the abovementioned tight network structure by micronized particles to overcome the separation force of buoyancy resulting from the difference in specific gravity between the dispersed and the continuous phases. The macronized dispersion tends to show phase separation as well as viscous instability due to insufficient formation of network structure.

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⁂Heavy-Duty Liquid Detergent

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ABSTRACT

A highly concentrated liquid detergent was developed. For the consumer, the quality and costs of this detergent correspond to the light-duty washing powders. The new detergent can be used in washing machines as well as for hand-washing. For the consumer, the liquid product is ready for immediate use, gives no solubility problems in the washing bath and saves both time and energy by excluding prewashing of textiles. Having a high concentration of surfactants and containing an enzyme, the liquid detergent is activated for stain removal. It is recommended especially for such stains as collar soil, blood, grass and many kinds of food stains. For the best result, the instruction advises the application of "Flytande Tvättmedel" directly on visible stains in a prespotting fashion.

A heavy-duty laundry detergent is a powdered or liquid product which is capable of removing heavy soil deposits from textiles during the washing process.

The first washing powders based on soap appeared at the end of the 19th century. The real built washing powders containing silicate and carbonate were not developed until the beginning of the 20th century. Many Europeans remember the first washing powder with a bleaching effect – Persil. Synthetic washing powders were not readily available until the 1950s.

Early liquid household detergents were principally potassium soaps of fatty acids or alcoholic solutions of soaps. The liquid detergents were mainly limited to personal use (shampoo, shaving cream, etc.) and medical use.

In the early 1960s, Nordtend produced a liquid light-duty detergent which was suitable primarily for hand-washing. The detergent consisted of triethanolamine salt of alkylaryl sulfonic acid, a small amount of ethoxylated nonylphenols, and potassium pyrophosphate. The active content was ca. 48% and pH of a 1% washing solution was neutral. Unfortunately, the time was not right for this innovation.

By the beginning of the 1970s the liquid detergents had already captured about a 4% share of the market in the USA, while Europe had to wait until the 1980s for the launching of the liquid detergents Liz and Vizir.

To answer the question whether the problems in the detergent fields in the United States and Europe really are different, it seems appropriate first to point out the factors influencing the washing process. The differences affect the detergent formulation.

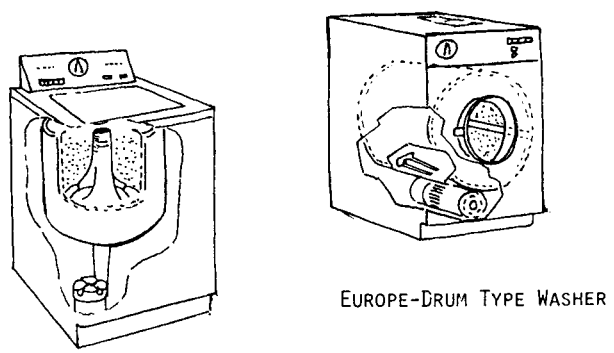


FIG. 1. Comparison of European and US automatic home washers.

There are differences in the washing medium, water. In the USA, only ca. 40% of the homes are affected by hard water. In Europe this number rises to ca. 80%, but in Sweden it falls to ca. 20%. The greatest differences between the United States and Europe are to be found in the construction of the washing machines. The top-loading agitator type of home washer is predominant in the United States. In Europe, on the other hand, the front-loading, horizontal drum type of washer is the most popular (Fig. 1). European automatic washers are fitted with electric heating elements and the washing process starts with cold water. American machines usually do not have a heating system, however – the washing starts with hot water. Consequently, these factors result in higher washing temperatures in European machines than in American machines. In Europe, more natural fibers, such as cotton, are used.

Currently, ordinary washing powders are still dominating the Swedish market and the total volume is estimated to be ca. 42,000 ton/year. The market shares for the major companies are as follows: Unilever (Sunlight), ca. 50%; Nordtend, ca. 20%; Colgate, ca. 8%; and Procter & Gamble, ca. 6%.

Nordtend has different kinds of washing powders which can be divided into the following main groups (Fig. 2). (a) "Alltvätt", an all-purpose washing powder containing a bleaching agent and enzyme. (b) Two liquid detergents, one with an enzyme and one without. Both detergents give good washing at 40 and 60 C by machine-washing and by hand-washing. (c) "Tvåltvätt", a washing powder with a low phosphate content.

At the end of 1981, Nordtend introduced a liquid washing detergent—"Flytande Tvättmedel"—on the market (Fig. 3). The detergent is suitable for all kinds of washing at 40 and 60 C, for hand-washing, and it can also be used at temperatures as high as 95 C (the normal European washing temperature for white fabrics). The liquid detergent is a highly concentrated detergent containing surfactants, enzyme, perfume, optical brightener and a sequestering agent.

The purpose of this discussion is to provide a brief survey of the ingredients, their functions, performance and evaluation of detergency. The main advantages over ordinary powder detergents for washing at 40 and 60 C will be discussed: the stain removal capability and the elimination of prewashing.

THE SURFACTANTS (Fig. 4)

Detergency is provided by a mixture of nonionic and anionic surfactants in a ratio of ca. 2:1. Alkylphenol ethoxylate with a suitable number of ethoxy units has the best performance at 50-60 C. Alkylphenol with a lipophilic character has a good laundering performance at 30-60 C.

Polyoxyethylene alcohol is an nonionic surfactant which is used as a hydrotrope for the remaining surfactants. It also acts as a viscosity-adjusting component, and has its best washing power at a temperature greater than 50 C. A secondary sodium alkane sulfonate (SAS) and a fatty acid mixture which is neutralized with ethanolamine are used as the anionic component. A small excess of ethanolamine is present to improve the detergency and the physical properties of the system.

ENZYME

Intensive work in the detergent enzyme field has resulted in the development of an enzyme slurry that can be incorporated in our liquid detergent. The enzyme has a broad activity range and hydrolyzes all proteinaceous substances normally present in the laundry such as blood, milk and egg.

A special procedure ensures that the active enzyme is protected against the action of the detergent components during storage. Tests have shown that after one year's storage at room temperature, the enzyme activity of our liquid detergent falls 40% (Fig. 5).

FIG. 3. A new, better way of washing.

FLUORESCENT WHITENING AGENT

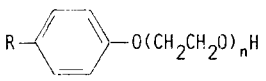
Fluorescent whitening agents are included in most powdered laundry products to increase the perceived whiteness of the laundered fabrics. They are substantive to fabrics and increase the absolute luminosity of the fabric by absorbing ultraviolet light and converting it to visible blue-white light. The amount of reflected visible light is increased and as a result laundered fabrics appear whiter or brighter. Yellowing and greying can be masked to some extent. A stilbene derivate (Fig. 6) which could successfully dissolve in our system was found effective.

Figure 7 shows that the whitening effect of our liquid detergent is comparable with that of our powder detergent.

FIG. 2. Nordtend washing powders.

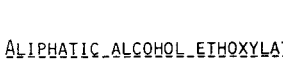
NONIONIC DETERGENTS

ALKYLPHENOL ETHOXYLATE



R = C_9H_{19}
n = 9-10 OR 6

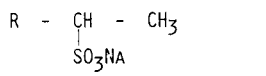
ALIPHATIC ALCOHOL ETHOXYLATES



R IS PREDOMINATINGLY C_{16}-C_{18}
n = 10

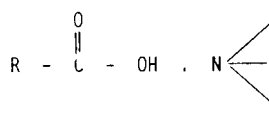
ANIONIC DETERGENTS

SODIUM ALKANE SULPHONATE



R = C_{12}-C_{16}

TRIETHANOLAMINE SALT OF FATTY ACID



R = C_{16}-C_{18}

FIG. 4. Nonionic and anionic detergents.

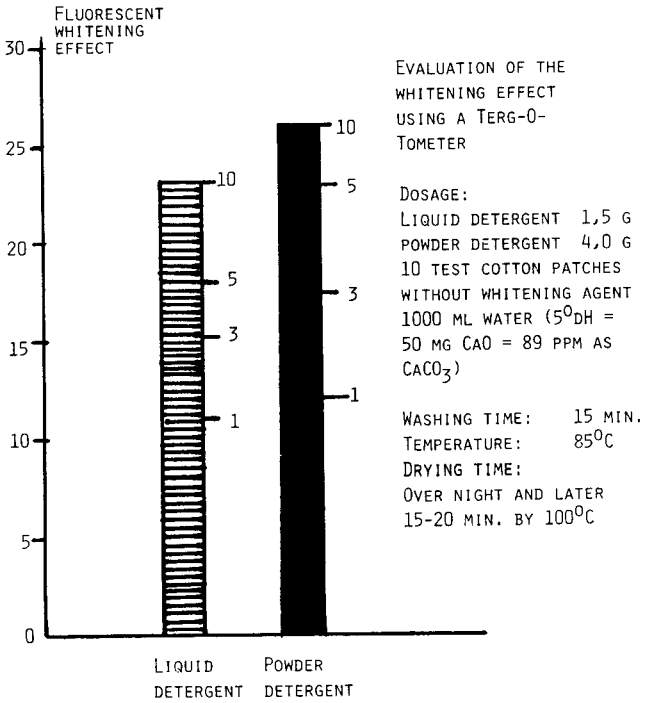


FIG. 7. Whitening effect in a liquid detergent in comparison with a powder detergent.

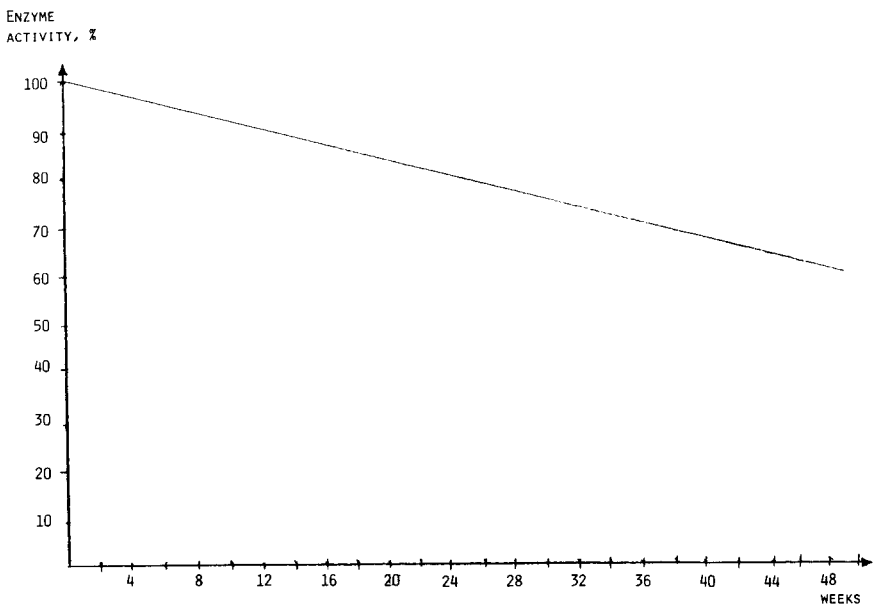


FIG. 5. Test of the enzyme activity in the liquid detergent.

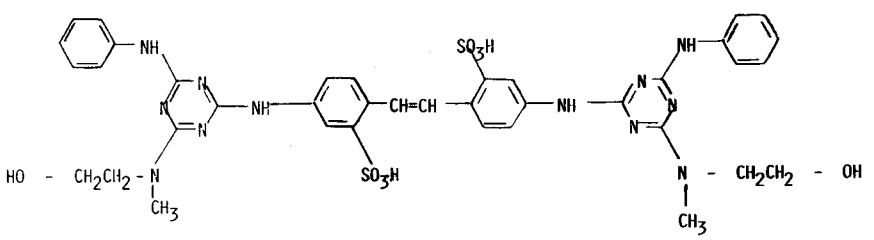


FIG. 6. Fluorescent whitening detergent.

TABLE I

Agent	Log. bacteria, number per mL				
	Total number aerobic bacteria	*Escherichia coli*	*Pseud. aureginosa*	*Staphylococcus aureus*	*Bacillus cereus*
"Flytande Tvättmedel"	–	–	–	<1.0	<1.0

BUILDER

Polyphosphates have been widely used in powder detergent formulations. In the 1930s it was discovered that 1-10 ppm of sodium hexametaphosphate could retard precipitation of $CaCO_3$ from supersaturated solutions. This so-called "threshold effect" is the prevention of precipitation from supersaturated solutions of builder salts in an aqueous medium with concentration of the inhibitor in the ppm level.

Phosphonates inhibit precipitation of much larger quantities of metal ions than can be explained by sequestration. In liquid systems phosphonic acid salts are superior to polyphosphates for threshold scale inhibition as they are significantly more stable in water.

SOLVENTS, PERFUME

Nordtend's liquid detergent contains 5% alcohol and a small amount of perfume. Perfume is incorporated to mask unpleasant odors in the detergent and to impart a pleasant aroma to the laundered articles. Alcohol is added in order to improve physical properties and to act as a preservative agent. A sample of "Flytande Tvättmedel" was grafted with a mixture of bacteria: *Staphylococcus aureus, Bacillus cereus, Escherichia coli* and *Aureginosa.* The total amount was 1000 bacteria/mL. The grafted samples were cultivated on agar plates and the results were recorded after 48 hr (Table I).

The complete composition of the light-duty liquid detergent is shown in Table II.

PRODUCT TESTING

The commercial success of a detergent product is determined by a variety of properties which are judged objectively and subjectively by the consumer. Tests are usually designed to determine physical properties, storage stability, detergency, etc.

The following discussion will include only the key elements of a liquid detergent testing: (a) detergency at different water hardnesses, (b) ash contents, and (c) stain removal.

Detergency was evaluated using a Cylinda 800 F washing machine (a front-loading washing machine from ASEA Scandia, Sweden) and was determined by the reflectance numbers which were measured using Elrephomat DEC 5 (from Zeiss, West Germany). The standard soiled fabrics include some types of pigmented materials, grease, carbon black, blood, milk, ink and cacao. The theory of Kubelka-Munk on which our measurements are based takes into consideration the light reflected from the fabric before and after laundering. The general formula for so-called "black content" is called the Kubelka-Munk equation, and is used for stain removal effectiveness:

$$K = \frac{(100 - R)^2}{2R} \cdot 100$$

where K = black content and R = reflexion.

$$\% \text{ stain removal} = \frac{K_f - K_e}{K_f} \cdot 100$$

where K_f = "black content" before the washing procedure, and K_e = "black content" after the washing procedure.

The evaluations of the laundry performance for liquid detergents are outlined in Figures 8-11.

TABLE II

The Chemical Composition of the Liquid Laundry Detergent

Component	Percentage
Nonionic surfactant	ca. 30.0
Anionic surfactant	ca. 5.0
Soaps of fatty acids	ca. 10.0
Ethanolamines, excess	ca. 6.0
Chelating agent	ca. 1.0
Fluorescent whitening agent	ca. 0.3
Enzyme	ca. 0.5
Alcohol	ca. 5.0
Perfume and water	ca. 42.0

Active content = 57%; pH, conc. = 8.5; viscosity = 200 cP.

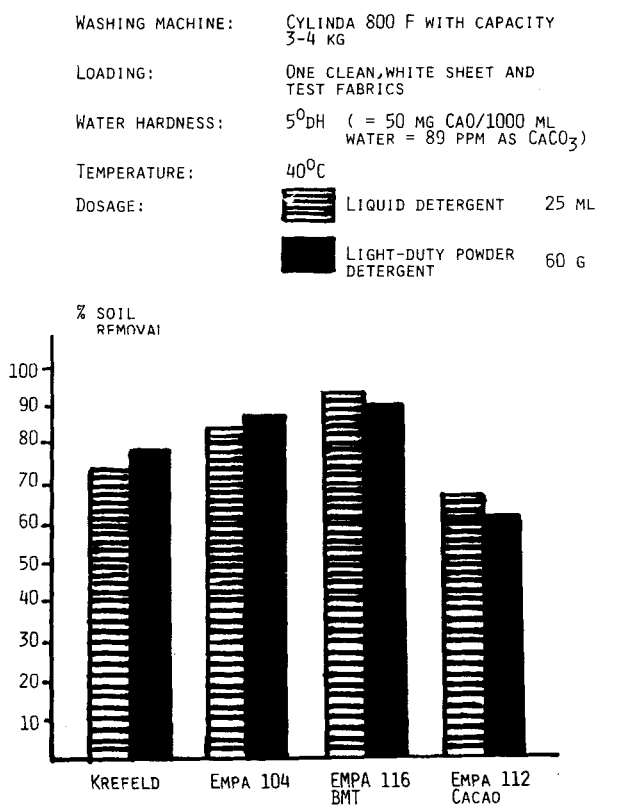


FIG. 8. Evaluation of the laundry performance for liquid detergents versus powder detergents.

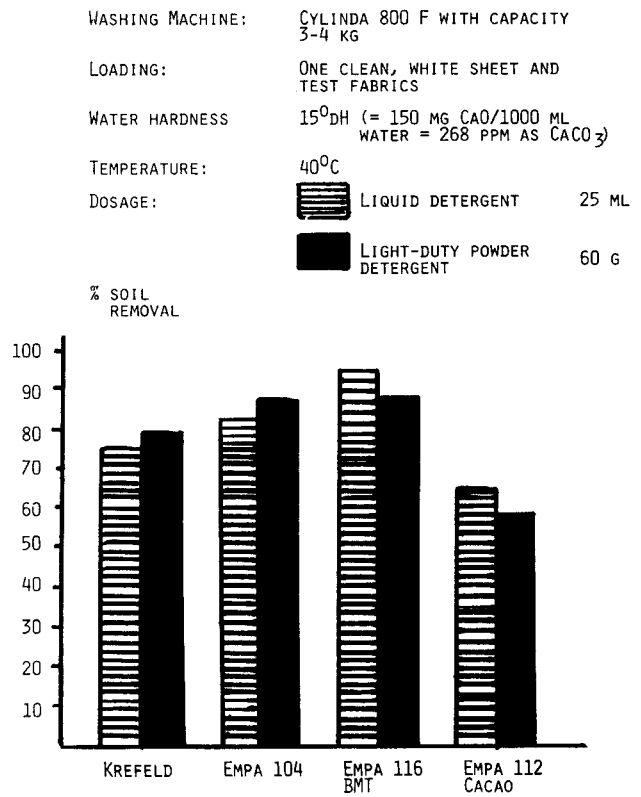


FIG. 9. Evaluation of the laundry performance for liquid detergents versus powder detergents.

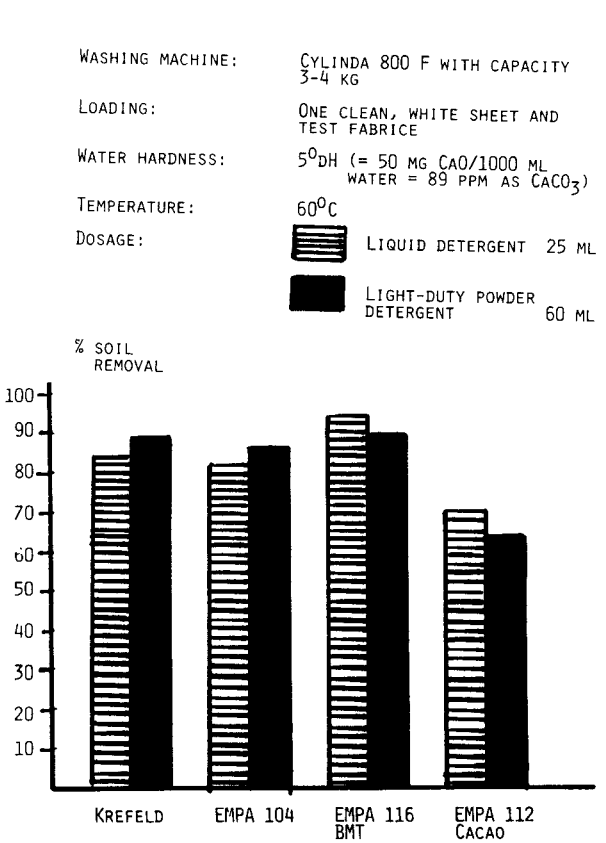


FIG. 10. Evaluation of the laundry performance for liquid detergents versus powder detergents.

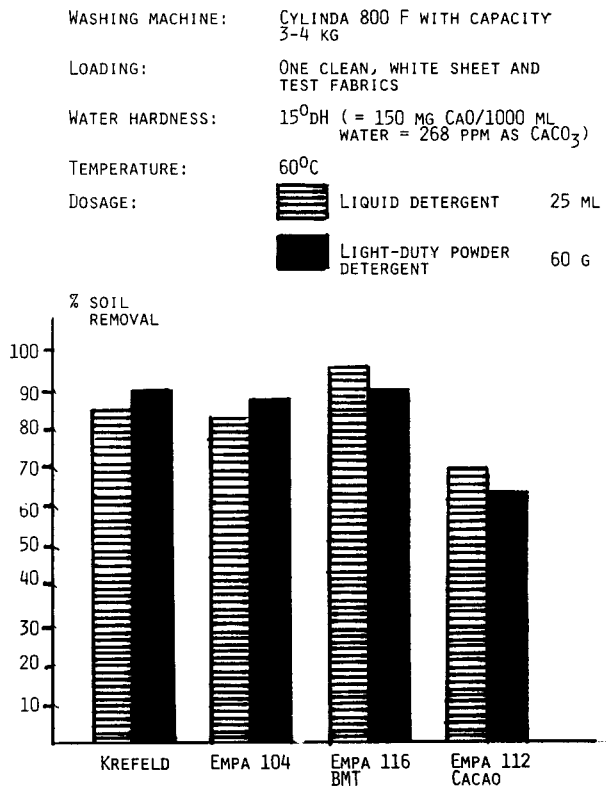


FIG. 11. Evaluation of the laundry performance for liquid detergents versus powder detergents.

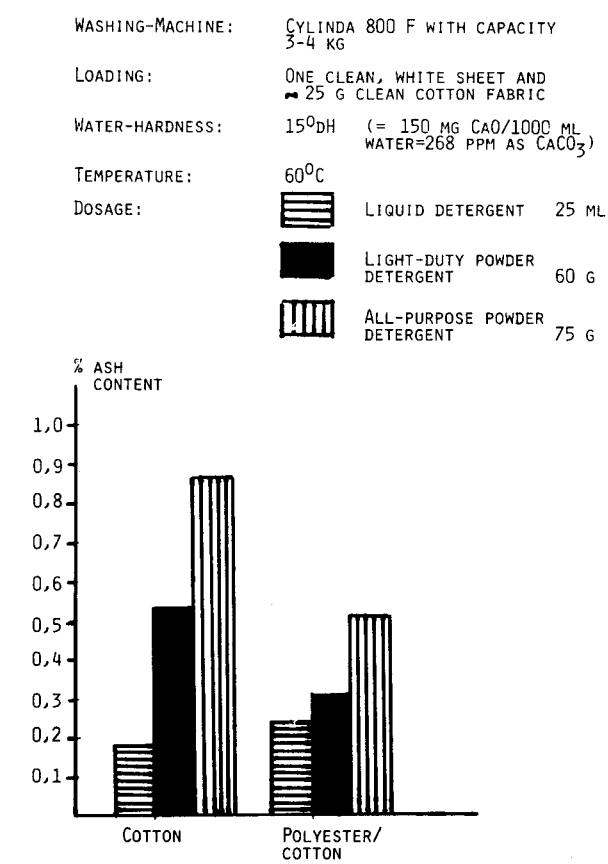


FIG. 12. Ash-content measurements.

The experiments show that the laundry performance for liquid detergents is comparable with conventional light-duty powder detergents. The reflectance values obtained in the separate experiments indicate that reflectance values obtained in the separate experiments indicate that there is no obvious greying of the fabrics. Since the liquid does not contain traditional builders in the form of sodium tripolyphosphate, the important purpose is to measure insoluble salt build-ups on cotton and polyester/cotton fabrics. The results of the ash-content measurements are shown in Figure 12.

From our results it can be concluded that the liquid detergent containing organic chelating agents gives a very low ash content after 10 laundries. It should be emphasized that the usual method recommends 20 laundries for estimation of the ash content. It is known that after 10 laundry cycles the ash content is about half of that found after 20 laundries.

As was mentioned at the beginning of this paper, our liquid detergent contains a proteolytic enzyme. It also has to be pointed out that the active content is very high (57%). These properties enhance its ability to remove stains and improve washing without a prewashing step.

By eliminating prewashing one shortens the time of the washing cycle, reduces the amount of energy required and thereby exerts a positive influence on the total energy balance.

Many tests have also been performed to check the prespotting performance of the liquid detergent.

Tests have been run on fibers soiled with different types of stain. The dried stains in the fibers were both prespotted with detergents and later also washed at 40 C with the same detergent. These results (Table III) were evaluated visually and compared with those of a light-duty powder detergent. This test indicates that the content of enzyme and the high concentration of surface-active agents improve the stain-removing capacity.

TABLE III

Stain Removal Capacity

	Liquid detergent		Light-duty powder detergent	
Kind of stain	Cotton	Polyester/ cotton	Cotton	Polyester/ cotton
Grass	1	1	1	0
Rust	2	0	1	0
Motor soil	2	2	3	3
Tomato	0	0	0	0
Strawberry	0	0	0	0
Peach	1	1	0	0
Raspberry	1	1	1	1
Coffee	1	0	1	1
Tea	2	1	1	0
Blood	0	0	0	0
Indian ink	1	1	3	3
Ball-pen	0	0	3	3
Ketchup	0	0	0	0
Mustard	1	0	1	0
Bilberry	1	0	1	0
Red beet	0	0	0	0
Dripping	0	0	1	0
Carrot juice	0	0	0	1
Nicotine juice	0	0	1	0
Salad dressing	0	0	2	0

0 = the stain totally washed away;
1 = very light, hardly visible;
2 = light but visible;
3 = clearly marked stain.