SESSION V
Performance Testing

Scanning Electron Microscopy in the Detergent Industry

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ABSTRACT

In 1965, scanning electron microscopes became available commercially. The use of these instruments and other new equipment (such as X-ray microanalysis and cathodoluminescence) created new possibilities for evaluation of detergent qualities permitting further insights into the morphology and inorganic chemical composition of powder particles, including the surfaces and the inside regions. The new instruments also can be used in testing procedures during product development. Use of scanning electron microscopy in evaluation of detergents was discussed using selected examples related to investigations concerning (a) stability of bleaching activator prills, (b) coating of enzyme marums, (c) distribution of optical brighteners, (d) distribution of the inorganic constituents of powder particles, (e) thermal stability of sodium triphosphate hexahydrate, and (f) development of sodium aluminum silicates (SASIL) as phosphate substitutes. The examples were chosen to show the possibilities of scanning electron microscopy. Together with its additional features and in combination with other methods of physical and chemical analysis, scanning electron microscopy can provide important information concerning solid surfaces, which are relevant in the field of detergent chemistry.

INTRODUCTION

In addition to other physical and chemical testing methods, the methods of light microscopy (both direct light and transmission mode) have long proven useful in detergent chemistry; they are now standard methods in all analytical laboratories. In production control, light microscopy is used to examine both raw materials, reaction batches, and finished products. In the evaluation of the washing performance of laundry detergents, the methods of light microscopy are of considerable importance in the study of dirt removal from textiles and the formation of deposits and incrustations (1). Aided by television cameras and magnetic recorders, dynamic processes, such as the dissolution of products or their individual constituents, may be recorded and analyzed in slow motion or single pictures. Another large field is the examination and analysis of textiles. Here, the various textiles are examined with regard to their finish and their behavior in various washing processes. The same applies to washer parts, which come into contact with de-

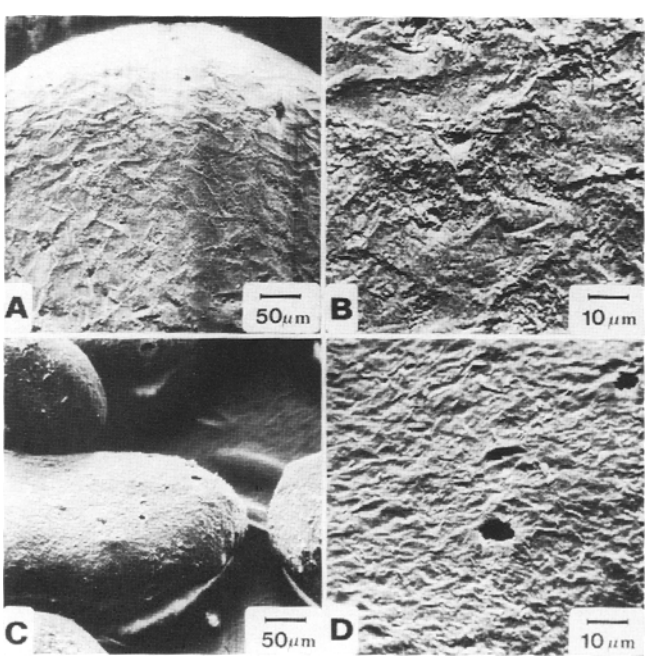

FIG. 1. Surfaces of bleaching activator prills (TAGU-prills).

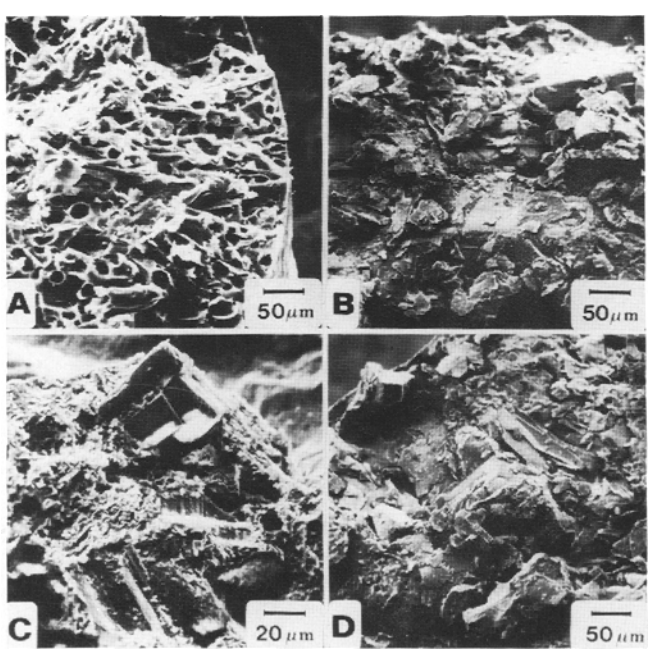

FIG. 2. Fracture surfaces of bleaching activator prills (TAGU-prills).

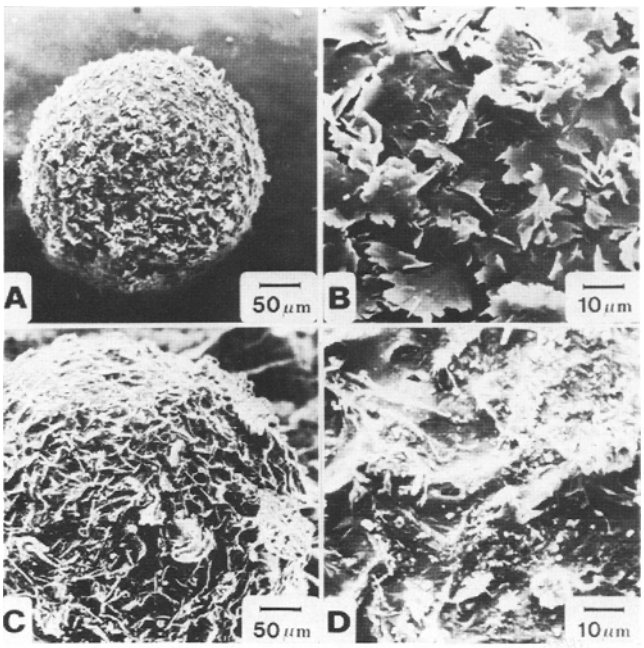

FIG. 3. Surfaces of TAGU activator prills after storage at elevated temperature.

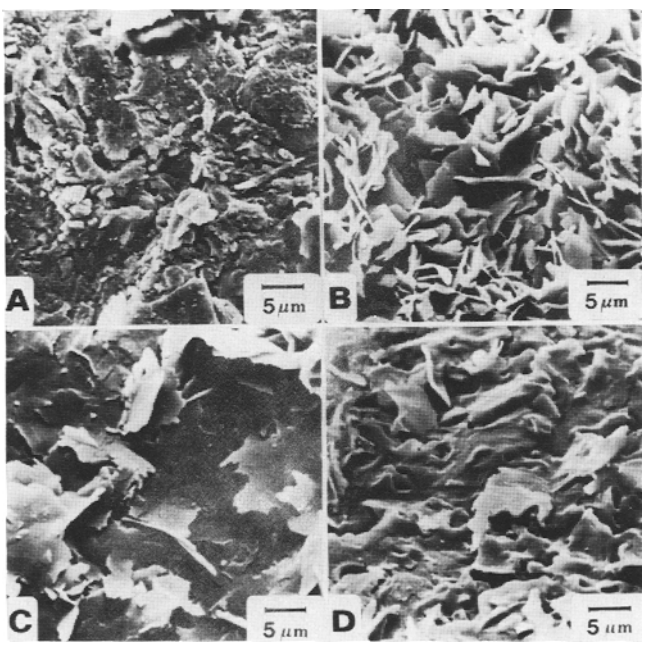

FIG. 4. Surfaces of TAGU activator prills after storage under various climate conditions.

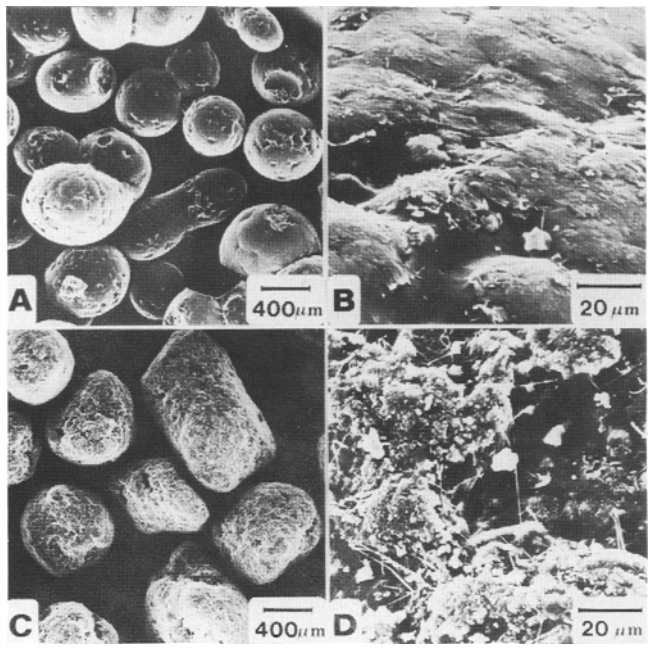

FIG. 5. Surfaces of enzyme-marums.

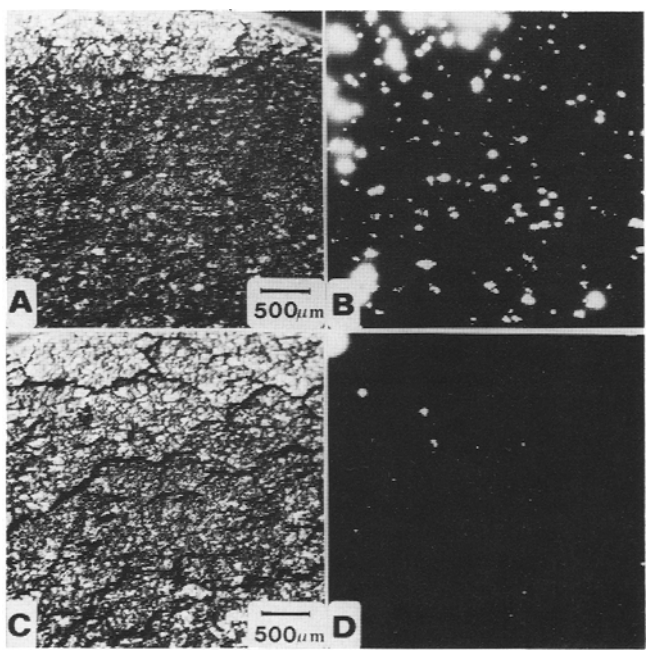

FIG. 6. Distribution of an optical brightener on tablet surfaces (A,C: secondary electrons; B,D: cathodoluminescence).

tergents or detergent solutions. Also, light microscopy is quite valuable in the handling of complaints and the examination of competitors' products.

The information obtainable in the examples above is not always optimal because of the limited resolution of light microscopy (~0.2 μm), which is restricted by the wavelength of light. Light microscopy is, therefore, not useful whenever smallest structural changes of products or their substrates are concerned. This is the field of transmission electron microscopy (2).

While its limits of resolution are better by three orders of magnitude (3 Å), the information obtained is not always unambiguous. This is mainly due to difficulties with preparation techniques, which are frequently both very difficult and full of possible trouble. Also, transmission electron microscopy is quite time consuming.

The commercial development of scanning electron microscopy in 1965 has closed the gap between light microscopy and transmission electron microscopy and provided a technique that gave new insights in all fields including detergent chemistry. Because of its high resolution (~50 Å) and its great depth of focus, scanning electron microscopy has become an extremely effective testing method with the particular advantages of ease of sample preparation and speed.

In the scanning electron microscopy the following signals mainly will arise in the interaction between the electron and the object examined: secondary electrons, elastically scattered primary electrons, cathodoluminescence, characteristic X-rays, auger electrons, and transmitted electrons.

Information concerning surface topography is obtained from secondary and elastically scattered primary electrons.

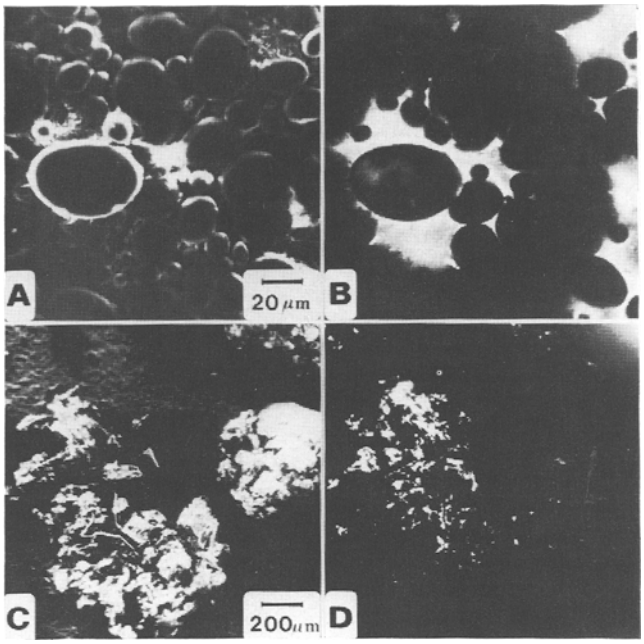

FIG. 7. Distribution of optical brighteners on a tablet surface (A: secondary electrons, B: cathodoluminescence). Distribution of optical brighteners on detergent powder surfaces (C: secondary electrons, D: cathodoluminescence).

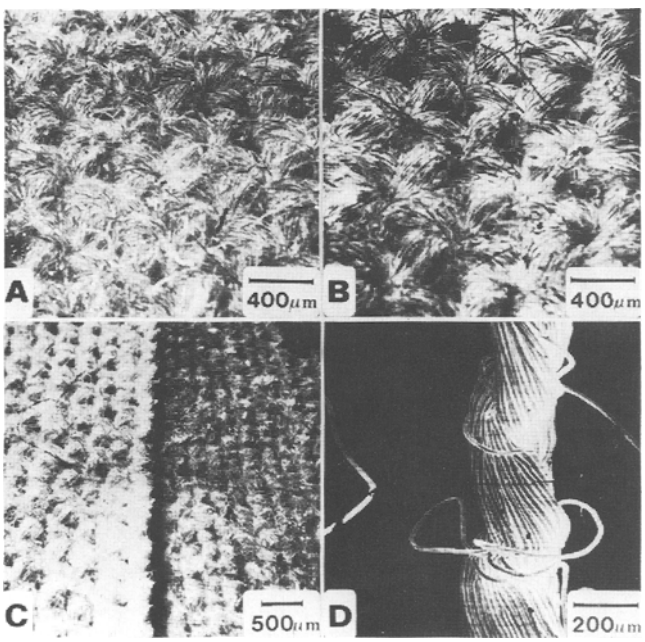

FIG. 8. Distribution of optical brighteners on textiles (cathodoluminescence).

Cathodoluminescence gives information on the distribution of UV-active substances, for instance, certain minerals and optical brighteners. X-rays allow qualitative and simultaneous elemental analysis and give information on the distribution of the elements within the sample. Auger electrons may be used for material analyses in the region of layer thicknesses between 2 and 10 Å. Transmitted electrons give information on specimen thickness.

Suitable collectors are used for the various signals, which are then processed electronically. We will skip the discussion of technical details of the equipment used, as these are largely well known and also to be found in the literature (3).

In the field of detergent chemistry, the micrographs ob-

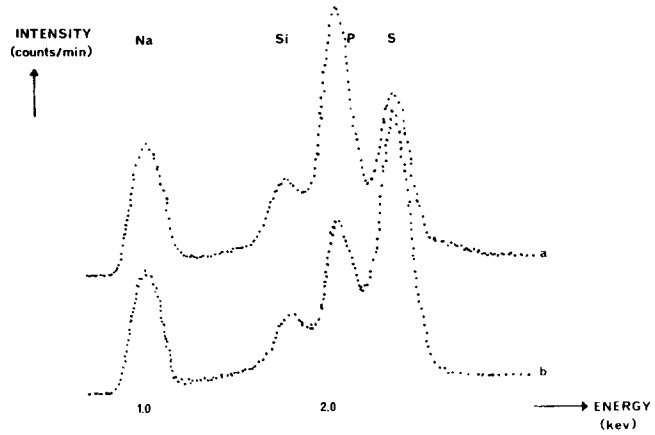

FIG. 9. X-ray spectra of a heavy duty laundry detergent (a) and a special purpose detergent (b).

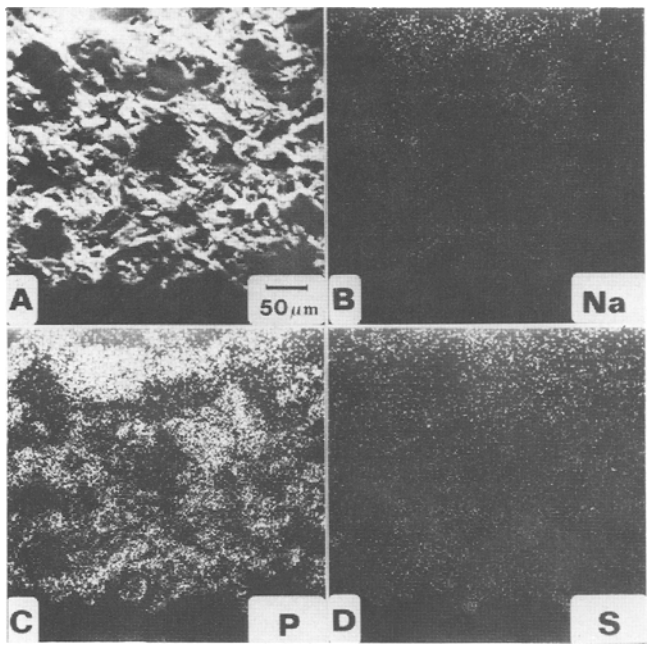

FIG. 10. Element distribution at the cut surface of a heavy duty laundry detergent particle; A: secondary electrons, B: sodium distribution, C: phosphorus distribution, D: sulfur distribution.

tained using secondary and/or elastically scattered primary electrons are particularly useful; the same applies to X-ray elementary analysis and the detection of UV-active substances, as well as the determination of their distribution by cathodoluminescence.

There is not enough time to present examples for all of the various methods we have mentioned. Rather we shall present a few selected examples from our own work in the attempt to show both the scope and the limitation of scanning electron microscopy in detergent chemistry.

The examples we have selected concern (a) the stability of perborate activator prills, (b) coating of enzyme marums, (c) the distribution of optical brighteners, (d) the distribution of inorganic constituents in detergent powder particles, (e) the thermo-stability of sodium triphosphate hexahydrate, and (f) the development of detergent phosphate substitutes.

STUDIES CONCERNING THE STABILITY OF BLEACHING ACTIVATOR PRILLS

Perborate activators for washing at temperatures of 60 C and below may be incorporated into perborate-containing

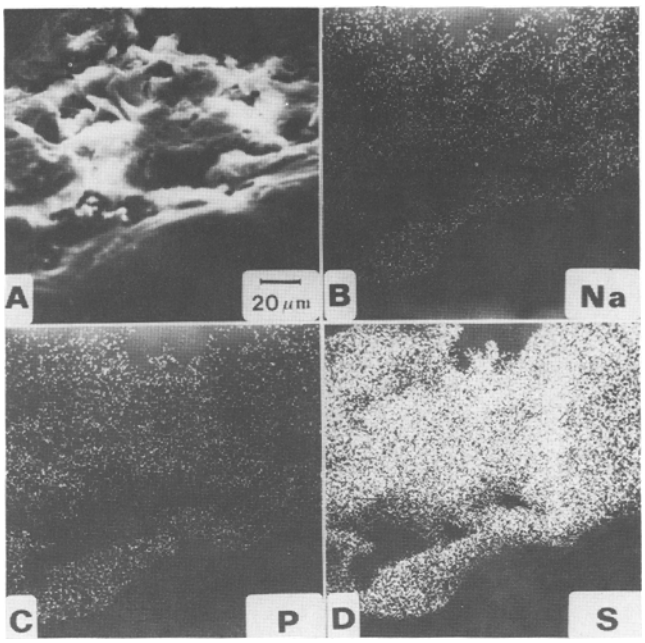

FIG. 11. Element distribution at the cut surface of a special purpose laundry detergent particle; A: secondary electrons, B: sodium distribution, C: phosphorus distribution, D: sulfur distribution.

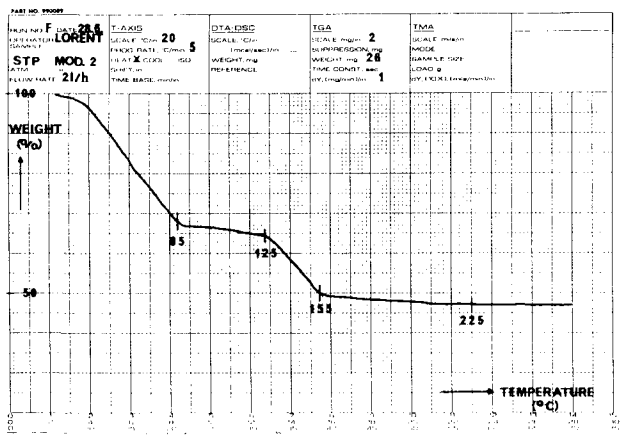

FIG. 12. Thermal diagram of sodium triphosphate hexahydrate.

detergents in the form of prills. A basic requirement is that these prills should be stable on storage. The particles must remain stable in the finished product over extended periods of time, and their properties should not be changed by variations in temperature or humidity.

The following scanning electron micrographs have been obtained in the course of the development of activator prills based in 1,3,4,6-tetraacetylglycoluril, which we call TAGU. Figure 1 (A-D) shows surfaces of TAGU prills with a larger magnification of the same particles on the right hand side. During the prilling process TAGU is processed as a slurry formed from substances melting in the region of 50 to 70 C and certain additives. This slurry is sprayed through a nozzle into the cold air of the spraying tower, in which the droplets solidify. In the present case the two samples differ in the chemical composition of the matrix material. As a consequence, the particles differ in shape and size. Mainly large, ball-shaped particles were obtained with material A (Fig. 1, A & B). Smaller and irregular prills, which consisted both of round and of ellipsoid particles, were obtained in the case of material B (Fig. 1, C & D). Apart from these differences in shape, quite noticeable differences in surface structure were also observed.

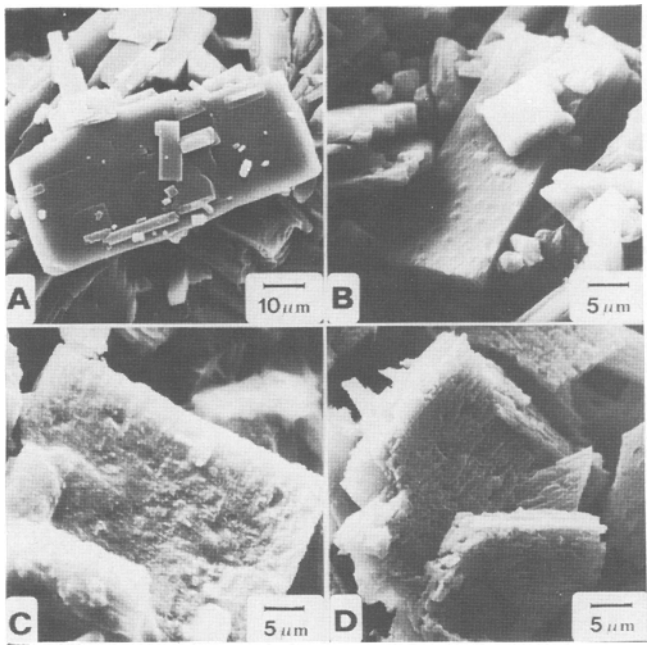

FIG. 13. Heated crystals of sodium triphosphate hexahydrate.

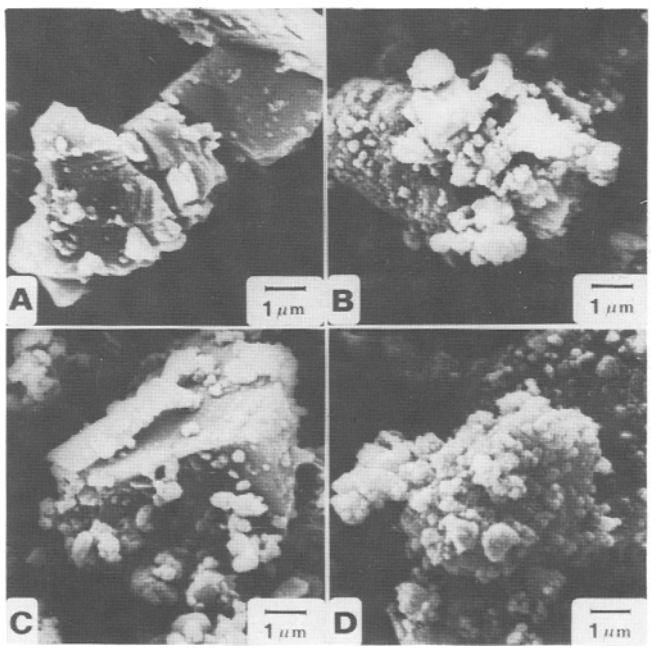

FIG. 14. Naturally occurring zeolites; A: nathrolite, B: analcim, C: mordenite, D: chabazite.

The particles prepared from material A had comparatively smooth surfaces with irregularly arranged straight elevations of almost equal lengths. Possibly, these elevations are the edges of TAGU crystals lying close to the surface. By comparison, prills obtained with material B had finely structured surfaces with few but large holes.

The chemical composition of the matrix material also influences the interior prill structure, as shown in Figure 2 (A-D). These micrographs show fracture surfaces. As shown in Figure 2A, a rather porous prill is obtained with the matrix material C. The other fracture surfaces show compact prill structures. It is clearly seen that some of the TAGU crystals – single crystals or agglomerates – lie rather close to the prill surface. This observation supports the assumption that the straight elevations observed before on the prill surface shown in Figure 2B are caused by TAGU crystals. TAGU crystals are also found in the sample cen-

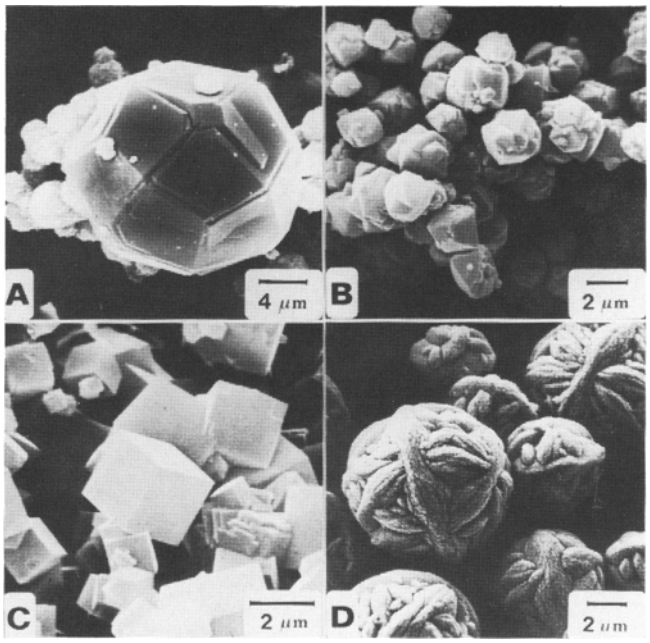

FIG. 15. Synthetic zeolites; A: analcim, B: zeolite NaX; C: zeolite NaA, D: potassium aluminum silicate.

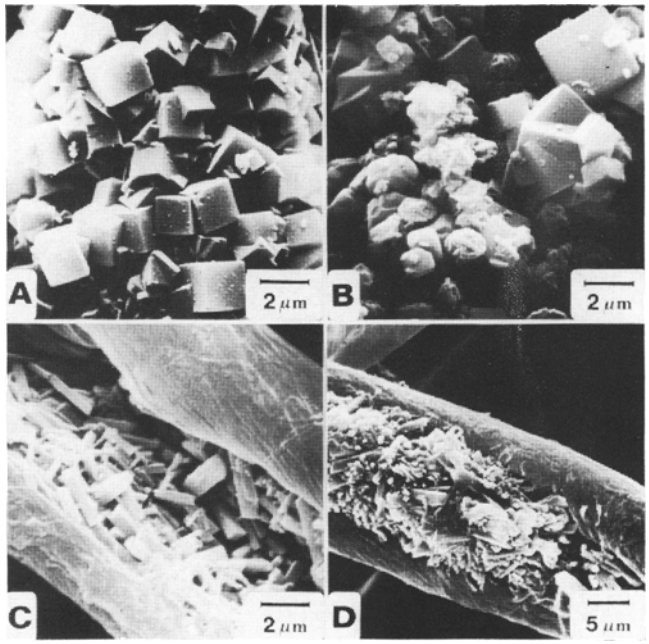

FIG. 16. A: zeolite NaA, B: zeolite NaA and sodalite, C, D: deposits of calcium carbonate on cotton fibers.

ters. It is also of interest that only fragments of TAGU crystals are seen on the fracture surface of the prill prepared from material C, whereas in the other cases there are generally either whole crystals or imprints of whole crystals. Obviously, material C has achieved an intimate contact with the TAGU crystals, which is not the case in micrograph C and only to some extent in the other examples.

The examination of samples from long term experiments under constant or variable conditions has also been very important. Figure 3 shows two prills differing in matrix composition (C and A) after an 8-week storage test at elevated temperature. Both examples show quite distinct signs of disintegration, which are totally different. Matrix material C shows a flaking off of lamellae. TAGU crystals are not exposed in this process. It is difficult to say, in which way material A decays, however, it is seen quite clearly how the phenomena observed initially are aggravated, and partially exposed TAGU crystals are observed.

Various climatic conditions also caused astonishing changes at the prill surfaces. Thus, at 30 C and 80% relative humidity the surface develops a jagged appearance with cracks and holes (4A). Climatic conditions alternating between 15 C and 90% relative humidity and 30 C and 50% relative humidity in a 12-hr rhythm again caused surface decay with the formation of lamellae (4B). The magnitude of the phenomena observed depends on chemical composition and the kind of external influences.

In some cases only very fine structural differences were observed, as seen in Figure 4 (C & D). In both cases lamella-like decay is observed with thin, pointed edges in one case and soft, rounded forms in the other.

These investigations gave valuable hints in the development of bleaching activator prills, which are stable in storage.

STUDIES CONCERNING THE COATING OF ENZYME MARUMS

The enzymes of major heavy duty laundry detergents and detergents for washing at 60 C are also coated with suitable substances in order to improve storage stability. Generally, granulates, prills, or marumerizer-pellets will be used. Surfaces of enzyme marums are shown in Figure 5 (A-D). Under low magnification (Fig. 5A) the particles are seen to be substantially round with a narrow size-distribution, with an occasional rod-shaped particle in between. These structures serve quite well to illustrate the marumerizer process. A slurry is extruded through narrow holes to form slabs or noodles, which are then cut into cylinder-shaped segments. These particles then undergo a surface melting due to the heat of friction developed in the marumerizer, which consists of a drum with vertical in-between walls and rotating bottom plate. In this process most of the particles become ball-shaped. To improve stability additional coatings are added, which may be achieved by adding the material in powder form to the marumerizer. Micrographs 5C and 5D show such pellets. The added coating consists of granular and fibrous substances and is not absolutely closed. Frequently titanium dioxide is incorporated to this outer coat to improve color. Titanium dioxide is most easily detected by a microanalysis system of the scanning electron microscope using the Ti-$K\alpha$-X-ray emission.

The inspection of the fracture surfaces does not allow determination of whether these enzyme marums are coated or not. At best it is possible to distinguish the outer zones that have undergone a surface melting from the inner zones of the particles, which are less homogeneous.

DISTRIBUTION OF OPTICAL BRIGHTENERS

Optical brighteners, which may be present in technical products or on textiles, may be detected and identified by cathodoluminescence, which is a kind of fluorescence microscopy with the depth of focus of scanning electron microscopy (4). The technique has been used, for example, in the determination of brightener distribution in optical brightener tablets as a function of the various production rates of the equipment used. The optical brightener powder was embedded in a matrix consisting of starch, powdered milk, carbowax, etc. Figure 6 (A-D) shows the tablet surfaces: the micrographs on the left hand side have been obtained with secondary electrons, while the right hand side shows the corresponding cathodoluminescence determination. It is seen that there is a drastic influence of the production rate on the optical brightener distribution. Similar observations were not made in the case of fracture surfaces. Under larger magnification (Fig. 7, A & B) it is seen that there is a superposition of starch granules and optical brighteners. On the other hand, the surfaces of the exposed starch granules are almost totally void of brightener. We

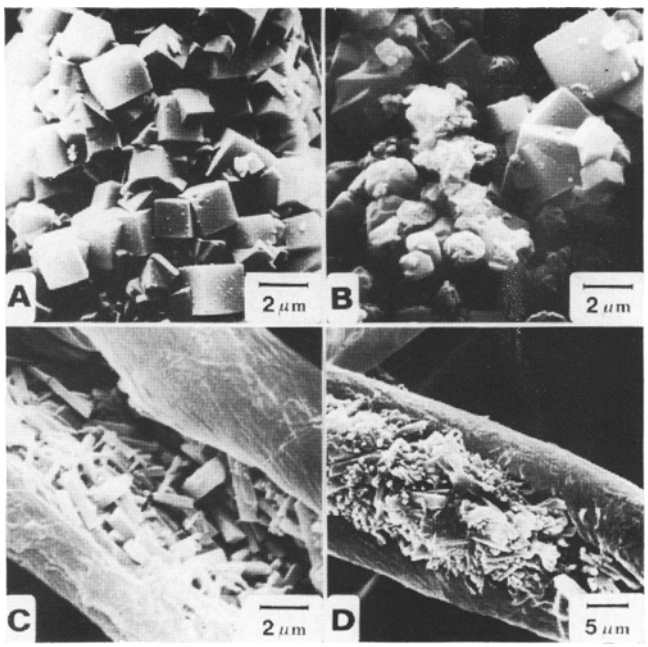

FIG. 17. NaA zeolites of different morphology (A-B) and different origin (A,B-C,D).

should note that the quality of the secondary electron micrographs is not nearly as good as in the more common applications, because in this case the samples have undergone little or no gold vapor treatment in order not to obstruct the UV-emission.

Laundry detergents containing optical brighteners are examined in the same fashion. An example is seen in Figure 7 (C & D). Here also the distribution of the optical brightener at the surfaces is rather inhomogeneous. With regard to textiles, questions concerning the substantiveness of optical brighteners are of great interest. Figure 8 (A & B) shows polyester/cotton after 10 and 50 wash cycles with a detergent containing optical brighteners. It is seen very clearly that considerably more optical brightener is adsorbed when the treatment is repeated more often. In both cases the brightener distribution is fairly regular. Light and dark spots are observed in various cases. The light spots are caused by agglomerated optical brightener particles, while the dark spots correspond to dirt particles. We see that the method of cathodoluminescence allows us to distinguish the presence of dirt particles from an irregular distribution of the optical brightener; this distinction cannot be made by secondary electron micrographs. Figure 8C again shows the difference in brightening obtained by a direct comparison of the two samples. Finally, Figure 8D shows a single thread with an even distribution of optical brightener and slight dirt deposits.

DISTRIBUTION OF THE INORGANIC CONSTITUENTS OF THE POWDER PARTICLES

The X-ray microanalysis facility of the scanning electron microscope is particularly useful for the determination of the inorganic constituents of laundry detergents and the determination of the element distribution at the surfaces or within the sample. Figure 9 shows X-ray data of a heavy duty laundry detergent and a detergent for special purposes in comparison. The intensity of the sodium peak should be tripled to account for the roughly 65% of the very soft Na-Kα-X-ray emission (1.04 KeV), which are absorbed by the detector window. From the intensities observed it is possible to estimate the elementary composition of the product; also, information concerning product quality may be obtained. Determination of element distribution gives information concerning morphological structure and homogeneity of the powder particles. Figure 10 shows a secondary electron micrograph and the distributions of sodium, phosphorus, and sulfur from the edge of the cut surface of a laundry detergent granule. The particles were carefully embedded in plastic and cut using a slide microtome. The plastic material penetrated into the granule is clearly visible. Also, it is seen that the inorganic materials are homogeneously distributed in the edge area. Figure 11 shows corresponding results obtained in the examination of the cut surface of special purpose laundry detergent. Here, too, a homogeneous distribution of the elements was observed.

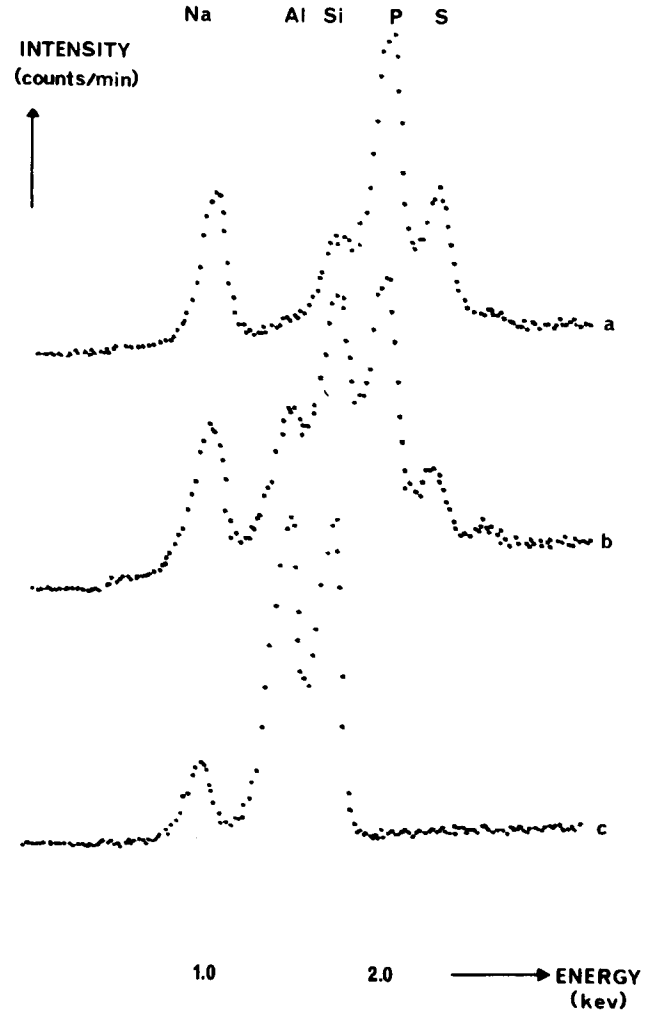

FIG. 18. X-ray spectra of (a) phosphate-based laundry detergent, (b) zeolite and phosphate-containing detergent, (c) zeolite NaA.

STUDIES CONCERNING THE THERMAL STABILITY OF SODIUM TRIPHOSPHATE HEXAHYDRATE

Sodium triphosphate as used in the manufacture of laundry detergents is made up of two crystalline modifications that must be present in a particular weight ratio if difficulties in processing are to be avoided. Nevertheless, problems such as variations of the slurry viscosity are occasionally encountered, which had not been well understood. We have recently observed that the two crystalline modifications give rise to crystals of different sizes and shapes upon hydration: modification I forms very small predominantly needle-like crystals, while very large plates are formed in the case of modification II. These results led us to further examination of the chemical and physical behavior of the two crystalline modifications under various experimental conditions. For example, we have been interested in the thermal behavior of sodium triphosphate hexa-

hydrate and studied the changes, which hexahydrate crystals undergo upon heating, as given in the thermo-diagram of Figure 12. Samples were taken at various points of this curve and studied by scanning electron microscopy. Figure 13A shows hexahydrate crystals, which have been obtained from modification II of sodium triphosphate. The very well-developed crystals have extremely smooth surfaces with few defects. Absorbed water was removed from the sample by heating to 85 C. A temperature increase by 40 to 125 C corresponds to the loss of 1 mole of water of hydration and causes slight changes at the surface (Fig. 13B). Slight cracks and blister-shaped elevations are observed. Increasing the temperature to 155 C, which corresponds to a loss of 4 moles of water of hydration, leads to a considerable degree of surface erosion and partial collapse of crystal structure (Fig. 13C). Finally, the release of the last mole of water of hydration, which is completed at 225 C, leads to a total breakdown of the crystal structure (Fig. 13D). Similar behavior is observed in the case of hydrate crystals obtained from modification I.

DEVELOPMENT OF PHOSPHATE SUBSTITUTES

The past 10 years have witnessed a worldwide search for suitable substitutes for laundry detergent phosphates. The compounds mainly considered were water-soluble, organic-complexing agents of higher or lower molecular weight. Very recently, water-insoluble ion exchangers have been studied which may serve as phosphate substitutes. In the study of such water-insoluble ion exchangers scanning electron microscopy has been used in the course of development, production, and product testing, as well as for analyzing market products.

Certain sodium aluminum silicates are particularly well suited as phosphate substitutes from the point of view of washing performance. They belong to the zeolite group of minerals. There are more than 40 naturally occurring and more than 100 synthetic types of zeolites.

Figure 14 (A-D) shows four naturally occurring zeolites in comminuted form:

A:	nathrolite	sodium aluminum silicates
B:	analcim	
C:	mordenite	
D:	chabazite	calcium aluminum silicate

In these examples sharp edges and rounded forms are observed, which originate both from single crystals and from crystal fragments; it is impossible to distinguish these by scanning electron microscopy. X-ray diffraction is used to identify these zeolites as discussed in great detail in the literature (5).

In the case of synthetic zeolites the characteristic morphological structure allows a distinction by scanning electron microscopy. Figure 15 shows four synthetic zeolites:

A:	analcim	sodium aluminum silicates
B:	zeolite NaX	
C:	zeolite NaA	
D:	potassium aluminum silicate	

The morphological differences are so characteristic that once recognized, a zeolite type may always be recognized again.

Zeolites A and X shown in Figure 15B and C have proven to be particularly suitable for the washing process. In addition to their water-softening action and the binding of multivalent metal ions by ion exchange, these ion exchangers show further advantages, which cannot be discussed here.

The properties of these crystals are significantly influenced by both morphology and particle size. This is true not only for the application discussed here, but also for other known fields of application, such as adsorption and catalysis. Therefore, scanning electron microscopy plays an important role in production control. The formation of secondary nuclei may lead to twinning or the formation of higher aggregates in the production process, as seen in Figure 16A. Such aggregates are easily distinguished by scanning electron microscopy from agglomerates, which are held together only by intermolecular forces; an unambiguous distinction is not always possible by other analytical methods. Furthermore, other modifications – desired or undesired – of the sodium aluminum silicates can be present that are not detectable by X-ray diffraction at low concentrations. Figure 16B shows the presence of sodalite crystals in addition to zeolite A. Obviously, it is possible to use scanning electron microscopy in the control of the production process.

The examination of washed textiles often shows that sparingly soluble substances such as calcium carbonate are deposited where the fiber has suffered injury or particularly within the cotton fiber lumina. Figure 16 (C & D) shows this very clearly. It is interesting to note that a deposition of sodium aluminum silicate has never been observed at these fiber sites, which are particularly preferred because of their large and active surfaces.

These and other investigations have led to laundry detergent formulations containing both sodium triphosphate and sodium aluminum silicate. It was possible to achieve a 50% phosphate replacement with comparable washing performance. In the course of these studies it has also been found that the use of sodium aluminum silicate crystals with rounded-off edges and corners is even more advantageous than using a product showing pronounced edges. Figure 17 (A & B) shows these morphologically different zeolites of the A type.

Before closing, it should be mentioned that the combination of scanning electron microscopy and energy-dispersive X-ray microanalysis provide quick qualitative information in the analysis of market products. For example, using the Al-Kα-line, one can demonstrate qualitatively the presence of 5% sodium aluminum silicate in laundry detergents. Figure 18 shows the X-ray spectra of a phosphate-based laundry detergent, a product with 10% sodium aluminum silicate, and a pure sodium aluminum silicate. Taking into account the water-insoluble residues of the samples analyzed, it is frequently possible to determine the origin (manufacturer) of the zeolite by scanning electron microscopy. Figure 17 (C & D) shows such an example. Figure 17C shows the water-insoluble residue of a competitor's product, while Figure 17D is part of a collection of micrographs showing zeolites from the production of various suppliers. It may be said that the microscopical identification is unambiguous.

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