Cotton fabrics in the U.S. have been largely replaced by synthetics (mainly polyester) or blends of synthetics with cotton. The blends are almost always treated with one or more polymeric materials to impart a "durable press" finish, soil-release properties and softness. These fabrics differ considerably from cotton in their susceptibility to particulate and oily soil redeposition. SCMC is only slightly effective or completely ineffective in preventing soil redeposition on these newer fabrics. Oily soil redeposition is a particular problem for synthetics and blended fabrics and has been mitigated to some extent by the treatment of these fabrics with various soil-release finishes at the textile mills. Nevertheless, oily soil redeposition on synthetics and blends, and release of oily soils and stains from these fabrics, continues to be major problems in laundering.

Greminger et al. (14) described experiments in which cellulose ethers such as methylcellulose, methyl hydroxypropyl and methyl hydroxybutyl cellulose were tested as antiredeposition and soil-release agents for polyester fabrics. Their data show considerable benefits for the addition of these cellulose ethers to a nonionic/carbonate detergent. In this particular example, the interaction between the surfactant and the hydroxybutyl methylcellulose was stated to be the critical factor in achieving antisoiling on polyester fabric. Their review of the patent literature points to a trend of using nonionic cellulose ethers containing increased levels of hydrophobic substitution to achieve both improved antiredeposition and soil release on synthetic fibers such as polyester.

Greminger (personal communication) noted that significant commercial acceptance of hydroxybutyl methyl cellulose as a detergent additive has resulted in the commercialization of this product.

Current research on methyl cellulose and its modifications involving interfacial tension measurements, using the spinning drop technique which allows observation of equilibria factors, show a correlation between the degree, the distribution, and the hydrophobicity of the substitution on the cellulose background, and the key benefit of inhibition and removal of oily staining on polyester and other synthetic fabrics (G.K. Greminger, Jr., personal communication).

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Detergent Enzymes: Developments during the Last Decade

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ABSTRACT

The decade of the seventies saw dramatic changes in the formulation of heavy duty laundry detergents. The reduction in the STPP content in laundry product formulations was a notable example. During the early 1970s, heavy duty liquid laundry detergents were introduced and today represent an estimated 20% of the heavy duty laundry detergent market. A significant trend during this decade toward lower wash temperatures also appeared. These developments in home laundry products and washing trends have been followed by collateral developments in detergent enzyme technology. During the 1970s, a new generation of high alkaline, active detergent enzymes were developed. This new group of alkaline proteases were characterized by greater activity and stability under conditions of alkalinity between pH 10.5 to near 12, thus favoring phosphate-free detergent formulations. These enzymes also were found to exhibit superior stability in nonbuilt liquid laundry detergent systems. Safety considerations at the plant operation level have resulted in a continual improvement in the quality of coated and encapsulated detergent enzyme granulates. During the past 10 years, detergent enzymes have passed through three generations of physical forms, from the powders to prills to encapsulates. The decade of the 1980s offers exciting possibilities for enzymatic laundry products. The trend toward lower wash temperatures, caused initially by the popularity of synthetic fabrics, is being compounded by a radical reappraisal of household energy consumption patterns. In this new atmosphere of energy conservation, detergent enzymes will offer energy-saving options in an assortment of laundry products. Finally, as we start this decade of the 1980s, the spiralling cost of petrochemical feedstocks will cause us to rethink laundry product formulations and here again, detergent enzymes offer an important alternative for the future.

Laundry detergent products have undergone changes in product formulation over the last 10 years. These changes have been well publicized (1), especially with regard to the shift toward reduced and zero-content sodium tripolyphosphate formulas (2). The trend to lower phosphate laundry products brought with it substitution or replacement builders, including sodium carbonate, sodium silicate, zeolite, NTA and others.

Another important development during the 1970s was the major growth of heavy duty liquid detergents. Liquid laundry detergents have gained substantial acceptance in the American household and, as the decade of the seventies closed, this product group held an estimated 20% market share (3). These liquids consist of two groups: those with builders and those without.

With the exception of the nonbuilt liquid products, heavy duty laundry detergents emerging in the mid-1970s were notably higher in alkalinity. For example, major U.S. detergent products in 1968 containing 49% sodium tripolyphosphate (4) exhibited a wash water pH of ca. 9.2. A "phosphate-free" heavy duty laundry detergent powder found in 1978 could usually be expected to have an initial wash water pH of 10 or higher. Technological developments for detergent enzymes during the 10-year period between 1970 and 1980 followed the developing trends toward higher alkaline products in the powdered laundry detergents. In addition, detergent enzymes were found to exhibit compatibility in some nonbuilt liquid products (5).

PERFORMANCE OR EFFICACY, STABILITY AND SAFETY

Consider just the properties of detergent enzymes that determine performance and efficacy. The older, and still quite popular, detergent enzyme used during the seventies is an alkaline, active proteolytic enzyme derived from *Bacillus licheniformis*. This enzyme is characterized chemically as a serine protease because it has the amino acid serine at the active site in the molecule of the protein substrate (6).

Figures 1 and 2 show the difference between wash efficacy and chemical activity for the alkaline detergent protease, ALCALASE. There is an identifiable difference between simulated wash performance and controlled reactivity in the ideal chemical environment of the test tube. For example, using the chemical assay procedure based on the hydrolysis of denatured hemoglobin substrate, the alkaline activity for ALCALASE is characterized, under carefully controlled chemical conditions, as being active in the pH range of 7 to ca. 11, while at the same time retaining over 80% of the enzyme's relative activity.

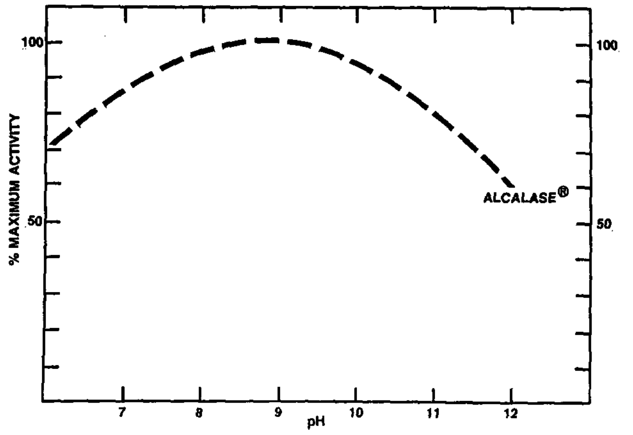

FIG. 1. Activity vs pH for the alkaline protease–Alcalase®. Test method, Anson assay; enzyme concentration, 0.2 Anson units/ℓ; substrate, denatured hemoglobin; reaction time, 10 min.

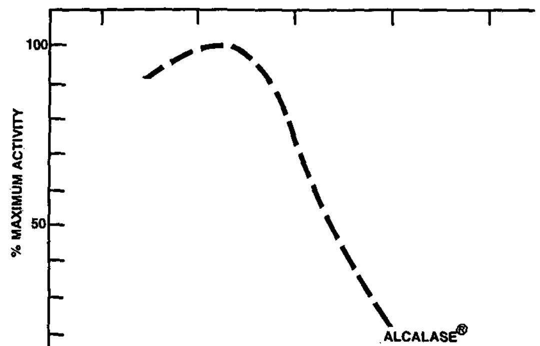

FIG. 2. Relative effect of pH on stain removal with Alcalase®. Test method, Anson assay; test cloth, EMPA 116 (blood, milk, ink); test, CSMA wash test; enzyme concentration, 0.2 Anson units/ℓ; detergent concentration, 2 g/ℓ.

However, when the activity or performance is examined under simulated wash conditions using the Terg-O-Tometer CSMA wash test on EMPA 116 test fabric, the enzyme activity assumes a somewhat different profile, especially under conditions of alkalinity above pH 10.2.

This fact becomes more relevant in context with the phosphate-free powdered formulations introduced in the 1970s which resulted in higher alkaline wash conditions. Examination of the thermal stability of this enzyme in Figure 3 demonstrates why the alkaline proteases are suitable for laundry wash conditions. In the area of exposure at 50 C for 10 min, ALCALASE is quite stable.

During the early 1970s, a series of newer, second generation alkaline proteases were investigated for laundry detergent formulations (7). As a result of this research, even higher alkaline active and stable proteolytic enzymes under the trade names ESPERASE and SAVINASE were developed for the industry. Figure 4 shows the biochemical activity, again based on the reduction of denatured hemoglobin, of the newer, higher alkaline protease, ESPERASE. This enzyme has a higher affinity for alkaline conditions, especially in the 10-11.5 pH range.

Figure 5 compares the washing profile with regard to pH for both ALCALASE (shown previously in Fig. 2) superimposed on ESPERASE, again using EMPA 116 test cloth. The detergent formulation also is included in this figure. Obviously, the higher alkaline enzyme is especially suited for the more alkaline formulation.

The chemical properties for two generations of bacterial alkaline proteases have been considered thus far in terms of relative activities under controlled analytical conditions and also under simulated wash conditions on protein stains.

Next, consider enzymes for heavy duty liquid detergents. In the beginning of the 1970s, it was discovered that two higher alkaline active proteases, ESPERASE and SAVINASE, exhibited improved stability in nonbuilt heavy duty liquid laundry detergent formulations (8). Examination of commercially available liquid laundry products to which the enzymes had been added indicated that the activity was maintained between 70 and 90% of the original activity after 6 months storage at room temperature. Working with both commercial and simulated nonbuilt liquid detergents, a significant improvement in stain removal was noted, again with the Terg-O-Tometer wash test on EMPA 116 test swatches (blood, milk and ink on cotton fabric) with the higher alkaline detergent enzymes.

The high alkaline stable and active enzymes added to overall performance by improving the liquid detergent's stain removal action on protein stains, both in the wash and when used simultaneously as a prespotting liquid.

Further investigations yielded information on the influence of some of the components commonly used in nonbuilt liquid formulations upon the stability of the enzymes. For example, the stability of SAVINASE was less sensitive to a higher water content than ESPERASE. On the other hand, the stability of ESPERASE at 37 C proved to be more sensitive to a water content of 44%. In general, the stability of ESPERASE was more sensitive to a higher water content in these formulations (9).

Factors affecting the stability of the higher alkaline active enzymes in liquid laundry products are therefore: (a) water content of the liquid system, (b) native pH of the liquid, (c) presence of chelating agents or liquid builders, and (d) surfactant system.

A review of detergent enzymes would be incomplete without at least a brief discussion of amylases. As a class, amylases represent one of the older commercial microbial-derived enzyme products found in industry. One method of classification of this enzyme group is by the living source. Generally, these are categorized as either fungal, bacterial, vegetable or animal in derivation. In surveying the commonly available industrial amylases, there is usually a relationship between a group of microorganisms (e.g., bacterial or fungal) and the active optimal pH range. The pH range, as well as availability and price, determine in large part the commercial viability of the enzyme for a particular application.

The well known bacterial α-amylase from *Bacillus subtilis* is characterized by a neutral pH activity profile and optimal thermal reactivity at ca. 170 F (10). This enzyme has had extensive use over the past 40 years in starch desizing for the textile industry, and more recently, for corn starch liquefaction.

In the 1970s, a unique bacterial amylase was developed (11) which exhibited improved tolerance to alkaline conditions. In Figure 6 the difference between the classical, bacterial α-amylase and the newer, alkaline amylase from *B. licheniformis* is described with respect to pH. The newer amylase retains activity at pH 10 whereas the older *B. subtilis* amylase is inactive above pH 9 on the starch substrate. This newer amylase has properties especially suited for chlorine-free heavy duty dishwashing detergents. Studies were performed in Europe using specially prepared dishes soiled with mashed potatoes, skimmed milk, egg yolk and vanilla pudding which had been dried on plates for 16 hr at 60 C. Various formulations were used with and without the alkaline amylase TERMAMYL 60. The results are summarized in Table I. Note on the bottom the scoring scale of 0 (best) to 80 (worst).

Next, consider the physical properties of detergent enzymes and safety conditions. As with all protein compounds foreign to the human body, detergent enzymes in the raw or exposed form have the capability of inducing allergic reactions in susceptible persons. Also, as protein active agents, alkaline proteinases, will cause irritations upon direct exposure to moist skin, eyes and mucous membranes.

The potential allergenicity and irritation has been largely eliminated by incorporating the enzyme in special granulated forms. In this way, the release of the free enzyme in the form of particulate dust, when handled in conjunction with proper ventilation and protective equipment, is virtually eliminated (12,13).

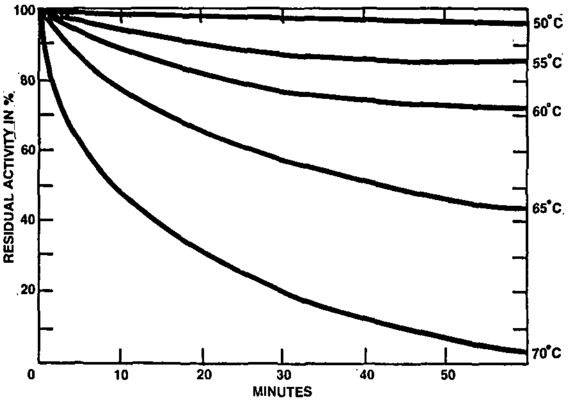

FIG. 3. Stability of Alcalase® at different temperatures. Test method, Anson assay; substrate, denatured hemoglobin; pH, 8.5 (tris-maleate buffer).

In order to better understand the high degree of safety achieved during the 1970s, it is necessary to review the state of the art of enzyme granulation technology as it developed throughout the decade.

Originally, detergent enzymes were introduced as powders, but by 1970, the enzyme was manufactured into tiny spherical-shaped prills. The principal properties of the

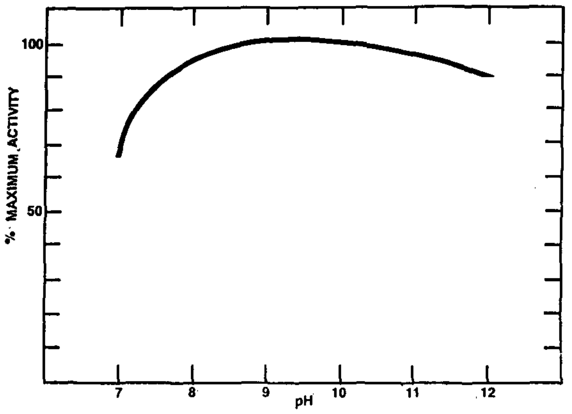

FIG. 4. Comparison of activity and pH for Esperase® 4.0 M (higher alkaline protease). Substrate, denatured hemoglobin; temperature, 25 C; enzyme concentration, 150 mg/ℓ; reaction time, 10 min.

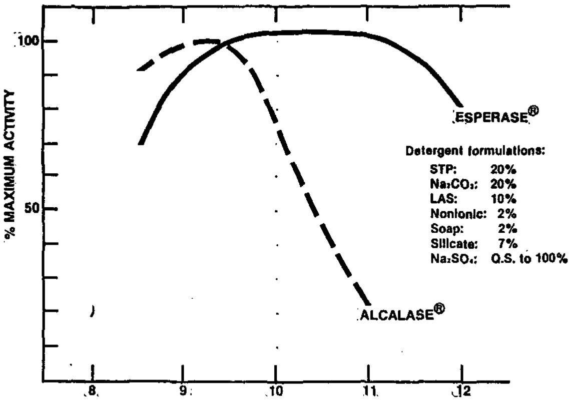

FIG. 5. Comparative stain removal for Alcalase® and Esperase® at different pH values. Test method, CSMA wash test; test cloth, EMPA 116; detergent concentration, 2 g/ℓ.

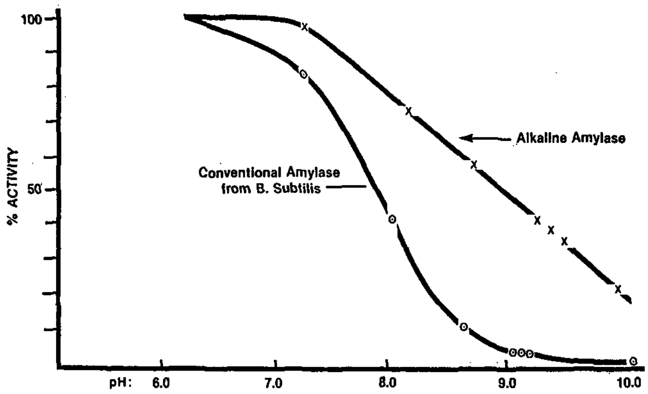

FIG. 6. Activity vs pH for alkaline and neutral bacterial α-amylases. Substrate, Merck starch; solution, 4.6 g/ℓ; STPP, 2.0 g/ℓ; temperature, 60 C.

TABLE I

Heavy Duty Dishwashing Detergent Formulations

Dose: 3 g/ℓ	(%, w/w)				
	A	B	C	D	E
STPP	30.0	–	–	–	26.7
Poly-(hydroxycarboxylate)-sequestering agent	–	62.0	–	–	–
NaPolysilicate (SiO_2/Na_2O = 2.4/ℓ)	–	–	50.0	–	–
Na_3-Citrate × $2H_2O$	–	–	–	30.0	–
Meta-silicate	10.0	10.0	–	10.0	26.7
Na-Bicarbonate	57.0	–	47.0	57.0	43.6
Borax	–	25.0	–	–	–
Nonylphenol-11EO	3.0	3.0	3.0	3.0	3.0

	0 = complete soil removal, best 5 = worst				
Cleaning result (sum of scores)	A	B	C	D	E
Detergent without TERMAMYL	63	75	74	76	73
Detergent with 4% TERMAMYL (60 KNU/g)	24	36	24	21	28

Range of points = 0-80

prill granulates are spherical shape, relatively small particle size and uniformity of composition. That is, the concentration of enzyme is about the same from the center or core to the surface of the particle. Enzyme prills are produced by spray-cooling a liquid mixture of enzyme and nonionic surfactant with a melting point above 38 C. Treatment after spray-cooling further reduces dust emission, e.g., the prill may have an additional organic coating on the surface.

Within several years after the introduction of the "prilled granulates," a second generation granulate was introduced to the international laundry detergent industry. This granulate differed from the prills in that the enzyme components were structured inside the particle with a nonenzyme coated skin of an organic compound and titanium dioxide covering or encapsulating the granulate. Physical properties include slightly elongated shape, core of sodium chloride and an outer "skin" casing of nonenzyme, inert material (14). Commercially, this type of granulate is referred to as an "M" granulate or marum, named for the process.

Finally, the close of the 1970s saw the development of a third generation encapsulated granulate similar in appearance and composition to the earlier "M" granulate, but having even superior properties with regard to resistance to abrasive degradation or "friability" (15).

It may be well to summarize the main advances regard-

TABLE II

Detergent Enzyme Summary

Generation	Optimum performance pH range	Optimum temperature range (F)	Enzyme description
1	7.5-10.5	100-135	Alkaline protease
2	10 -11.5	100-140	Alkaline protease
1	6.5- 8	140-160	Neutral α-amylase
2	7 - 9.5	180-212	Alkaline α-amylase

Granulation Summary

Generation	Description	Primary component
1	Prill	Nonionic surfactant
2	Encapsulate	Inorganic salt, organic binder
3	Improved Encapsulate	Inorganic salt, organic binder

TABLE III

Energy Consumption and Savings

Oil consumed/day for residential water heating = 1,000,000 barrels

Conservation measures	Oil savings in barrels/day
(a) Adoption of cold water laundering	100,000
(b) Replacement of existing water heaters with more efficient units	300,000
(c) Other devices (e.g., shower flow and faucet restricters)	160,000
Total estimated savings in barrels/day	560,000

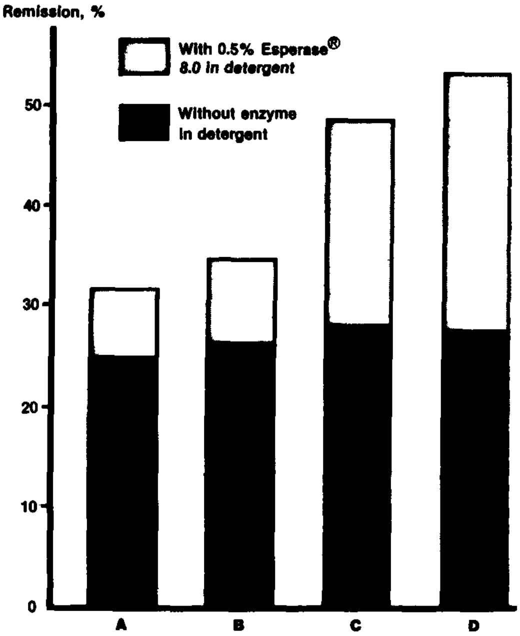

FIG. 7. U.S. cold water wash, EMPA 116. A–U.S. cold water wash (20 min/25 C). B–Soaking 3 hr (20 C) + U.S. cold water wash (20 min/25 C). C–Soaking 17 hr (20 C) + U.S. cold water wash (20 min/25 C). D–Prespotting 10 sec + U.S. cold water wash (20 min/25 C).

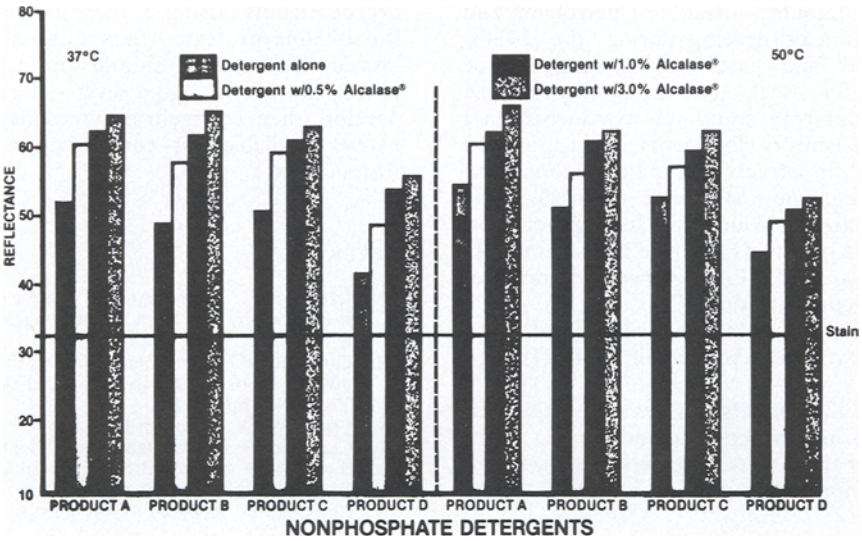

FIG. 8. Effect of enzyme concentration on wash efficacy. Wash conditions, 10 min, Terg-O-Tometer; soil, EMPA 116 (blood, milk, ink on cotton).

ing detergent enzymes during the 1970s. Table II presents a summary of developments during this period. Two new alkaline proteolytic enzymes were introduced. These exhibited superior performance under more alkaline conditions. Also, a more alkaline stable bacterial amylase was introduced. Granulation technology has continued to develop. The detergent enzymes marketed at the start of the 1980s contrast markedly with the detergent enzyme powders in use at the beginning of 1970.

Examine the future and apply the experience of the 1970s to the next decade. Consider, for example, energy savings with lower wash water temperatures. The technological developments of the 1970s offer opportunities for enzymatic laundry products during the 1980s. Concern over future energy availability and the growing need for energy conservation offers possibilities for the application of enzymes, including those for the laundry detergent industry.

In 1977, the concept of employing enzyme detergents for lower energy consuming laundry washing was reviewed (5) at the World Conference on Soaps and Detergents, held in Montreux, Switzerland. Energy savings in the home laundry can be achieved via several methods, including cold- or warm-water presoaking followed by cold-water wash and prespotting treatment of heavily soiled garments with a liquid enzyme laundry detergent, followed by a cold-water wash.

For background, oil consumption in the U.S. for residential water heating has been estimated at one million barrels/day (16). Daily savings in oil of 500,000 bpd should be possible without severely affecting our lifestyles. Table III lists the largest energy savings potential offered by the measures that could be followed.

Figure 7, a simulated wash study was made using the Terg-O-Tometer on EMPA 116 fabric. Clearly, two factors contribute to the removal of protein soil from the test fabric in the absence of heat: time (with presoaking) or a high enzyme concentration on the stain via prespotting.

Finally, consider detergent enzymes as detergent ingredient

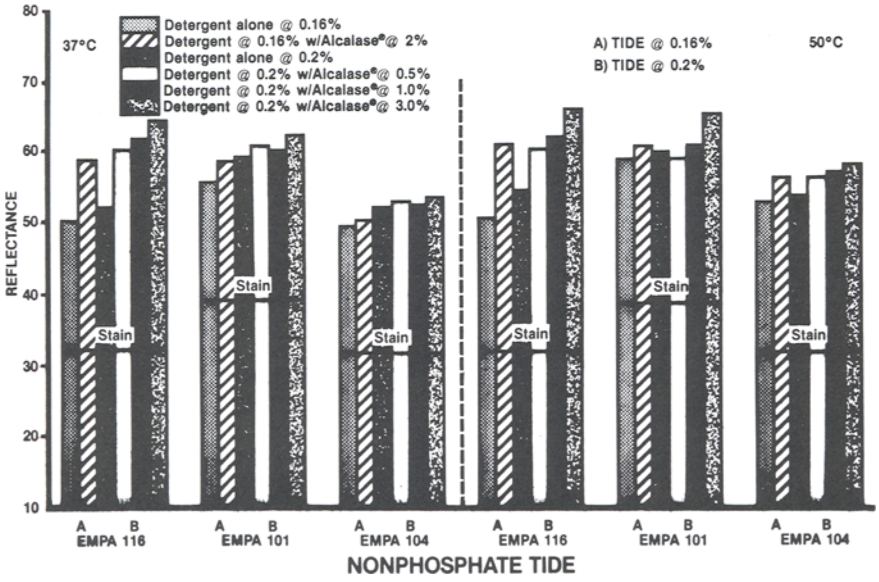

FIG. 9. Effect of enzyme concentration at standard and 20% less detergent levels.

options for the 1980s. Should shortages of petroleum and petroleum-derived chemicals develop during the 1980s, emergency supplements and partial substitutes will be needed in the event that surfactant availability will be limited. In 1978, a laboratory study was conducted on a series of nonphosphate laundry detergents, again using the Terg-O-Tometer, where the effects of expanded concentrations of the detergent enzyme ALCALASE up to 3% in the formulation were evaluated on four of the leading nonphosphate laundry detergent powders (17). The improvement in detergency on protein-soiled EMPA 116 swatches increases with increased enzyme concentration.

Figure 8 summarizes the increased contribution of detergency on a typical enzyme-susceptible soil swatch (EMPA 116).

The performance of all products was favorably enhanced under warm, as well as hot, water wash conditions. Again, it should be noted that these tests were performed without presoaking using the normal 10-min wash period in the Terg-O-Tometer.

Next, studies were made with nonphosphate Tide on the following soil swatches: EMPA 116—blood, milk and ink on cotton; EMPA 101—vegetable oil on cotton; EMPA 104—vegetable oil on polyester/cotton. Again, wash conditions included both hot (50 C) and warm (37 C) water washing (Fig. 9).

The test was repeated at a 2% enzyme level (wt/wt detergent basis) whereas the detergent concentration in the wash water was reduced by 20%. The effect of ALCALASE on protein stain removal at 37 C and 20% less detergent also was significant. Under hot water conditions, detergency was improved at 2% enzyme on oily soil (EMPA 101 and 104). The effect was noted even with the reduced detergent levels (20% less).

Nonphosphate Tide showed improvement in performance on EMPA 116, even at the lower detergent concentrations in the wash water.

This type of study underscores the potential advantages of formulating with high concentrations of enzyme in laundry detergents. Using a lower concentration of surfactant, the alkaline protease offers a partial compensation for the loss in detergency. Should the worst situation happen during the 1980s, e.g., a severe shortage in petroleum does develop, then detergent enzymes may be one of a few alternatives available for consideration by laundry detergent formulators.

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Detergent Builders

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ABSTRACT

A highlight summary of the chemistry of commercial manufacturing processes, relative effectiveness, economic comparison and present uses of the various detergent builders of industrial significance to the soap and detergent industry are presented and reviewed. Builders discussed include the inorganic phosphates, silicates, carbonates, zeolites, and the organic citrates and other polycarboxylate salts (NTA, CMOS and "Builder M").

INTRODUCTION

Detergent builders contribute to improved washing performance in a number of ways (1). They reduce the deleterious activity of hardness ions (Ca^{++} and Mg^{++}) introduced via the wash water and the wash fabric, provide excess basicity to convert sebum fatty acids to effective soaps, which assist in the emulsification and removal of nonpolar components of oily and greasy soils, deflocculate particulate soils, buffer in the optimum detergent pH ranges (9-10.5), and decrease soil redeposition by stabilization of the dispersed soil (adsorption, increased zeta potential).

The complex phosphates became the major builder ingredient in detergents after World War II because of their overall superior ability to perform the functions outlined. By the early 1970s, however, phosphate levels in household laundry products in the USA had been significantly and increasingly reduced because of the eutrophication problem attributed mainly to high levels of phosphates in certain lakes and streams. Legislation in the USA has resulted in many areas of the country allowing essentially no phosphate in household detergent formulations. In Japan, and in Germany more recently, legislation also is resulting in lower phosphate usage.

Considerable research and development activity has been undertaken in the past decade and longer on new organic (2) and inorganic (3,4) builders to replace phosphates in