spent these days on safety testing.

Be that as it may, we must have safe products. Basic guidelines and some specific rules toward attaining this goal are provided by a variety of safety regulations which govern the soap and detergent industry at this time. However, the industry often goes well beyond these regulations to ensure that all its consumer products are indeed safe. An attempt will be made to present an overview of the many regulations and actions taken by the industry to ensure the safety of its products.

The first act passed in 1938 by the newly formed Federal Drug Administration (FDA) and updated regularly since, was designed, as the act is called, to control the safety of foods, drugs and cosmetics. In the detergent industry, soap bars are split into three groups—conventional soap bars, such as Camay, Ivory and Lux; cosmetics, such as Dial, Irish Spring and Safeguard; and drugs, such as Caress, Dove and Neutrogena. Basically, the act states that such products have to be safe and use FDA-approved materials.

The next act, the Federal Hazardous Substances Act, became law in 1960 essentially to protect consumers against the indiscriminate use of highly alkaline cleansers. The act came under the aegis of the newly formed Consumer Product Safety Commission in 1972 and today covers all hard surface cleansers, detergents and light duty liquids among a variety of other products. The act, together with the Poison Prevention Packaging Act passed in 1970 and also administered by the CPSC, provides both guidelines and specific instructions as to when a product is considered hazardous and in what way, and what one has to do about it.

In 1970, the Department of Labor passed the Occupational Safety and Health Act (OSHA) which is designed to protect workers against unsafe working conditions. The record of the detergent industry in this respect is enviously high but we must continue to ensure by all possible means that it remains high.

Finally, in 1977 two acts—the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA)—came into being through the Environmental Protection Agency (EPA). These are designed to prevent, as far as possible, unsafe chemicals from getting into the marketplace or from being disposed of in potentially hazardous ways.

In a capsule, one has to ensure the safety of products from development through manufacture, use and final disposal. The practical effects of these regulations on the development of a new detergent product can be illustrated in the following example.

Our scientist has had a brilliant idea. Adding compounds X and Y to a detergent powder produces a marvelous new product. Unfortunately X and Y are new compounds, or significant new uses of known compounds, and under the TSCA, we have to satisfy ourselves that they are safe. Previously, only the 50th percentile lethal dose test (LD_{50}) would have been determined. In the LD_{50}, we feed varying amounts of the material to prestarved young healthy rats and determine the amount necessary to kill half of them. A material with a very low oral LD_{50} would either not have been used or used cautiously, with adequate warnings. Nowadays, that is only the beginning.

Currently, there are a variety of short-term (a few days to a week), medium-term (a few weeks to a few months) and long-term (2-3 years) tests that often have to be made to be assured that a material is safe for use. Short-term tests would include acute toxicity, skin and eye irritation and mutagenicity; medium-term tests would include subacute toxicity, sensitization and teratology; long-term tests would include carcinogenicity. The extent that one proceeds through these depends upon the product's structure, how it will be used and its ultimate fate in the environment. One now also routinely looks at the material's propensity to cause mutations or teratological changes, starting with the relatively simple Ames test, but going on to a number of complex procedures on the basis that these tests are relatively fast and inexpensive. One can be pretty certain that the compound is not a carcinogen if all results are negative.

In the Ames test, one looks for a greater than normal reversion of specially prepared bacterial cells growing on a specific medium. Increased growth indicates reversion, mutagenic activity and, hence, possible carcinogenic activity.

Negative results, on the other hand, do not necessarily mean that the compound being tested is completely safe. The particular bacteria used in the Ames test may be insensitive or too sensitive, it may even be killed by the compound being tested, and despite the use of liver extracts in one of the forms of the Ames assay, the bacteria may not pick up potentially harmful changes in the compound being tested via, say, metabolic transformations. Thus, in addition to the relatively simple Ames test, one also carries out similar types of tests on fungal cells and other cells, both in vitro and in vivo, in the so-called host-mediated assays, where the host animal provides the various living enzyme systems to metabolize the material if it is going to be metabolized.

One must also guard against possible harm to offspring or teratogenic effects. To check fully for this, a series of feeding experiments have to be made. The material is fed to newly pregnant animals, usually rats, from day 6 to day 13 of their pregnancy, which is the most sensitive period for formation of birth defects; then the pups are either extracted via caesarian birth or allowed to be born naturally. In both cases, one looks for any skeletal or other differences from a control group. Since the problem may not always derive from the dame, male animals are also fed the material for some time before mating (usually 90 days) and again the offspring examined.

So, after some months and the expenditure of considerable money and, providing all these test results are negative, one can proceed with fair confidence that the material is reasonably safe. However, before moving ahead with larger scale development, manufacture, laboratory and consumer testing one must be sure that all the remaining areas of safety have been covered.

Compounds X and Y eventually will be used in the plant. Under OSHA one must be sure that the compounds are handled safely and are safe to handle. The various tests done so far indicate no acute, mutagenic or teratogenic problems for the plant worker, but a solid material may be dusty and a liquid material may splash and could get into the eyes, lungs or irritate the skin.

The controversial, but essential, Draize Rabbit Eye Test is used for determining any potential eye problems and various kinds of patch tests are used to determine potential skin irritation. Simple irritation may be annoying but is not a very serious matter. Much more serious is the potential of the compound to cause sensitization—that is, cause a person eventually to become essentially allergic to even minute quantities.

Several tests have been devised to check for this and probably the most widely used and accepted one is the Magnusson-Kligman test. In this, guinea pigs are injected just below the skin with slightly irritating doses of the material with and without an antigen. Some days later the areas above the injected sites are patched with the material being tested to stimulate the skin to react. The animal is then repatched some weeks later on a virgin site. If the animal reacts positively to this repatch then the material can be presumed to be a sensitizer.

A final sensitization that one has to guard against is photosensitization—that is, sensitization caused by the compound plus sunlight. The Harber test is used to evaluate this. Guinea pigs are open-patched a number of times with the compound and exposed to UV light each time. After a 2-3 week rest period, the animal is repatched on a virgin site and again exposed to UV light. If the animal reacts positively, then the material is probably a photosensitizer.

The potential problems of inhalation have been omitted, but obviously these may not be neglected. If the material is water-soluble and simply slightly irritating, it would not be necessary to go any further except, perhaps, to recommend suitable masks for workers exposed to the material on a continuing basis. However, if the material is insoluble and the particles are small enough to get into the lungs, then virtually the only way of determining whether this can cause any problems is to carry out animal inhalation studies, starting at a couple of weeks to look for gross effects, then proceeding to 90 days and, if indicated, lifetime studies.

So much for compounds X and Y for the moment. What about the finished detergent product?

Under the FHSA, the product must be accurately labeled. To determine whether an ingestion warning is needed, and what kind or whether child proof packaging is necessary, one has to do an acute toxicity test on the finished product. If the LD_{50} is less than 5 g of body weight, the product must be labeled with an ingestion warning. Furthermore, the label must list the compound or compounds responsible for the ingestion problem and recommend, for the use of poison control centers, the best antidote for accidental ingestion.

Similarly, a Draize test reveals whether an eye warning is needed and what should be done to minimize potential damage.

It is possible that the new product will be used for pretreatment and so irritation and potential sensitization tests must be made on the finished product just as was done for compounds X and Y. In addition, even if the product is not recommended for pretreatment, one usually does a human sensitization test on 100-200 people to confirm that these are no problems and incidentally confirm the animal test results. The Draize-Shelanski procedure generally is used for this test. The upper forearms are patched every other day for a total of 10 times, then the person is challenged on the back after a two-week rest period.

Obviously, if all these tests are negative one can be reasonably certain that neither the product itself nor minute residues left on clothes will cause any problem.

Is the safety testing finished at this point? Certainly not!

After the wash is through, the product goes down the drain and, hence, to septic tanks or sewage works and eventually to ground or open waters. To ensure safety to man and the environment, a whole additional series of tests may be carried out from simple to complex biodegradation (BOD) studies, to determining the amount that will kill half a fish population, the LC_{50}, and even to determining the long-term, or chronic effects, on fish and crustations.

Although finished products may be tested in this way, TSCA requirements demand that specific materials, e.g., compounds X and Y, which are a significant percentage of the finished product, be selected for testing. If, in doing these tests, it is found that the compound persists in the environment for some time, it may then be necessary to do chronic animal feeding studies to check long-term carcinogenic effects.

One can now understand why detergent products are so relatively safe to man and the environment. But can one be completely satisfied at this point? From the point of view of the various regulations, the answer must be yes, but from the point of view of a concerned manufacturer, not necessarily.

Consider the package of detergent—assuming someone has spilled some product on the floor. The question may be asked, how did it get there? The answer could be that someone dropped an open package, and it can be asked whether this could conceivably give rise to any safety problems. Obviously it does depend on what is in the product but, some years ago, for an enzyme product, a large detergent company thought it worthwhile to monitor the amount of enzyme that could be inhaled by a person who had had such an accidental spill. Happily, the results indicated virtually zero risk. Since then, the enzymes themselves have been improved even more from the point of view of dustiness so today we would not need to do such an experiment to prove products made with them are safe.

There are additional steps to maintaining a thoroughness in assessing potential risk. For instance, the LD_{50} of a product can be determined and from that one can form a reasonable picture of its safety after ingestion. Indeed, even if the LD_{50} is below 5 g/kilo it would be difficult for a person to keep down a lethal dose because of all the salts in our products. However, rats do not have an emetic response and cannot give us information on this. Is this a concern?

Since some nonionics are known to have anesthetic effects, it was thought to be a possible concern for detergent products based on nonionics. By theoretically depressing the emetic response, the possibility was raised that a dose close to or above the LD_{50} could be tolerated. Some time ago, it was thought that this should be checked. Dogs are much more like humans in possessing normal emetic response and so appropriate experiments were run. It was possible to show that the nonionics used in the detergent industry have no depressive effect on emetic response.

Similar experiments have to be designed for other potential problems.

In summary, various governmental regulations from a number of agencies mandate the safety of household products from manufacture through use, or possible misuse, to eventual disposal. This paper has shown how we meet this need and how we often go much further to satisfy our desires to market truly safe products.

Surfactant Raw Material Outlook for the Eighties

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ABSTRACT

Over the next decade, the surfactant industry should be able to secure an adequate supply of the raw materials necessary to provide its need for surfactant intermediates. Since the U.S. will continue to rely on foreign imports for marginal crude supplies, periodic disruptions in raw material supply are likely to occur. World crude prices are expected to rise more rapidly than the general U.S. inflation rate and surfactant feedstocks are expected to track world crude prices as a whole. Over the next few years, ethylene prices should increase faster than other surfactant feedstocks. This should occur as a result of natural gas price decontrol and improved ethylene profit margins. Otherwise, in the long term, the major driving force for all three synthetic feedstocks should be the price of world crude. Of course, short term perturbations, e.g., plant shutdowns and over-supply situations, may cause one feedstock or the other to increase at somewhat higher or somewhat lower rates for short periods of time. Natural oils may represent an interesting alternative to crude-oil-based alcohols. Longer term, average prices for natural oils should increase at lower rates than world crude oil. However, natural oil prices have historically been much more cyclic than crude prices and "natural" alcohol producers run the risk of being noncompetitive during tight supply/demand periods.

INTRODUCTION

In the midst of the current recession with spot prices, even of refined products, below contract prices and falling, petrochemical producers are now more interested in maintaining volume and margins than in future feedstock supply security. Still, having experienced the sharp price increases and supply shortages of 1974 and 1979, a lingering concern over future feedstock availability and pricing remains. In general, the surfactant industry has done well in its battle with the fuels industry for its needed feedstocks. The surfactant industry's success, like most petrochemicals, can be attributed to its value added, labor and GNP advantages vis-a-vis the fuels markets (1,2). These advantages will continue and, therefore, the detergent industry should continue to acquire the feedstocks necessary for growth. However, prices, which are driven by world crude prices, should rise significantly higher in the next few years.

SURFACTANT INTERMEDIATE RAW MATERIALS

Basic surfactant intermediates are produced from petroleum (or natural gas liquids) products and natural oils. Detergent intermediates produced from petroleum-derived ethylene, benzene and normal-paraffins are usually referred to as "synthetic"; alcohols produced from agriculturally derived fatty acids are referred to as "natural."

SYNTHETIC SURFACTANT FEEDSTOCKS

"Synthetic" feedstocks are produced from refined petroleum products or natural gas liquids—ethane, propane or butane. Crude oil is processed in refineries into various "virgin" products, e.g., naphtha, kerosene and various gas oil or distillate streams (3). Natural gas liquids (NGL) are extracted from "wet" natural gas streams (either "associated" or "unassociated" with crude oil production). NGL, naphtha and gas oil are common feedstocks for ethylene "steam crackers" (3-7). Naphtha also can be "reformed" into highly aromatic gasoline range products that yield significant quantities of benzene (3,9,10). Normal paraffins are extracted from refinery kerosene streams (3).

NATURAL SURFACTANT FEEDSTOCKS

Naturally derived, long chain fatty acids also are used as raw materials for the surfactant industry. The preferred fatty acids are lauric types derived primarily from coconut oil, and minor amounts from palm kernel oil. These natural oils can be hydrolyzed or reacted with methanol to produce glycerine and either methyl esters or fatty acids.

U.S. ENERGY DEMAND

Natural oils now represent less than 5% of the total raw material requirement (including ethylene oxide) for the surfactant industry. Therefore, at least in the foreseeable future, surfactant feedstock availability and price will be influenced primarily by the three petroleum derived feedstocks—ethylene, benzene and *n*-paraffin.

These products share two significant characteristics that influence their availability and price: (a) each is petroleum-derived; (b) each is produced "on-purpose." "On-purpose" means that each is the primary product from a particular production facility, as opposed to being a "coproduct" or "byproduct." For this reason, the price, over the long term, is going to be cost-related and the availability (long term) will depend on the relative margin above cost, i.e., demand drives price and, hence, supply.

Since all are petroleum-based, the U.S. and world crude oil situation is extremely important to the surfactant industry. Will the detergent industry continue to import a majority of its crude oil? Will OPEC continue to control the price? To answer these questions one must look at the total U.S. energy picture—today and over the next decade or so. In 1980, the U.S. can be expected to consume about 76 quadtrillion BTUs (Quads) of energy (only 2% greater than the 1973 pre-embargo peak). Over the next 10 years, total energy demand is projected to increase less than 1.5%/yr. This projected growth rate is significantly lower than in the 1960s (4%) and is the result of increased conservation brought about by higher relative energy costs and lower overall economic growth.

Coal is expected to provide a greater proportion of the U.S. Energy needs. Coal's share of the total energy supply