# Building Action of Various Types of Inorganic Electrolytes

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## Abstract

The builder effects of a series of condensed phosphates and other types of electrolytes on the detergency for standard soiled cloth have been measured. The detergency highly depends on the type of electrolytes and, in general, increases with increasing pH of detergent solutions. The building action of phosphates is greater than that of other electrolytes when it is compared at the same pH. The alkalinity, including alkali buffering capacity, of various electrolytes and the sequesteration capacity of phosphates for calcium ion have also been determined. From the results, the building action of inorganic electrolytes in a detersive system has been discussed in connection with the suspension stability of colloidal particles reported in previous papers. The following factors are at least important in the building action of inorganic compounds: (a) the suspension of soil particles in a detergent solution, (b) the sequesteration of heavy metal ions, and (c) the alkalinity including buffering action to keep the solution alkaline. Condensed phosphates, in particular sodium tripolyphosphate, have an ability to satisfy these three factors although their alkalinity is not so strong.

## Introduction

Although the building action of inorganic compounds in a detersive system involves many phenomena, which are related in a complicated way, and these phenomena and their interrelations are not well understood, a number of approaches have been attempted to characterize this action. Among inorganic compounds, sodium tripolyphosphate has been widely used because of its considerable building action (1–3). Therefore, the elucidation on the mechanism of building action for sodium tripolyphosphate is considered to be one of the approaches to understanding the builder effect of inorganic electrolytes commonly used as builders on detergency.

In previous works (4,5), the effect of various electrolytes on the stabilities of solid particle suspensions has been studied in connection with the electrophoretic mobility of suspended particles, the rate of sedimentation, the volume of sediment particles, and the optical absorption of suspensions. It has been shown that the stabilizing ability in suspension of condensed phosphates is relatively high as compared with that of other electrolytes, and this is indicative of strong adsorption of phosphate ions onto the surface of colloidal particles (4,5).

In the present work, the builder effects of a series of condensed phosphates and other types of electrolytes on the detergency of detergent solutions containing these electrolytes have been discussed in relation to the pH of the solutions, the alkalinity including alkali buffering capacity, the sequesteration capacity towards calcium ion, and the stabilizing ability in suspensions, which was reported previously (5).

## Experimental Section

### Materials

Polyphosphates, metaphosphates and most of other inorganic compounds were the same samples as those described in previous papers (4,5). Sodium oxalate, trisodium salt of nitrilotriacetic acid (NTA) and tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) were of special reagent grade, obtained from Wako Pure Chemicals Co. Sodium alkylbenzene sulfonate (Na-LAS), the average alkyl chain of which was $C_{12}$, was the same sample as that used in a previous work (6). Beef tallow [acid value (AV), 3.2; saponification value (SV), 205; iodine value (IV), 42.6], lanolin (AV, 2.0; SV, 89.3; IV, 35.1) and oleic acid (AV, 201; SV, 203; IV, 89.6) were specially prepared commercial samples. Bentonite clay and carbon black used for standard soiled cloth were supplied from Hojun-Youko Co. and Tamagawa Co., respectively.

The fabric used was a polyester/cotton blend of 60/40 which was desized, bleached and unfinished. It was extracted for 12 hr in a Soxhlet apparatus with a 1:1 mixed solvent of ethanol and benzene. The fabric was cut into 5 × 10 cm swatches.

### Soiled Cloth

An artificial soil was formulated, having a composition of 6% oleic acid, 6% beef tallow, 8% lanolin, 8% carbon black and 72% bentonite clay. Oleic acid, beef tallow, lanolin and carbon black were mixed well, and then bentonite clay was added to this blend. The mixture was milled for 2 hr in a mortar. The soil thus obtained was a free-flowing powder. In a knobbed vessel of 2 liters capacity, 1.6 g of the soil and 40 swatches of the fabric were blended, and shaken up and down for 1 hr. Then both sides of the soiled swatches were brushed several times in the same direction and ironed. The swatches soiled in this way were kept for a week in a desiccator at 25 C before use.

### Laundering Experiments

The laundering experiments were performed in a Launder-O-Meter, using 100 ml of hard water with a built detergent and washing for 15 min at 40 rpm at 25 C. The hard water contained calcium and magnesium ions in a mole ratio of 2 to 1 having a total hardness of 72 ppm as calcium carbonate. Each Launder-O-Meter beaker contained 2 soiled swatches and 10 quarter inch stainless steel balls. The swatches washed were rinsed once in the same hard water for 5 min. Three replicate runs were made for each washing solution to obtain reliable averages. The swatches were then air dried and ironed.

The change in reflectance due to variation in blackness of carbon on a swatch has been taken as an index of detergency. Reflectance readings were made with a Color Machine Model CM-30 reflectometer (Color Machine Kaisha, Ltd., Tokyo, Japan) using a plate of magnesium oxide as a reference. The result was expressed as per cent detergency (7).

### Emulsion Stability Measurements

Emulsions were prepared as follows. In a 150 ml beaker, 50 ml of benzene solution, containing 0.01 or 0.10 *M* oleic acid and a very small amount of Waxsoline Red as an indicator, were added to a 50 ml of distilled water containing a definite amount of sodium hydroxide. The mixture of benzene-oleic acid-water was agitated with a magnetic stirrer at a fixed speed for 15 min. The emulsion thus prepared was

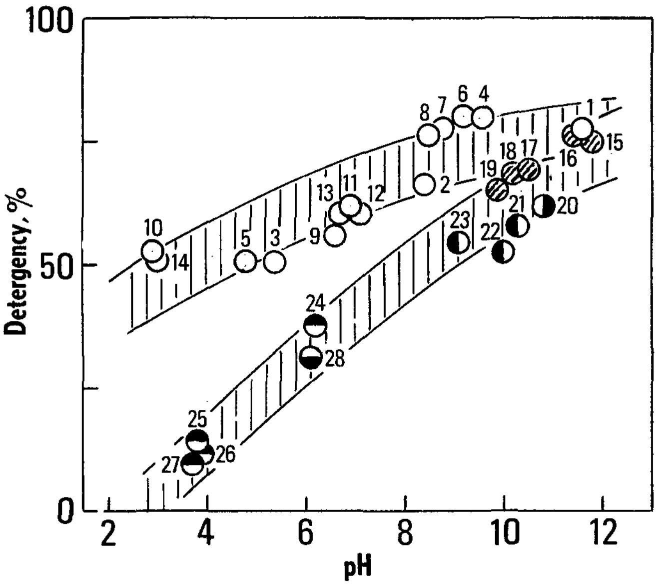

FIG. 1. The dependence of detergency on the pH of 0.20% detergent solutions with phosphates (○), silicates (⊘), carbonate (◑), borates (◐), sulfates (◓) or chloride (◒) at 25 C. (The number attached to each point refers to the sample number given in Table I.)

poured into a graduated glass-stopped cylinder of 100 ml capacity and 20 cm height. The cylinder was allowed to stand and the readings of the benzene phase, emulsion phase and water phase were taken at various intervals.

### Buffering Capacity Measurements

pH Titrations were made of the solutions of inorganic electrolytes, using an automatic pH meter, Potentiograph E-336, with Beckman standard buffers. The solutions, the concentration of which was 1.0%, were titrated with 2.82 N hydrochloric acid solution at 25 C. The buffering capacity B, which is expressed as dB/dpH where B is the amount of the acid added, was calculated from the pH titration curve at each pH (8).

### Calcium Sequestration Measurements

In a 200 ml beaker, a solution containing 0.10% sodium oxalate and 0.10% sample compound (phosphates or aminocarboxylates) was prepared and the pH of the solution was adjusted to pH 9.5 ~ 10.0 by adding either 0.1 N HCl or 0.1 N NaOH solution. A definite volume of the sample solution was pipetted into a 100 ml beaker. Nephelometric titration was performed with 0.25% calcium chloride solution at 25 C by thoroughly stirring so as not to give a high localized concentration of the titrant and not to mistake the judging of the attainment of equilibrium (9). The end point was determined with the naked eye. The pH of the solution was controlled by periodic additions of 0.1 N NaOH solution.

## Results and Discussion

### The Builder Effect of Inorganic Electrolytes on Detergency

Table I summarizes the builder effects of various types of inorganic electrolytes, i.e., phosphates, silicates, carbonate, borates, sulfates and chloride, on detergency towards standard soiled cloth. The building action of phosphates is in general higher than that of other electrolytes. Among phosphates, polyphosphates exhibit a better building action than metaphosphates, and the normally alkaline salts are better than the acid or the neutral salts. With other electrolytes, this builder effect is in the order of silicates > carbonate > borates > chloride, sulfates. The action of silicates is relatively high which would be closely related to the pH of the solutions, as will be described later.

Theories of soiling and soil removal involving electrostatic attraction or repulsion are often employed because of the ubiquity of electrokinetic phenomena and the success of the Verway-Overbeek-Derjaguin theory in explaining colloid stability in other systems (10,11). In a previous paper (5), the suspension stability of solid particles such as titanium dioxide and ferric oxide in the presence of various types of electrolytes has been discussed in relation to the electrophoretic mobilities or zeta potentials of these particles. The higher the zeta potential of particles, the greater the stability of their suspension, although a few exceptions were found. In the process of washing the electrical potential causes a repulsion between dirt and fabric so that the dirt worked loose by mechanical washing action can not redeposit on the fabric. The zeta potentials of solid particles in the solutions of phosphates are higher than those in the solutions of other electrolytes. This could partially explain the remarkable builder effect of phosphates on detergency.

### The Importance of Alkalinity in Detergent Solutions

The extent of the building action of inorganic electrolytes depends on the pH of the detergent solution containing them. The effect of pH on detergency is shown in Figure 1 where the detergencies of various inorganic electrolytes are plotted against the pH of the detergent solutions. It is seen that the detergency increases with increasing pH of the detergent solution, and this tendency is more remarkable in inorganic electrolytes other than phosphates.

As reasons for importance of the presence of alkali

TABLE I

Builder Effects of Various Inorganic Electrolytes on Detergency Towards Standard Soiled Cloth at a Concentration of 0.20% Detergent[a]

| Electrolytes | | Sample No. | pH[b] | Detergency % |
|---|---|---|---|---|
| Polyphosphates | $Na_3PO_4$ | 1 | 11.6 | 77.3 |
| | $(Na_2HPO_4)$ | 2 | 8.4 | 66.7 |
| | $(NaH_2PO_4)$ | 3 | 5.4 | 50.2 |
| | $Na_4P_2O_7$ | 4 | 9.6 | 79.8 |
| | $(Na_2H_2P_2O_7)$ | 5 | 4.8 | 50.5 |
| | $Na_5P_3O_{10}$ | 6 | 9.2 | 80.0 |
| | $Na_6P_4O_{13}$ | 7 | 8.8 | 77.5 |
| | $Na_7P_5O_{16}$ | 8 | 8.4 | 76.0 |
| Metaphosphates | $Na_3P_3O_9$ | 9 | 6.6 | 55.6 |
| | $(Na_2HP_3O_9)$ | 10 | 2.9 | 52.8 |
| | $Na_4P_4O_{12}$ | 11 | 6.9 | 61.9 |
| | $Na_5P_5O_{15}$ | 12 | 7.1 | 60.3 |
| | $Na_6P_6O_{18}$ | 13 | 6.7 | 60.1 |
| | $(Na_3H_3P_6O_{18})$ | 14 | 3.0 | 51.0 |
| Silicates | $Na_2O \cdot 0.5SiO_2$ | 15 | 11.8 | 75.0 |
| | $Na_2O \cdot 1.0SiO_2$ | 16 | 11.4 | 76.1 |
| | $Na_2O \cdot 2.0SiO_2$ | 17 | 10.5 | 69.4 |
| | $Na_2O \cdot 2.5SiO_2$ | 18 | 10.2 | 68.8 |
| | $Na_2O \cdot 3.3SiO_2$ | 19 | 9.9 | 64.9 |
| Carbonate | $Na_2CO_3$ | 20 | 10.8 | 61.9 |
| Borates | $NaBO_2$ | 21 | 10.3 | 57.8 |
| | $NaBO_3$ | 22 | 10.0 | 52.2 |
| | $Na_2B_4O_7$ | 23 | 9.1 | 54.4 |
| Sulfates | $Na_2SO_4$ | 24 | 6.2 | 37.5 |
| | $Al_2(SO_4)_3$ | 25 | 3.8 | 14.0 |
| | $K_2Al_2(SO_4)_4$ | 26 | 3.9 | 11.7 |
| | $(NH_4)_2Al_2(SO_4)_4$ | 27 | 3.7 | 9.5 |
| Chloride | NaCl | 28 | 6.1 | 31.0 |

[a] Detergent formulation: Na-LAS/inorganic electrolyte/$Na_2SO_4$ = 20/40/40 (When $Na_2SO_4$ was used as an inorganic electrolyte, Na-LAS/$Na_2SO_4$ = 20/80).
[b] The pH of 0.2% detergent solution before washing.

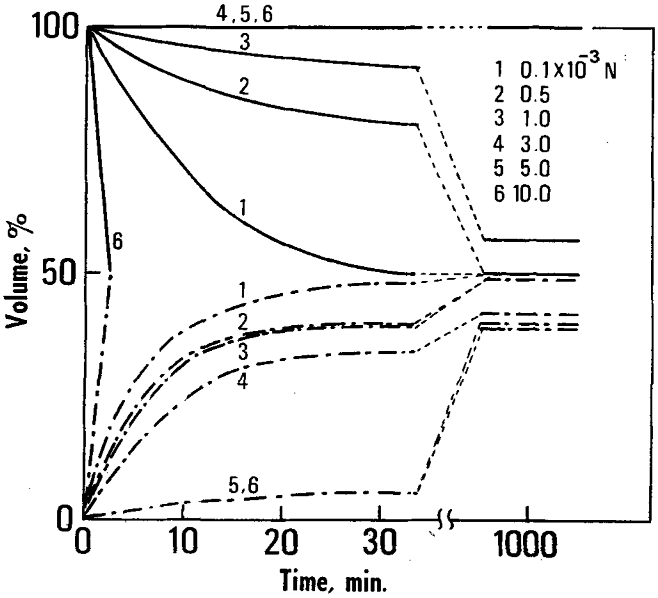

FIG. 2. The effect of the concentration of sodium hydroxide on the stability of benzene-water emulsion in the presence of 0.005 M oleic acid: ———, interface between benzene and emulsion phases; — · — ·, interface between water and emulsion phases. (The number in the figure indicates the concentration of sodium hydroxide. No. 6 indicates no oleic acid.

in detergent solution, several factors are considered. Among these factors, the emulsification of oily materials in soils attached to a substrate may be one of the major ones. Natural domestic dirts generally contain oils, greases and fats, 30% of which are free fatty acids (12,13). These free fatty acids are supposed to play an important role in emulsification, under alkaline condition, to remove oily materials from the substrate.

Figure 2 shows the effect of the concentration of alkali, NaOH, on the stability of a benzene-water emulsion containing 0.005 *M* oleic acid as a function of time. The volume of the emulsion phase at a given time after preparation, which is a measure of the stability of the emulsion, increases with increasing concentration of NaOH. In the absence of oleic acid, however, a stable emulsion could not be obtained even at high concentrations of NaOH. Oleic acid in the benzene phase will react with alkali in the water phase at the interface to produce sodium oleate. In the present case, this nascent sodium oleate would enhance the emulsification of the oily material (benzene). The result obtained here suggests that free fatty acids in soils have a close relation to alkali in detergent solution in the process of washing. A similar result has been obtained for the emulsion in the presence of 0.05 *M* oleic acid. The effect of alkali on the stabilization of the emulsion is more remarkable than that shown in Figure 2.

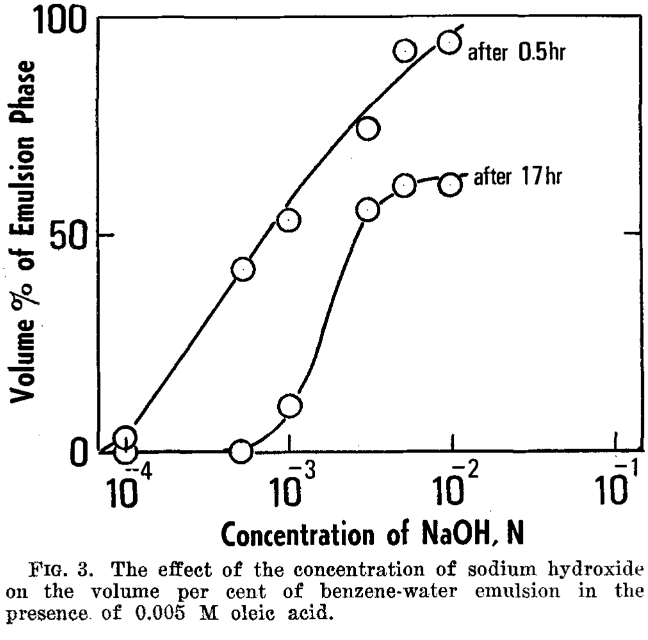

FIG. 3. The effect of the concentration of sodium hydroxide on the volume per cent of benzene-water emulsion in the presence of 0.005 M oleic acid.

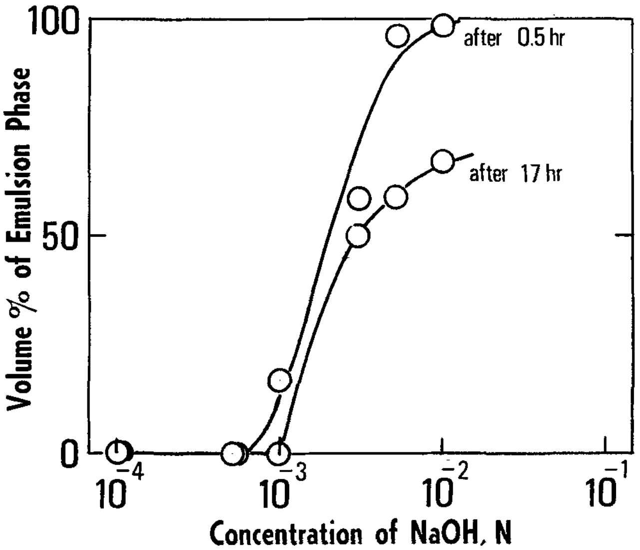

FIG. 4. The effect of the concentration of sodium hydroxide on the volume per cent of benzene-water emulsion in the presence of 0.05 M oleic acid.

Figures 3 and 4 give the relation between the volume

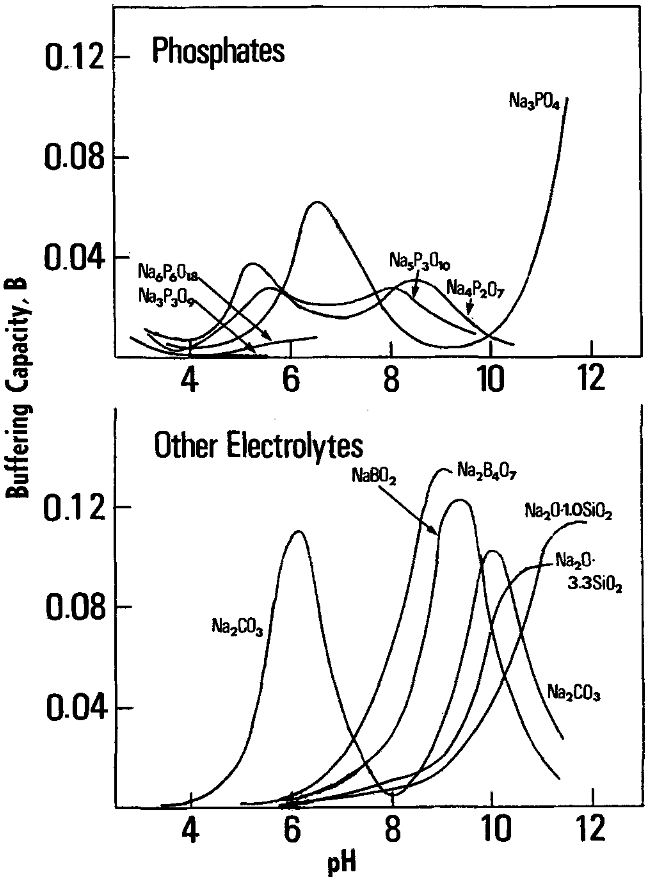

FIG. 5. The relation between buffering capacity $\beta$ and pH for 1.0% inorganic compound solutions at 25 C.

TABLE II

Buffer Indexes of Various Inorganic Electrolytes at a Concentration of 1.0% at 25C

| Electrolytes | | Initial pH | Buffer Index[a] | Electrolytes | | Initial pH | Buffer Index[a] |
|---|---|---|---|---|---|---|---|
| Phosphates | $Na_3PO_4$ | 12.0 | 3.82 | Silicates | $Na_2O \cdot 0.5SiO_2$ | 12.4 | 9.85 |
| | $Na_2HPO_4$ | 9.2 | 0.31 | | $Na_2O \cdot 1.0SiO_2$ | 12.3 | 6.63 |
| | $Na_4P_2O_7$ | 10.5 | 0.38 | | $Na_2O \cdot 2.5SiO_2$ | 11.5 | 3.42 |
| | $Na_5P_3O_{10}$ | 9.3 | 0.80 | | $Na_2O \cdot 3.3SiO_2$ | 11.0 | 3.35 |
| | $Na_7P_5O_{16}$ | 8.5 | 0.74 | Carbonate | $Na_2CO_3$ | 11.4 | 2.01 |
| | $Na_3P_3O_9$ | 5.6 | 0.12 | Borates | $NaBO_2$ | 11.2 | 1.26 |
| | $Na_6P_6O_{18}$ | 6.7 | 0.45 | | $Na_2B_4O_7$ | 9.2 | 4.51 |

[a] The milliliters of 2.82 N hydrochloric acid required to decrease the initial pH of the solution by 1 pH unit.

per cent of the emulsion phase and the concentration of sodium hydroxide at a definite time after the preparation of the emulsion to show more clearly the concentration effect of alkali on the emulsification of the oily material. Figure 3 refers to 0.005 *M* oleic acid and Figure 4 to 0.05 *M* oleic acid. In both cases, emulsification takes place at $10^{-4} \sim 10^{-3}$ N sodium hydroxide (pH 9 ~ 10): the larger the amount of oleic acid present, the higher the concentration of sodium hydroxide required. This implies that when the cloth to be washed is heavily soiled, a greater amount of alkali is needed to obtain a satisfactory detergency.

### The Buffering Capacity of Inorganic Electrolytes

The results presented above suggest that a high pH value is needed in the process of washing. Figure 5 shows the relation between the buffering capacity $\beta$ and pH for solutions of 1.0% inorganic compounds. The buffering actions of borates, silicates and carbonate are greater than those of phosphates. With phosphates, the first effective pH, at which the buffering action is remarkable, for ortho-, pyro- and tripolyphosphate is approximately >11, 8.5 and 8.0, respectively. Their buffering capacity depends on the chain length of the phosphate molecule. It has been reported that the buffering action of chain phosphates comes only from the ends of the chains where there is a weakly acidic replaceable hydrogen (1,9). Therefore, the shorter the chain, the better the buffering action per unit weight of the phosphate. This means that the buffering action of the pyrophosphate is better than that of the tripolyphosphate and that both of these are much better buffering agents than glassy phosphates. Trimetaphosphates have essentially weak buffering action because there is no end-group.

Table II also gives the buffer index and initial pH of inorganic electrolytes at a concentration of 1.0% to show more clearly their alkalinity. The buffer index given in Table II is defined, in this case, as the milliliters of 2.82 N HCl required to decrease the initial pH of the solution by 1 pH unit.

### The Sequesteration Capacity of Phosphates

Unless calcium and magnesium ions are sequestered, they will form insoluble salts called 'soap curds' with anionic surfactants and present deleterious effects such as soil redeposition (14,15). Among the builders examined, phosphates except orthophosphate have an ability to sequester calcium, magnesium and other heavy metal ions. Table III gives the sequesteration capacities of phosphates for calcium ion at pH 9.5 ~ 10.0, i.e., the number of milligrams of calcium carbonate sequestered by one gram of the phosphate at pH 9.5 ~ 10.0. For comparison, the sequesteration capacities of trisodium nitrilotriacetate (NTA) and tetrasodium ethylenediaminetetraacetate (EDTA) are also given in Table III. The ability of pyrophosphate for the sequesteration of calcium ion is about a half of the ability of tripolyphosphate. The tri-, tetra- and pentapolyphosphates have nearly the same value which is roughly comparable to the value for EDTA. Trimetaphosphate is not so effective, as seen in Table III. The ability to sequester heavy metal ions is very important in practical detersive systems. The building effect of polyphosphates on detergency is higher than that of silicates in spite of lower pH of their solutions. This may be partially attributed to the sequestering ability of polyphosphates although other abilities such as suspending power should have some relation to the building action.

TABLE III

Sequesteration Capacities of Phosphates and Aminocarboxylates for Calcium Ion at 25C (The pH of the solution was adjusted to pH 9.5 — 10.0)

| Samples | Seq'n capacity $CaCO_3$ mg/g | Samples | Seq'n capacity $CaCO_3$ mg/g |
|---|---|---|---|
| $Na_3PO_4$ | 0 | $Na_3P_3O_9$ | 18 |
| $Na_4P_2O_7$ | 136 | $Na_6P_6O_{18}$ | 233 |
| $Na_5P_3O_{10}$ | 270 | $Na_3$-NTA | 390 |
| $Na_6P_4O_{13}$ | 261 | $Na_4$-EDTA | 264 |
| $Na_7P_5O_{16}$ | 269 | | |

From the results reported previously (4,5) and presented here, it can be concluded that the following factors are at least important in the building action of inorganic compounds: (a) The suspension of soil particles in a detergent solution, (b) the sequesteration of heavy metal ions, and (c) the alkalinity including buffering action to keep the solution alkaline. The reason why phosphates, in particular tripolyphosphate, have been used widely as a major builder of detergents is probably due to their ability to satisfy at least the above three factors (although their alkalinity is not so strong). This concept will be proved without the use of tripolyphosphate in a forthcoming paper. The importance of the combination of these three factors, the suspension of soil particles, the sequesteration of deleterious ions, and the alkalinity including alkali buffering capacity, in building action will also be demonstrated in more details in the next paper of this series.

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