Detergent Enzymes — Past, Present and Future

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Enzymes are not a new phenomenon. They play a key role in all fermentations — from anibiotics to the manufacture of cheese, to say nothing of all living processes. Enzymes are a vital part of our lives.

Enzymes were first used in laundry wash products more than 50 years ago in Germany in a product sold under the trade name Burnus. From an historical point of view, enzymes as home laundry product ingredients are considerably older than the major chemicals found in laundry products today.

Although Burnus did not achieve great success by contemporary standards, it did endure in several European markets for over 50 years. The product consisted mainly of soda ash and small amounts of pancreatin — a crude mixture of enzymes derived from the pancreatic glands of animals. However, its proteolytic activity was low due to the relatively high alkalinity of the wash water which damaged the activity of the enzymes.

Years later, during World War II, enzymatic washing agents attained importance because of the severe shortages of fats and soap. Scientific interest in Switzerland during the 1940s was spurred by reports that enzymes could be used to reduce soap consumption. As the 1940s came to a close, the high demand for pancreatic glands for the manufacture of insulin limited the use of trypsin in laundry products. The relative instability of pancreatic enzymes in the presence of laundry wash ingredients led scientists to conclude that an enzyme derived from a bacterial fermentation would offer advantages over the pancreatic trypsin. This new enzyme, a neutral bacterial protease, was a significant improvement over the trypsins, but still had relatively poor stability in the pH range of 9-10.

Around this time the first alkaline stable proteolytic enzyme was developed in Denmark from the microorganism *Bacillus licheniformis*, a morphological relative of the common soil organism *Bacillus subtilis*, and marketed under the trade name Alcalase®.

Detergent enzymes gained steadily in Europe throughout the late 1960s (Fig. 1). From a technological point of view, enzymes were to the 1960s what optical brighteners were to the 1950s for the laundry industry in Europe.

Over 20 years after its original development, alcalase and its congeners continue to enjoy widespread acceptance throughout the world and serves as a reference standard in the investigation and evaluation of new detergent enzymes for protein related stains.

The properties of detergent enzymes that determine performance in laundry products are: pH dependence, thermal reactivity, a relative nondependence on calcium or magnesium ions for performance, and compatibility with surfactants and the sequestrant builders.

For an enzyme to perform viably in laundry detergents, it should be stable in the presence of sequestrants (Table I).

Figure 2 provides a comparison of the calcium binding ability of STP and NTA covering the pH range of 6-12. The performance of detergent enzymes at various conditions of alkalinity as expressed by the pH is equally important when considering final performance.

MARKET DEVELOPMENT OF HEAVY DUTY ENZYMATIC LAUNDRY DETERGENTS IN THE U.S. — EUROPE AS A % OF TOTAL MARKET

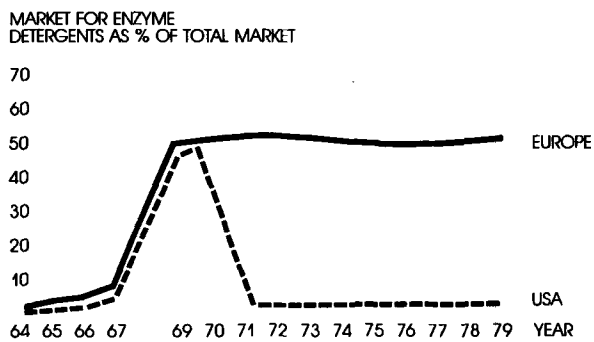

FIGURE 1

TABLE I

Stability of Alkaline Proteolytic Enzymes in the Presence of Calcium Ions and Sodium Tripolyphosphate (STP)

Enzymes	Residual activity in % after 30 minutes 122 F & pH 9.0	
	0.01 $MCaCl_2$	0.1% STP
Pancreatic trypsin	94	11
Bacterial Proteases		
Alcalase	98	44
Esperase	97	89

COMPARISON OF CALCIUM SEQUESTRATION ABILITY OF STP AND NTA $Na_3 \cdot H_2O$

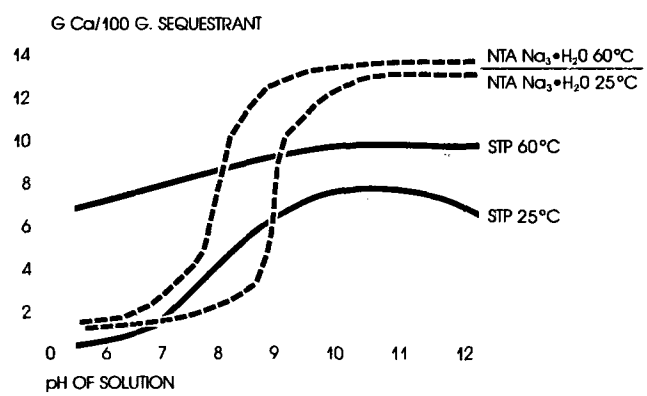

FIGURE 2

The chemical activities of the alkaline protease, Alcalase®, is shown in Figure 3.

Figure 4 shows the higher alkaline properties of Esperase® – an even more alkaline active proteolytic enzyme introduced into laundry products in the 1970s. Both Alcalase® and Esperase® demonstrate the conformance to the pH performance demands of the well known laundry builders including STP, NTA and sodium carbonate.

Another point is that performance is a function of time, temperature and concentration within limits of an enzyme's optimum thermal activity. Enzyme performance increases with either temperature or increased enzyme concentration.

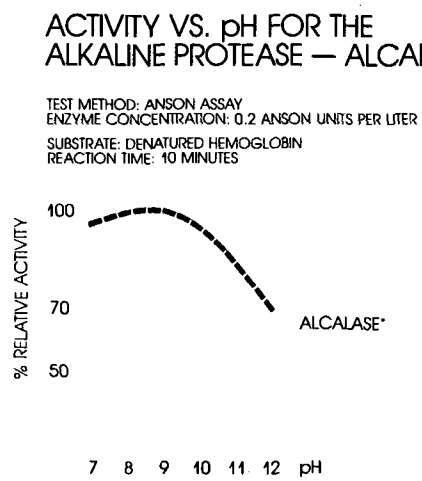

FIGURE 3

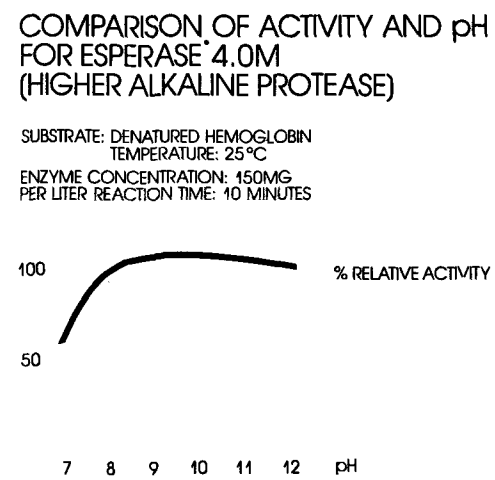

FIGURE 4

Using 122 F (50 C) as a typical hot water condition in this country, the amount of enzyme required to produce the same degree of hydrolysis or protein degrading action at 100 F (38 C) is approximately twice the concentration at the higher temperature.

Laundry washing temperatures determine the performance objectives and therefore the level of enzyme formulated into the product.

There is a considerable difference in the laundry wash water temperatures in different countries. Water temperatures are considerably lower outside of Europe where a hot water temperature of 200 F (94 C) is not uncommon. In this country, water may range from 65 F (18 C) to 125 F (55 C). In Japan, a water temperature of 68 F (20 C) may be usual. Of course, washing cycle times, machine design, to say nothing of the fabric trends, affect laundry detergent washing performance.

Over the past 15 years, countries in the hot water zones have been the largest market for detergent enzymes.

The difference in the washing conditions in different regions of the world with regard to actual time in the washing machine and average temperature will affect the type and also concentration of detergent enzyme.

In this country, there are a variety of laundry products in addition to heavy duty detergents. Two criteria to be considered in formulating enzymes into a laundry product are immediate or reactive compatibility and also the stability or shelf-life over the life of the product. Today a heavy duty detergent liquid may be found on a supermarket shelf in a number of product types. These include: nonbuilt liquids – usually having a high nonionic surfactant system and relatively mild alkalinity; built liquids – these are higher in alkalinity and may be either further divided into phosphate and nonphosphate categories; or liquid detergents containing fabric softeners.

Most laundry products in the market today, although not all, are compatible with detergent enzymes.

Enzymes can be formulated into nonbuilt products with a water content of between 40 and 60%. Liquids containing builders generally are not a stable matrix for enzymes primarily due to sequestering of the divalent cations needed for the stability of the enzyme molecules in the solution. A second factor affecting the poor stability of enzyme in built liquid detergents is the higher alkalinity of the formulation. This latter factor is not as critical for the enzyme's stability since it is possible to formulate around this problem by moderating the degree of alkalinity and by the selection of the most suitable alkaline active detergent enzyme. The effect of sequestering agents on the stability of alkaline proteases is demonstrated in Table II.

Enzymes are not stable in liquids containing organic fabric softeners due to the reaction of the cationic fabric softener with enzyme when exposed in solution over extended periods of time.

Aqueous liquid prewash products can use the stain dissolving properties of detergent enzymes provided the total water content is less than 60%. This is due to the stability requirements of the enzyme when stored in solution for

TABLE II

Stability of Several Alkaline Proteolytic Enzymes in the Presence of NTA

Enzyme	% residual activity after 30 min 130 F at pH 9.5	
	0.03% NTA	0.1% NTA
Pancreatic trypsin	28	32
Alcalase	71	50
Esperase	73	70

long periods of time.

Enzymes should never be considered for use in gas-driven aerosol products because of the possibility of enzyme inhalation. Enzymes are not compatible with chlorine compounds such as hypochorites and cyanurates. The activity of Alcalase in a solution of hypochlorite shows rapid inactivation of the protease after 5 minutes at 100 F (38 C) about 2 ppm available chlorine.

In the case of peroxygen compounds, detergent enzymes do exhibit compatibility when incorporated in granulate powders. However, in liquid products, the enzyme deteriorates and loses activity when stored for an extended period of days. Subject to these various limitations, detergent enzymes do offer an effective role in many of today's laundry products and the future look quite promising.

Enzymes and Safety

Before an enzyme is formulated into a laundry product, it is necessary to consider its toxicological properties in detail. Extensive screening studies must be performed to ensure suitability of a particular enzyme product.

Concern for safety does not end at the enzyme product's design and manufacture. This concern takes on the form of product education, surveillance and monitoring recommendations that are passed on to and maintained by the laundry detergent producer. Since the early 1970s, detergent enzymes have been manufactured in encapsulated granular form to suppress the emission of airborne enzyme dust in the factor.

The key elements in the proper use of detergent enzymes at the factory level are: routine monitoring of airborne dust in the factory, a well defined program of instruction for the safe and proper handling of this material, and periodic monitoring of employees via medical examinations. Companies not prepared or willing to follow this protocol of safety should not consider the use of detergent enzymes in their factories. This regimen should be adopted by all detergent manufacturers regardless of enzyme usage.

As the world market for detergent enzyme granulate products continues to increase, the burden is on the enzyme producer to increase production efficiencies without sacrificing quality. In this regard, let's look at a recent breakthrough in enzyme granulate technology. Novo's flagship "T" granulating facility employs the latest in advanced encapsulating technology. The design of the equipment was done internally by company staff engineers and incorporates the latest concepts in computer technology, automation and gravity aided flow control.

The detergent "T" granulate produced in this new facility offers an improvement over the existing encapsulated granulates is what we call "friability." This is the property of elasticity of the granulate to flex or yield to mechanical stress. This elastic characteristic contributes to an even further reduction in possible dusting that can result when the granulate particles are broken by mechanical abrasion.

Product forms of this type will contribute even further to the record of safe usage of enzymes in detergent factories. It is important to note, however, that granulation technology employing even these latest techniques in encapsulating are not, nor were they intended to be, a substitute for good manufacturing practices in the factory.

Where do we go from here? What will the 1980s offer to the laundry product formulator in terms of new enzyme products and performance advantages?

We can only offer clues since the decision on product ingredient selection is ultimately up to the major formulators in the industry.

There are, however, trends in laundry washing, for example, lower wash temperatures that are putting greater demand on the performance of laundry detergents. Stains that years ago yielded more easily to the hot water temperatures are more resistant in lower wash temperatures. It is, therefore, possible to speculate that enzymatic detergents of the future will be multienzyme-systems which will include not only proteases for protein soil but also lipase for animal and vegetable oil soils, amylases for starch containing soils and possibly even other enzymes for both the hydrolase and oxidase categories. Researching new enzymes is a long term, high risk venture with no guarantee of success after years of effort and investment.

Over the seven-year period from 1976 to 1981, Novo's capital investment has exceeded income in five of the six years.

Other Aspects of Enzyme Technology and Research

Organisms have been found that attack or modify hydrocarbons and it may be possible, in the future, to isolate and identify enzyme complexes from these organisms that will breakdown waxy paraffin substances as well as linear hydrocarbon enzyme catalysts would be of considerable value to many industries.

Another area of interest in the future may be the production of carbohydrate-based surfactant systems from natural products. Enzymes could play a critical role in such technology starting with the production of glucose or modified glucose polymers. Commercially, enzymes have a largely unexploited potential in the field of organic synthesis, i.e., as a catalyst for converting smaller molecules into larger chemical compounds having specific functional properties.

Another area is the modification of protein molecules into functionally more valuable compounds to produce surfactant properties. Using enzyme technology that is already established. As an example, proteins are converted into shorter chain length polypeptides. These peptides have better water solubility and also surfactant properties. By linking these compounds to lipophilic chemical groups — new families of surfactants can be developed.

Lipolytic enzymes have been identified are capable of removing one, two and even all three of the fatty acid side chains on the triglyceride molecule of both animal and vegetable fats and oils. The technology of enzymatic lipid transformation offers a very real potential for this decade.

One novel example of lipid-related enzymatic transformation is an enzyme which Novo isolated from the pancreas of animals: phospholipase A-2. Enzyme selectivity removes the second fatty acid ester from the triglyceride structure in the phospholipid lecithin. The reaction product was found to improve surfactant properties. This is just an example of how we may employ enzymes in the future to improve the usefulness of raw material products.

We are only beginning to appreciate the potential of enzyme biotechnology in the transformation of organic molecules into more useful (and valuable) compounds.