Technical

The Benefit of Detergent Enzymes under Changing Washing Conditions [1]

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ABSTRACT

The influence of two commercial proteolytic enzymes, Maxatase® and PB-92, were studied viz à viz changing phosphate content and washing conditions. (Maxatase® is a registered trademark of Gist-Brocades N.V.; PB-92 will be sold under the trademark Maxacal™.) In the USA and Western Europe, detergent phosphate content is decreasing because of environmental considerations/legislation. Washing conditions are changing towards lower temperatures because of the increased use of synthetic fibers and the need to conserve energy. Both Maxatase and PB-92 are shown to improve significantly the performance of US detergents, even at temperatures as low as 70 F. This conclusion is based on Terg-O-Tometer tests on EMPA 116 cloth using US detergents and presoak products.

INTRODUCTION

The use of proteolytic enzymes in detergents has been generally accepted in Europe. Nowadays, ca. 80% of the European detergents contain enzymes. The washing conditions in Europe in contrast to those in the United States can be characterized by higher washing temperatures, a longer washing cycle including a warming-up period, a more concentrated washing solution and the use of perborates in the detergent as bleaching agent.

Although the use of enzymes to improve detergents is prevalent under European washing conditions, this is not the case in the USA. Therefore, it is worth investigating to what degree these enzymes could contribute to the performance of US laundry products under present and future washing conditions. Two major trends in the present market for laundering products are apparent: first, a move towards lower washing temperatures; secondly, a change in the composition of the laundry detergents to lower phosphate levels.

The change towards lower washing temperatures is the result of the growing use of synthetic fibers and energy conservation. In Western Europe, it is expected that the average washing temperatures will decrease further during the next five years as is shown in Table I (A.M. De Jong, Gist-Brocades N.V., Delft, Holland, personal communications).

Between 1985 and 1990, washing at the boil will be reduced by half; 25-30% of the washings will be carried out at temperatures up to 40 C (104 F).

In the United States there has been a shift from hot water washing to warm water washing over the past 10 years. Table II shows that by 1985 the percentage of wash loads using hot water will be cut in half, whereas the percentage of cold water washing will increase proportionally (1).

A second trend is the changing composition of the laundry detergents. Environmental considerations led to the partial or complete replacement of phosphates by other sequestrants or alternate builders. A commonly employed builder system in zero-phosphate detergents is a carbonate/silicate mixture. Zeolites now play an important part in the detergent formulation (2).

[1]Paper presented by F.W.J.L. Maase at the 72nd AOCS annual meeting, New Orleans, 1981.

TABLE I

Washing Temperatures in Western Europe

	% of wash loads	
	1980	1985/90 (estimated)
+/- 90 C (195 F)	40-50	20-25
+/- 60 C (140 F)	30-35	+/- 50
≤ 40 C (105 F)	15-20	25-30

TABLE II

Washing Temperatures in the USA

	% of wash loads	
	1980	1985 (estimated)
Hot (50-55 C/120-130 F)	20	10
Warm (30-40 C/85-105 F)	60	60
Cold (15-30 C/60-85 F)	20	30

In Europe, the situation with regard to the use of phosphates differs from country to country. In ca. 40% of the Western European laundry detergent's market, a reduction in the phosphate level is taking place either voluntarily or enforced by legislation.

This situation does not differ much from the one in the United States, where in ca. 40% of the detergent's market nonphosphate products are sold. In 22% of the market this is due to a phosphate legislative ban (1).

As a result of the changed composition of the laundry detergents, the pH of the washing solutions shows a marked increase of 0.3-0.5 pH units to values above pH 10 (3). Both this pH change and lower washing temperatures are expected to show an effect on the action of detergent enzymes.

The purpose of this paper is to show the effects of these changing washing conditions on the performance of two commercial proteolytic enzymes: the alkaline protease Maxatase, and a new high alkaline protease which was recently developed and was given the code name PB-92.

MATERIALS AND METHODS

Enzymes

The enzymes used were: Maxatase, Gist-Brocades' alkaline protease, and PB-92, Gist-Brocades' high alkaline protease.

The enzymes are commercially available as dust-free encapsulates as well as in liquid form.

Detergents

US heavy-duty detergents, either phosphate or zero-phosphate, were used. The influence of a US presoak product the US cold water wash for 30 min was superior to that of the other conditions shown. The addition of the enzyme Maxatase to the heavy-duty detergent increased the remission value by as much as 80% in the case of the hot (122 F) water wash in Figure 3.

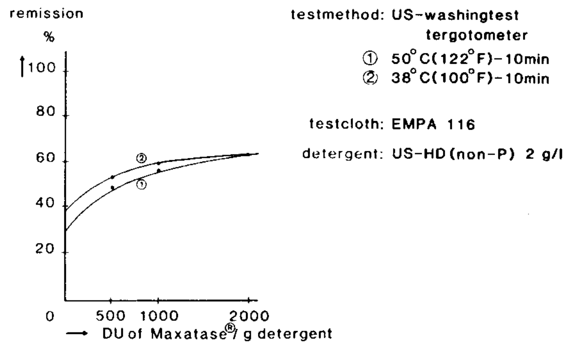

FIG. 2. The effect of the addition of Maxatase on the washing result.

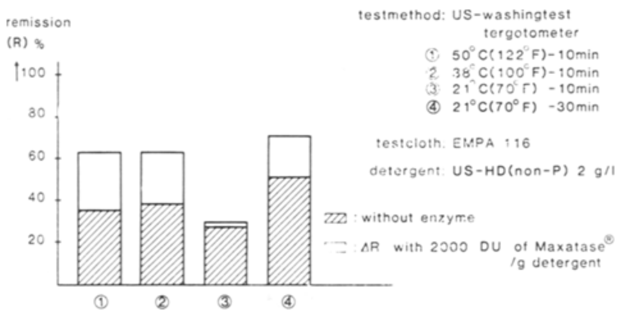

FIG. 3. The effect of the washing temperature and time on the cleaning result (Maxatase).

This contribution of the enzyme, expressed here as delta remission, depended on the temperature and the wash time: the effect was greater at 122 F than at 100 F and 70 F. The effect after 30 min at 70 F was greater than after 10 min at the same temperature.

The influence of the temperature of the washing water was less pronounced when using the new enzyme PB-92, which is presented in Figure 4. The overall result at 100 F (second column) in this case was slightly higher than that at 122 F (first column). Even under cold washing conditions the remission value was improved by 25% of the level of the detergent without enzyme. This experiment indicates that the new enzyme PB-92 is suitable for improving detergency at moderate and low temperatures.

The influence of wash time can be demonstrated when using a presoaking procedure. Presoaking is practiced in the USA and special presoak products were developed to meet this need. As the degree of enzymatic breakdown of the protein stains is proportional to the reaction time, it is obvious that prolonging the reaction time by introducing a presoaking procedure will have a favorable effect on the results.

In Figure 5, the effect of the addition of Maxatase in a presoaking procedure for 16 hr at room temperature is presented. The detergents used in the test were a US heavy-duty detergent and a US presoak, both containing phosphate. The addition of the enzyme improved the performance of these detergents on the protein-soiled test cloth by 65-90%. The maximum level reached was almost equally high in both cases. In case of the presoak, curve no. 2, only 1 g of detergent per liter was used, therefore the base performance was at a lower level. It is interesting to note that in the latter

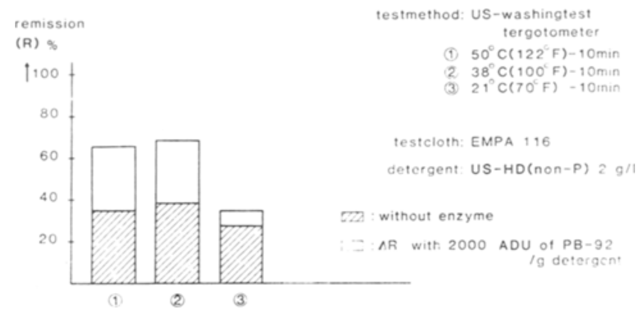

FIG. 4. The effect of the washing temperature on the cleaning result (PB-92).

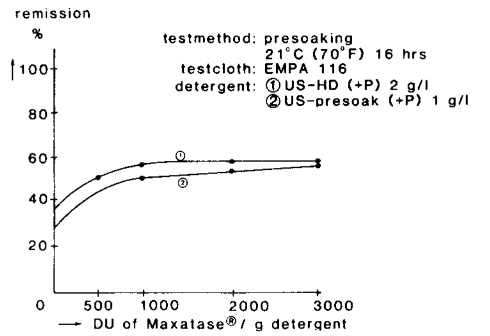

FIG. 5. Presoaking: the effect of the addition of Maxatase on the washing result.

case the enzyme's contribution to the performance was greater.

How a presoaking step relates to a normal wash period is shown in Figure 6. A comparison has been made between presoaking and cold and warm water washing.

The overall washing result of presoaking with an enzymatic detergent was between the results of a cold water wash during 30 min, the column on the left, and a warm water wash during 10 min, the column on the right. Thus, presoaking with a detergent containing Maxatase offers an alternative for getting good washing results at low temperatures.

The reduction of the phosphate content of laundry detergents may lead to a reduction in cleaning performance, since phosphates not only act as a sequestering agent but also make a positive contribution to the total detergency of the formulation. This is shown in Figure 7, in which the washing performance of a US heavy-duty detergent with or without phosphate is presented under different washing conditions.

The reduction in cleaning performance of a nonphosphate detergent can be compensated to a great extent by the addition of a detergent enzyme as presented in Figure 8. The

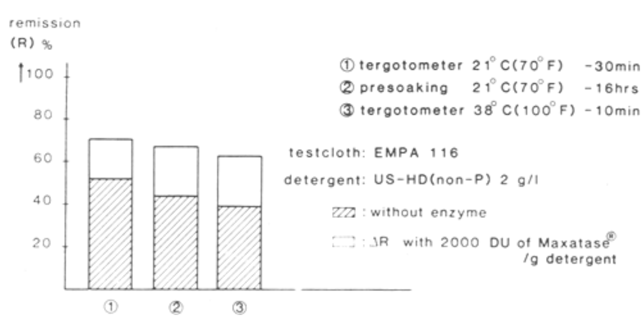

FIG. 6. Presoaking vs US warm/cold water washing (Maxatase).

was also studied. The detergents were dissolved in synthetic tap water of 15° German hardness.

Test Material

As test material EMPA 116, cotton homogeneously soiled with blood, milk and black ink was used. The material was obtained from the Eidgenössische Materialprüfungs- und Versuchsanstalt für Industrie, Bauwesen und Gewebe, St. Gallen, Switzerland. It is generally accepted that the effect observed on this test cloth correlates well with the results in practice.

Washing Procedures

US washing test. US washing tests were carried out in a Terg-O-Tometer. This laboratory washing machine contains four 1-L beakers placed in a thermocontrolled water bath. During washing, vigorous agitation was achieved by four stirring devices (one per beaker) that move back and forth (100 rpm). Each beaker contained two EMPA pieces of test cloth of 10 × 12 cm.

Gist-Brocades washing test. This European washing test was done in conical flasks containing 250 mL of suds. The concentration of the heavy-duty detergent was 4 g/L. The flasks were kept in a water bath at 45 C (113 F) for 60 min where occasional agitation took place. Each flask contained one EMPA piece of test cloth of 5 × 5 cm.

Reflection (remission) measurement. After washing, the test clothes were rinsed with tap water for ~ 15 min and dried between filter paper. The whiteness was measured at both sides of the swatches at every corner using an Elrepho reflectometer. The average value of 16 measurements was expressed as a percentage of the reflection of a piece of test cloth that was washed and bleached as clean as possible. The reflection value of this specially treated piece of test cloth (70% when measured versus MgO) was arbitrarily set at 100%. Graphs were generally obtained by plotting the amount of enzyme, expressed as DU (Delft units) or ADU (alkaline Delft units) per gram of detergent, versus the percentage of remission (reflection).

Determination of Proteolytic Activity

The proteolytic activity of Maxatase and PB-92 was determined according to the Delft method at pH 8.5 and 10.0, respectively, using casein as a substrate at 40 C for 40 min, after which the enzyme activity was stopped by the addition of trichloroacetic acid. After filtration, the optical density was read at 275 nm. Enzyme activity assayed at pH 8.5 was expressed as DU and as ADU in case the incubation pH was as high as 10.0.

The DU and the ADU are arbitrary units which are defined as follows. If one mL of a 2% solution of an enzyme preparation gives a Δ optical density of 0.400 under the test conditions, the enzyme preparation has a protease activity of 1,000 DU/ADU per gram.

Experimental Set-Up

Well known US heavy-duty detergents and presoaks were used either with or without phosphates in Terg-O-Tometer washing tests at different temperatures and times with different amounts of both enzymes. The experimental protocol is presented in Table III.

RESULTS AND DISCUSSION

Maxatase and PB-92 have different pH profiles (4,5). Compared to alkaline proteases, like Maxatase, PB-92 has a relatively high pH optimum. This indicates that PB-92 is suitable for use in more alkaline detergent formulations. This is demonstrated in Figure 1, in which the results of an European washing test at different pH values are shown.

The results, expressed as a percentage of maximum value, showed a better performance of PB-92 as compared to Maxatase, at pH values above 8.5. PB-92 showed fine washing results in a broad pH range from pH 8 to 11.

The effect of the addition of Maxatase to a nonphosphate heavy-duty detergent in a US hot (122 F) and warm (100 F) water washing test is shown in Figure 2. The curves represent the effect of an increasing concentration of the enzyme in the detergent. The detergent enzyme contributed significantly to the performance of this detergent. It can also be seen that the effect of a warm water wash at 100 F, at the highest concentration of the enzyme applied, was almost equal to that of a hot water wash at 122 F.

The contribution of the detergent enzyme Maxatase to the cleaning result can also be observed in Figure 3. The effect of different washing temperatures and times on the cleaning result is presented. The result in remission value of the detergent with and without 2,000 Delft units of Maxatase per gram of detergent is given. Cold washing, using water of 70 F, for 10 min gave unsatisfactory results, as shown in the third column of this graph. However, by prolonging the duration of the washing cycle from 10 to 30 min, the result could be improved as shown in the fourth column of Figure 3. It is evident that the overall result of

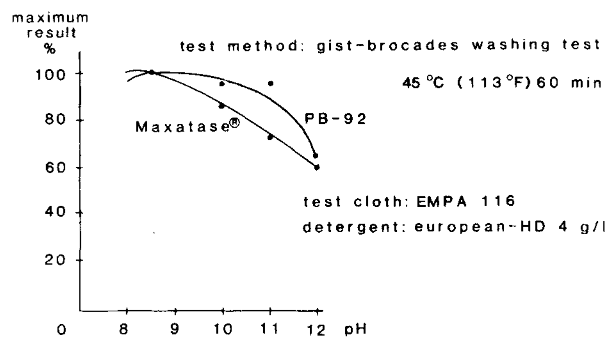

FIG. 1. The effect of pH on washing result (Maxatase vs PB-92).

TABLE III

Experimental Set-Up

Detergent	Dosage (g/L)	Temperature 70 F (21 C)	100 F (38 C)	122 F (50 C)
		Time (min)		
US heavy-duty nonphosphate	2	10/30/960[a]	10	10
US heavy-duty phosphate	2	10/30/960[a]	10	10
US presoak phosphate	1	960[a]		

Enzymes: either Maxatase® or PB-92. Enzyme dosage: 0-500-1000-2000 DU (or ADU)/g of detergent.
[a]960 min refers to a presoak (no agitation).

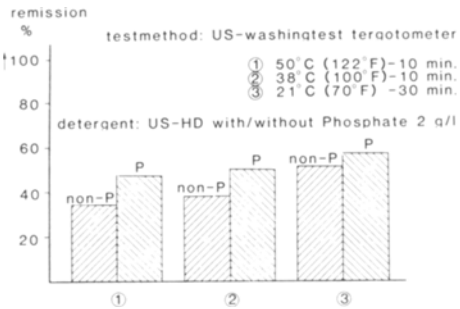

FIG. 7. The effect of phosphate and washing condition on cleaning of EMPA 116.

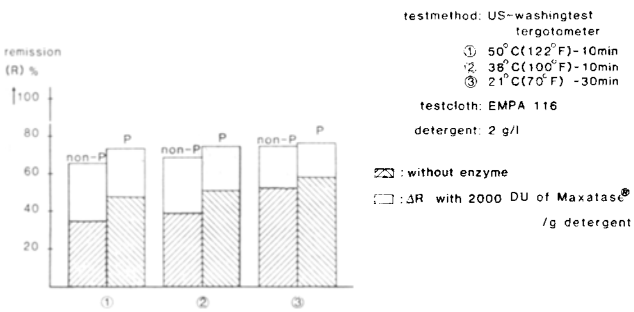

FIG. 8. The effect of Maxatase in US heavy-duty detergent with/without phosphate.

effect of the addition of Maxatase to these formulations is shown. It is clear that the application of the enzyme reduced the differences due to the elimination of phosphates by 50% or more, resulting in equal performance of the detergents.

The removal of phosphates in detergents often leads to a builder system composed of a carbonate/silicate mixture. Consequently, the pH of the washing water is raised considerably. A nonphosphate detergent may give a pH higher than 10 in the washing solution.

Because Maxatase and PB-92 have different pH profiles, it is interesting to know the effect on detergency when using these enzymes in such a highly alkaline detergent. In Figure 9, results of a comparison between the two enzymes are given. The pH of the solution of this heavy-duty nonphosphate detergent was pH 10.2, whereas in the earlier results the detergent solutions had a pH of 9.8-10.0.

The increase in washing performance by the addition of the detergent enzyme PB-92 was obviously much higher than in the case of Maxatase. Hence, PB-92 is more suitable

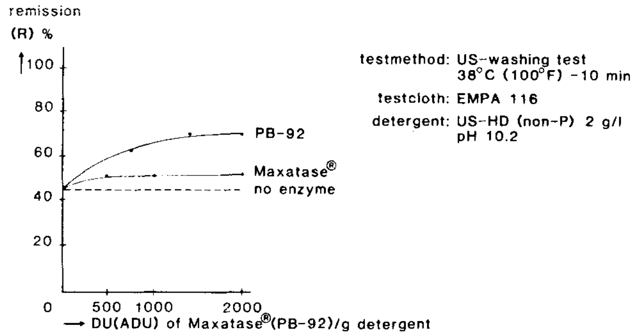

FIG. 9. The effect of the addition of Maxatase/PB-92 on the washing result of a high alkaline US heavy-duty detergent.

for use at more alkaline conditions. These results confirm those presented in Figure 1.

In conclusion, the following points are mentioned.

– The addition of the proteolytic enzyme Maxatase to US detergents, both heavy-duty and presoaks, increased the performance of those detergents in removing protein-based stains.

– The improvement in performance was not only true for US hot and warm water washing, but also for cold water washing at longer wash times.

– Presoaking with enzymatic detergents containing Maxatase gave results comparable to those obtained under normal washing procedures.

– The negative effect of the removal of phosphates from detergents can be compensated by the addition of a proteolytic enzyme to the detergent.

– The characteristics of the new enzyme PB-92 make it particularly suitable for use in the more alkaline detergent solutions, above pH 10, and in both moderate and low temperature washing.

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