Measurement of Enzyme Laundry Product Dust Levels and Characteristics in Consumer Use

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Abstract

Prior to the adoption of improved dust control measures, some factory workers developed allergic respiratory symptoms during the manufacture of enzyme laundry detergents. Since then, the industrial hygiene problem is being brought under control by maintaining dust exposure below levels where allergic respiratory symptoms develop. However, the fact that enzyme allergies could develop in manufacturing plants prompted questions from outside the soap and detergent industry regarding consumer safety of enzyme detergents. Although detergent dust levels in consumer use were known to be very low, a comprehensive testing program was undertaken to place quantitative dimension on the difference between home use and factory operation. Levels and characteristics of detergent dust and enzyme dust generated during home use of laundry detergents have been measured using specialized equipment and procedures. Data from laboratory and in-home studies confirm that laundry products containing an agglomerated enzyme complex are safe from the standpoint of potential consumer exposure to enzyme dust. Even under conditions of excessive home use, consumer exposure is extremely low and can be compared to only a minute fraction of the industrial exposures which are considered to be safe.

Introduction

The successful development and utilization of safe, stable and effective enzymes in laundry products represents the greatest advance in soap and detergent industry technology in the past 20 years.

FIG. 1. Typical enzyme laundry products. Over 160 enzyme-containing laundry products are available worldwide. These include at least 31 in the United States, 97 in Europe, 10 in Asia and 2 in Africa. In July, 1969, in the United States alone, nearly 50 million households were using one or more enzyme laundry products.

Enzymes are not new since they cause and control numerous chemical processes in all living organisms. Likewise, their controlled use by man precedes recorded history in such "natural processes" as the fermentation of wine, the making of cheese and the yeast raising of bread dough.

In more recent years, enzymes have become commercially available from various animal, vegetable and microbiological sources and are employed for purposes ranging from the treatment of milk, to make it more digestible, and the inversion of sugar in candy manufacture, to the improvement of tough cuts of meats by meat tenderizers. In addition, proteolytic enzymes are used in medicine in many diverse applications such as wound debridement (1).

The first known application of enzymes in consumer laundry products occurred in 1913 with the sale of a presoak product in Germany, but it was not until 50 years later in Holland that the first really successful enzyme product for laundry use was formulated and introduced.

In the United States the first enzyme laundry products were introduced in early 1967. Since that time there has been a dramatic growth in the number of enzyme brands sold and in their popularity with consumers, both in the United States and worldwide (Fig. 1). This success directly reflects the opinion of the majority of women everywhere who consider the addition of enzymes to laundry detergents a significant improvement in home laundry products.

Much has been published in the literature concerning the nature, use and function of enzymes in laundry detergents (2–4). Likewise, extensive investigations have shown that dermatological and toxicological influences of enzyme detergent solutions are equivalent to comparable nonenzyme formulations under consumer usage conditions (5). Finally, the trouble-free use of enzyme detergents in the homes of millions of consumers around the world has confirmed the overall safety and effectiveness of these products in consumer use.

The purpose of this review is to compare consumer use conditions with industrial situations, demonstrating the continuing validity of the conclusion that enzyme detergents are safe in consumer use. This is done in view of reports of respiratory symptoms among workers in enzyme detergent manufacturing in Europe, and because recently the United States detergent industry recognized that industrial exposure to high concentrations of enzyme dust could result in allergic respiratory symptoms among some manufacturing employees (6–8). (These symptoms are comparable to those found in other kinds of industrial exposure to dusts with antigenic properties.) Among affected workers, enzyme-related allergic conditions have responded readily to standard medical treatment and symptoms disappeared after reduction of dust exposure. No evidence of any permanent effects on the respiratory system has been found. The subsequent adoption of improved dust control measures, coupled with the use of proper personal pro-

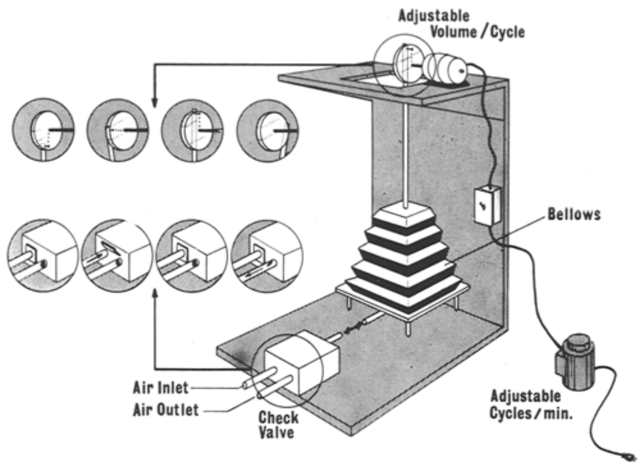

FIG. 2. Schematic diagram of bellows breathing simulation device.

tective equipment if abnormal manufacturing conditions exist, are bringing the problem under control (9).

Experimental Procedures

The basic experimental approach can be outlined as follows: (a) Airborne dust was collected in consumers' homes during normal use of laundry detergents. Dust collection was conducted in a manner that permitted determination of the amount of detergent dust to which housewives were exposed during the use of detergents. (b) Consumer use of laundry products was simulated in the laboratory to permit collection of sufficient samples for analyses of the amount of enzyme in detergent dust, and for detergent dust particle size distribution determinations and persistence measurements.

Products Tested

The enzyme laundry products used in these studies were representative of those sold by the Procter & Gamble Company. Both warehouse samples and samples purchased from retail outlets were tested.

Background on Manufacturing Processes

Enzymes are added to Procter & Gamble products in a way that ensures a minimum potential for dust development in both manufacture and consumer use. Specifically, enzymes are agglomerated with carrier granules composed of conventional detergent ingredients. These carrier granules are dedusted by spraying with a nonionic surfactant. The agglomeration processes used securely bind the enzymes to the carrier granules. [The Procter & Gamble Company has decided to dedicate its patents on agglomeration processes to the public (10,11), so that anyone may freely use these methods for dust control.]

The agglomerates produced by this process are both less fragile and, on the average, coarser than the base formula itself; hence, they have a significantly reduced potential as a source of dust. Of additional importance is the fact that this agglomeration process produces the highest enzyme concentration in the largest particles. The agglomerates are then blended with the base formula to provide the desired enzyme level in the finished product. The base formula is also dedusted by spraying with a nonionic surfactant.

The use of these processing techniques results in a relatively dust free finished product, the very small

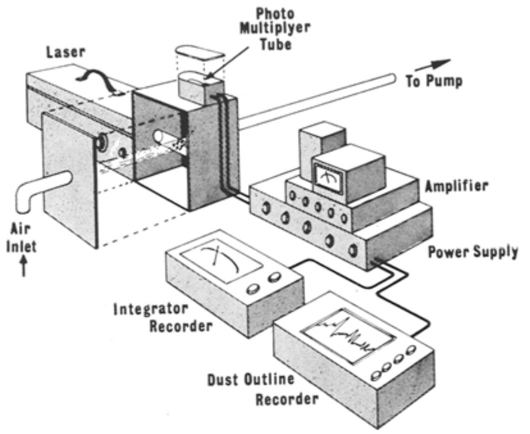

FIG. 3. Schematic diagram of laser dust detection device.

amount of dust that can be produced being significently lower in enzyme content than the finished product itself.

Air Sampling

A variety of air sampling and dust collection systems (e.g., filters, cyclones, impactors) are available. However, experience has shown that an electrostatic precipitator is best for this application. Some key advantages of precipitators are: high collection efficiency for all particle sizes, portability and operability over a range of air flow rates, low flow rates approaching the breathing rates of people at work. The precipitator used in this work was a Bendix Electrostatic Air Sampler, Model No. 959. (Bendix Corp., Cincinnati).

A bellows device (Fig. 2) for simulating the cyclic nature of breathing, i.e., inhalation and exhalation, was developed to help validate the use of the Bendix precipitator. This apparatus reproduced a broad range of breathing volumes and frequencies corresponding to those of women doing light work. Dust was generated by simulating home use conditions, and sampled by the Bendix precipitator with its constant air flow rate and by a Bendix precipitator attached to the simulated breathing device. Equivalent weights of collected dust were found per volume of air sampled, thereby confirming the validity of using the Bendix precipitator at a constant air flow rate.

The collection efficiency of the Bendix precipitator in this application was evaluated by placing an in-line filter (99.95% collection of 0.3 μ particles) in the exhaust port of the unit and sampling the dust generated from the simulated pouring of laundry detergents. It was necessary to use a very powerful vacuum pump to supplement the fan in the Bendix unit. At an air flow of 3–4 cfm the collection efficiency of the Bendix unit was found to be 99.7%.

A further evaluation of the Bendix unit was conducted to determine if potential ozone generation by the high voltage could affect enzyme activity. With the Bendix unit operating at 12 kv and 3 cfm, no degradation of enzyme activity was found.

It was also of interest to determine how long dust persisted after generation. An exceptionally sensitive detection device was developed for this purpose (Fig. 3). A helium-neon gas laser with an output of 0.1 mw at a wavelength of 632.8 nm was used as a light source. Since all the energy is contained in a beam of 2.5 mm diameter, it represents a source of very high luminous flux. The beam passes through a dark

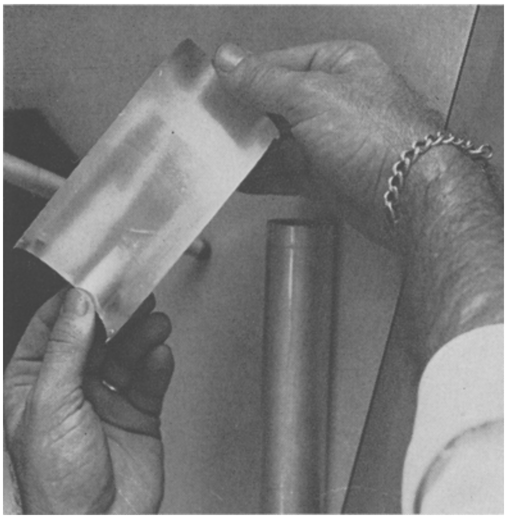

FIG. 4. Dust on the foil liner from the electrostatic air sampler. Dust collects as a stripe near the end of the foil. The dust shown here represents that collected from more than 75 simulated pours.

chamber through which the air being tested is drawn. A photomultiplier tube is positioned at 90° to the laser beam. As dust particles pass through the beam they scintillate, causing an output from the photomultiplier detector which is amplified and displayed on strip chart recorders. Recorders can produce a curve displaying the peak value of the dust, followed by a gradual return to a steady base line as the dust settles or, using an integrator circuit, the integral of the peak-persistence curve can be displayed. The sensitivity of this device is such that a single speck of dust passing through the light beam is easily detected. Although the minimum size particle detectable by this device has not been determined, it is known to be very small since the device can readily detect the difference between the breaths of nonsmokers and smokers several minutes after smoking.

Dust particle size distribution was determined by advanced microscopic techniques. Samples from simulated consumer use were collected on foil liners placed inside the precipitator collection tubes (Fig. 4). Since laundry product dust is generally spherical in shape and its specific gravity has been found to be only slightly higher than 1.0, aerodynamic particle size would be about the same as that determined microscopically.

The level of enzymes in various particle size fractions of detergent dust was estimated by a procedure (Fig. 5) which consisted of, first, very carefully screening samples of laundry products through a 65 mesh screen. Next, particles smaller than 200 μ passing through the screen were air-elutriated in a modified Roller Analyzer where particles larger than about 20 μ were removed. The effluent air stream containing dust particles smaller than 20 μ then passed into an Andersen air sampler (Model No. 705–1), which classified the dust particles into size fractions of interest. This procedure was continued until the quantity of sample collected in each size fraction was adequate for enzyme analysis.

In-Home Studies

Air was sampled during actual home use of laundry products with the Bendix unit operated from a battery power source. Air was sampled continuously from the time each housewife began to pour laundry

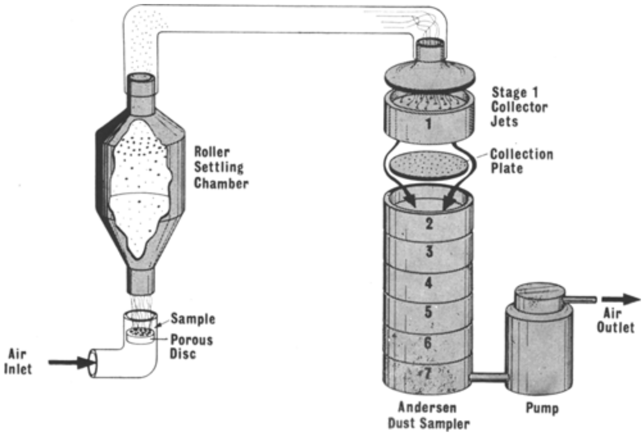

FIG. 5. Schematic diagram of apparatus for dust particle size classification.

product for use until she left the laundry area. During each in-home sampling, the entry orifice of the dust collection device was located at a distance from the point of dust generation spatially equivalent to the direction and distance of the housewife's nose from the point of dust generation (Fig. 6).

Laboratory Simulation of Consumer Use

Since only minute levels of dust are produced in home use of laundry products, it was necessary to simulate consumer use in the laboratory to secure sufficient and satisfactory dust samples for enzyme analyses, particle size measurements, and dust persistence determinations. For instance, it would be necessary to combine dust samples taken from thousands of home uses in order to have an adequately sized sample for a single enzyme analysis.

Laboratory simulation of consumer practices was based upon extensive consumer habits data developed by a variety of conventional techniques. This was supplemented by a program of observation of consumer behavior in homes to determine such details as the geometry of pouring product into a cup. In general, laundry detergent dust was generated in the laboratory by simulating the most common housewife

FIG. 6. Collection of dust in consumers' homes. An electrostatic air sampler is held at nose level as housewives pour enzyme laundry product.

method of dispensing detergent granules for machine laundry, that is, by pouring the product from the carton into a measuring aid and then to the washing machine. This practice is followed by over half of all U.S. housewives. Other housewives use methods, such as dipping a cup into the box or pouring directly into the machine, which are less likely to generate dust. In fact, the double-pour machine laundry practice involves equal or greater potential for consumer contact with some dust than does any other normal use of laundry product for any common task in the home.

In pouring from box to cup, most women rest the carton on the edge of the cup, while others pour from a height of one to three inches. A range of one to three inches was used in this work. The cup of product was then poured into a shallow pan from a height of 12 to 18 in. (the shallow pan was used to simulate pouring product onto a filter pan or agitator post near the top of the machine, a practice expected to generate more airborne dust than, for example, pouring onto the bottom of the empty machine tub). Finally, in all laboratory simulations the orifice of the dust-collecting device was located at distances from the dust-generating operations equivalent to the minimum distance between the home operation being simulated and the typical consumer's nose, as determined by in-home observations. Air sampling at this minimum distance was conducted for 2 min, whereas the typical housewife keeps this minimum distance for only a few seconds.

Overall, the laboratory methods generated detergent dust at substantially higher levels than would be encountered in typical household practice. Even with the greatly exaggerated dust levels produced in the laboratory simulations, each simulation procedure had to be repeated many times at each test condition in order to produce adequate sample sizes for the desired analyses.

A housewife inhalation rate of 16.3 liters/min was used in all calculations.

Throughout this report, enzyme concentration is expressed in terms of a commercially available material, which has been standardized to a proteolytic activity of 1.5 Anson Unit Equivalent (A.U.E.).

Findings

The soap and detergent industry has long been interested in, and has spent considerable effort towards reducing laundry product dust to minimum levels in order to minimize any adverse quality impression that could be associated with laundry product dust. This continuing interest and effort had reduced laundry product dust to the point where laundry products were relatively dust free even prior to the addition of enzymes. The results of the in-home studies place quantitative dimension on laundry detergent dust in home use. At most, detergents contribute only 5% of the dust present during the time detergents are dispensed for laundering. On average less than 3% of the dust collected during in-home studies was laundry detergent. The remaining 97% is believed to be mainly lint.

It has long been believed that any airborne dust generated from laundry detergents in home use does not persist very long. Using the laser dust detection device this judgment was confirmed. Even in extreme conditions, virtually all detergent dust settles in less than 2 min. More than 95% of detergent dust settles in 100 sec.

From laboratory simulation of consumer use, it was determined that there is less than 0.05% enzyme (1.5 A.U.E.) in dust generated from the laundry detergents tested.

From in-home studies conducted during typical consumer use, it was found that there is on average 0.27 μg detergent dust exposure per cup of product used for double-pour machine laundering. Nonetheless, 1.0 μg was used in calculations to ensure that the conclusions reached would be clearly conservative.

Analysis

Since there is less than 0.05% enzyme in these detergents' dust and since detergent dust exposure is less than 1.0 μg per double-pour machine laundering, it is calculated that there is less than 0.0005×1.0 or less than 0.0005 μg enzyme (1.5 A.U.E.) exposure per machine laundering.

There is wide variation among households in both frequency and amount of laundry product usage for a number of tasks. This situation is best handled by considering the total weekly consumption of laundry products for all these purposes. Total consumption was determined as follows. Comprehensive studies on habits and practices have been conducted by the Procter & Gamble Company among tens of thousands of consumers. These studies provided task frequency and usage data for laundry products in each of the following individual tasks: machine laundry, presoaking, use of presoak products as laundry additives, hand laundry, dishwashing, floor and wall washing.

Using a sophisticated computer programming technique, joint task frequency and usage data were developed which showed the following total consumer usage for all these tasks to be: median, 7.8 cups/week; upper 95th percentile, 22.5 cups/week.

As discussed earlier, a double-pour machine laundering can result in consumer exposure to less than 0.0005 μg of enzyme. This exposure estimate applies for a usage of one cup; if it is conservatively assumed that all other purposes and practices involve the same exposure estimate, it can be calculated that potential total consumer exposure is: median, 7.8 cups/week $\times$ 0.0005 μg/cup or less than 0.0039 μg enzyme (1.5 A.U.E.) per week; upper 95th percentile, 22.5 cups/week $\times$ 0.0005 μg/cup or less than 0.0113 μg enzyme (1.5 A.U.E.) per week.

At this point it is appropriate to introduce a basis for judging whether or not these infinitesimal quantities of enzymes could represent a hazard if inhaled by consumers.

Based on experience in the soap and detergent industry, it appears that factory employees can be exposed to an airborne enzyme concentration of at least 5 $\mu g/m^3$ (1.5 A.U.E.) without developing enzyme-related respiratory symptoms. This safe level was used as described below in order to have a tentative and conservative basis for evaluating the significance of the consumer exposure data.

A female factory worker breathing at about 16.3 liters/min in an environment containing an apparently safe enzyme level of 5 $\mu g/m^3$ would inhale 195.6 μg of enzyme (1.5 A.U.E.) during a 40 hr week. This weekly industrial exposure is compared to the potential weekly consumer exposure as follows.

Potential Weekly Exposure (μg enzymes 1.5 A.U.E.): (a) Consumer, 50th percentile, less than 0.0039; upper 95th percentile, less than 0.0113. (b) Factory worker, 195.6.

Consumer Exposure: Fraction of safe factory level, 50th percentile, less than 1/50,000; upper 95th percentile, less than 1/17,000.

These large differences between the industrial and home situations are not surprising. In home use, only very low levels of dust can be generated from laundry products and even less enzyme dust is produced from these products due to the special methods of dedusting and incorporating enzymes into them. Further, dust is generated in home use only very occasionally, and when generated, it settles very quickly.

Discussion

To place added dimension on potential enzyme exposure, dust was generated in a manner that would exceed any level likely to be developed by consumers in home use. Laundry detergent was dumped onto the floor from a height of 6 ft. The detergent was then vigorously swept with a brush for 5 min. Dust was collected at "nose location" with the Bendix precipitator for the entire time beginning with the dumping of the product. Even in this very extreme situation, if 3 lb. of laundry were dumped, potential consumer exposure to enzyme dust would be only about 1/500 of a safe weekly dose for a factory worker.

To provide a basis for relating this extreme spill situation to actual consumer experience, over 100 housewives were interviewed in depth. About half of the housewives claimed to never have spilled a laundry detergent. Of those that could remember ever spilling some, four out of five reported that the amount spilled was no more than one cup, with the majority of these reporting a few granules or a few spoonfuls at most. The largest spill reported was estimated to be about 2 lb. of detergent that spilled out when the housewife stumbled over a box sitting on the floor.

There is an additional factor of significance in the consumer dust exposure situation: the particle size of any dust that consumers might be exposed to in home use is relatively large. Specifically, only about 4–6% by weight of dust generated in consumer use was found to be less than 15 μ in diameter while a maximum of only 0.2% dust was found to be less than 5 μ. (Particles larger than 5 μ are generally considered to be too large to be respirable.)

These findings are fully consistent with the very low persistence of consumer dust. Thus, to the extent that dust particle size and respirability is of significance from the standpoint of safety to the respiratory system, consumer dust is even farther from representing a safety concern than the minuscule exposure estimates suggest.

Another important finding is that enzyme concentration in consumer dust decreases as particle size decreases. Specifically, it has been determined that there is only ⅛ the percentage of enzyme in dust in the 10–20 μ range compared to the percentage in the complete finished laundry detergent, and only 1/10 as much in the 5–10 μ range. Since there was essentially no detergent dust generated smaller than 5 μ, enzyme levels in this particle size range were not determined.

In our research and development laboratories there are many laundry technicians who perform successive home-type laundry operations all day long. These people have the same kind of exposure as the housewife but at a much more exaggerated level. A survey of 93 laundry technicians at several locations in the United States and abroad has been made. Some technicians have done 50–75 washings per week with enzyme products for upward of two years. This corresponds to the laundering it would take the average American housewife 20–30 years to do. None of these people has had any respiratory symptoms or other evidence of inhalant allergy.

Information regarding other respiratory allergies can provide further perspective on the difference between the industrial and consumer situations with enzyme products. Intensity of exposure is an important factor in the development of allergy. Thus, as might be expected, many agents responsible for industrial problems have caused only a very low incidence of problems in the general public. As a specific example, it is reported that a large proportion of bakers and workers in flour mills develop a respiratory allergy to wheat flour (12), but centuries of experience have shown flour to be completely safe for use by the general public. Since this example is similar to that which exists between the industrial and consumer situation with enzyme laundry detergents, a comparison of consumer exposure to flour in home use vs. enzyme exposure in laundry product use was made. Flour dust was collected in an appropriate manner with a precipitator during the making of two loaves of bread and a batch of cookies. In the 30 min required to prepare the bread and cookies, the potential consumer inhalation of flour was 3830 and 2690 μg of flour, respectively, or (on average) about 300,000 times the upper 95th percentile level of enzymes to which housewives are exposed during one week's use of enzyme laundry products. The medical significance of this finding is not known, but these results at least serve to put dimensions on the very low levels of enzymes to which consumers of laundry products are exposed.

The several years of trouble-free consumer use of enzyme laundry products previously was mentioned as being very meaningful evidence of the safety of these products. Although enzyme products have been in use several years longer in Europe than the United States, the Procter & Gamble Company has gained considerable experience over two years of marketing these products in the United States. The few instances of consumer reports on symptoms suggestive of an allergic reaction have been carefully studied, including clinical investigations by physicians whenever possible. Similar investigations were carried out as part of pre- and post-marketing consumer usage tests of the products. During this entire period enzyme products have been used by many millions of people, yet this continuing program of surveillance has revealed no case of allergy or other respiratory problem traceable to their use (13).

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