Recent Studies on the Roles of Silicate Builders in Detergent Formulations

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Abstract

In today's detergency silicates are called upon to perform more roles than in the past. The providing of alkalinity and soil suspension properties remain important, but the less obvious properties of silicates are often unrecognized.

Interaction between silicates and phosphates in solution lead to enhanced builder properties over each component alone. Additionally, silicate acts to slow down the reversion of high-molecular-weight phosphates. Silicate solutions may be used to hydrate sodium tripolyphosphate commercially in order to provide useful particles containing both builders in easily soluble form. The alkalinity of sodium silicate may be used to convert sodium trimetaphosphate to tripolyphosphate, again providing a particle with both builders present.

Silicates prevent corrosion of metals, especially in the presence of phosphates. This corrosion prevention is discussed in regard to the effect of alkali-to-silica ratio and the influence of neutral salts on the system. The prevention of insoluble formation can be achieved by increasing the quantity of silicate in the formulation or by providing a vapor-barrier package.

This paper also reviews the fundamental properties of sodium and potassium silicates that have importance from the standpoint of detergency.

Introduction

THE PRESENT-DAY EMPHASIS on using combinations of many ingredients in cleaning formulations in order to obtain the best possible cleaning properties leads naturally into research efforts to define how these properties are obtained and the role that the various ingredients play. This paper will show that the silicates play many roles, some of them rather complicated, providing a rational basis for the inclusion of silicates in modern cleaning formulations and indicating that their continued use is not only justifiable but highly desirable.

About 100 years ago silicates were first introduced in order to act as builders for laundry bar soaps, where it was found empirically that foam stability was improved and the insoluble soaps formed by water hardness were decreased by the presence of soluble silicates. Their use was later expanded into the fields of synthetic detergents, metal cleaning, and other suspension problems, such as ore flotation and clay dispersion. Although many popular formulations are basically simple from the chemical standpoint, it is true that today the household cleaning formulations, in particular, are becoming more and more sophisticated so that the contribution desired from silicate is subject to change in emphasis. Metal-cleaning formulations however have remained fairly static over the past several years although these too are expected to undergo changes as new metals are introduced to commerce in larger quantities.

The usual way of expressing the chemical composition of silicates is by the SiO_2:Na_2O weight ratio. Commercial silicates are available from a ratio of 0.5 to 4.0. Crystalline ortho-, meta-, and sesquisilicates are available in hydrated and anhydrous form or in both. Ratios above 1.0 are glassy in nature and are available as either anhydrous or hydrous solids; the water contents are designed to give rapid solubility. The liquid silicates, actually water solutions of sodium silicates, are the most widely used form. These are available in various ratios up to 4.0; the solids content is chosen to provide densities and viscosities consistent with convenient handling. Potassium silicates are also available in solution as well as in solid form, but readily soluble crystalline potassium silicates are not known.

The chemistry of silicate solutions involves what has become known as the crystalloidal-colloidal balance. Below a mole ratio of 2 SiO_2:Na_2O the silicate anion consists of either one or two silicate tetrahedra. The ortho- and metasilicate structures are well characterized; the metasilicate exists in many different hydrated forms, and the most common one is a 5 hydrate. Sodium disilicate can be prepared and has low solubility in cold water; but it is readily soluble in hot water and represents a well-characterized crystal structure. Above a mole ratio of 2 the molecular weight of silicates increases as polymerization takes place. The transition from simple anions to more complex polymer structures is a sharp one, as shown below.

Some recent results on molecular-weight determination are shown in Table I. Fig. 1 shows the dependence of molecular weight on mole ratio, indicating strongly the difference in behavior between sodium silicates with higher than a 2 ratio and those below the disilicate ratio. This behavior carries over into intrinsic viscosity measurements, as shown in Fig. 2, where a break is also obtained at the 2 ratio. Additional light-scattering studies have shown that the high-molecular-weight polyelectrolyte particles in the high-ratio sodium silicate are spherical and that the electrical charges are uniformly distributed about the particles. The data in Table I show also that potassium silicates have much higher molecular weights than sodium silicates for equivalent mole ratios and are therefore more highly polymerized.

This dual nature of soluble silicates has often been termed the crystalloidal-colloidal character and is responsible for considerable duality in the behavior of silicates in solution, a duality which is pertinent in the field of soil removal. It is therefore ambiguous to make blanket statements about silicates in general without defining the ratio at which the silicate is applied or becomes effective. In practice it is necessary

TABLE I

Molecular Weight of Soluble Silicates from Light Scattering

Wt. ratio SiO_2/M_2O	Mol. ratio SiO_2/M_2O	Molecular weight	Type
3.98	4.11	550	Sodium silicates
3.22	3.32	322	
2.56	2.64	265	
2.04	2.11	158	
1.65	1.70	118	
0.98	1.01	90	
2.50	3.92	1538	Potassium silicates
2.10	3.30	1150	

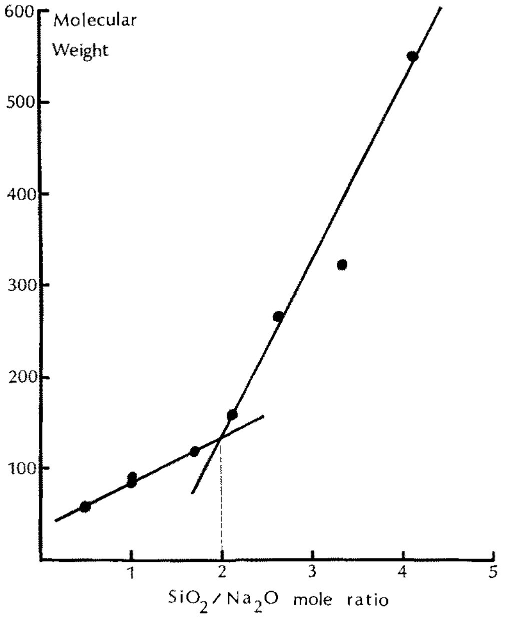

FIG. 1. Variation in silicate molecular weights with mole ratio.

to take into account the other components, particularly such components as either raise or lower the pH of the system. The dynamic equilibrium between the crystalloidal and colloidal silicate anions is such that compounds which increase pH will increase the crystalloidal or monomeric character of the silicate whereas compounds which lower pH will increase the colloidal or polymeric character of the silicate.

The dynamic character of this equilibrium is taken advantage of by formulators in practice. It is possible, for example, to include a metasilicate in a formulation in such a way that, once placed in solution, the metasilicate will generate strong alkalinity and therefore is an excellent cleaner for steel surfaces. But the same metasilicate placed in solution in combination with some other ingredients will, in effect, become a high-ratio silicate and function as a soil-suspending agent and a corrosion inhibitor for soft metals. Thus the behavior of the silicate cannot be described on the basis of silicate alone but must be considered in terms of total formulations and conditions of use. It is the complexity of this system, in a chemical sense, that has made silicates such a versatile class of compounds and so popular in detergency throughout the periodic formulation changes of the last hundred years.

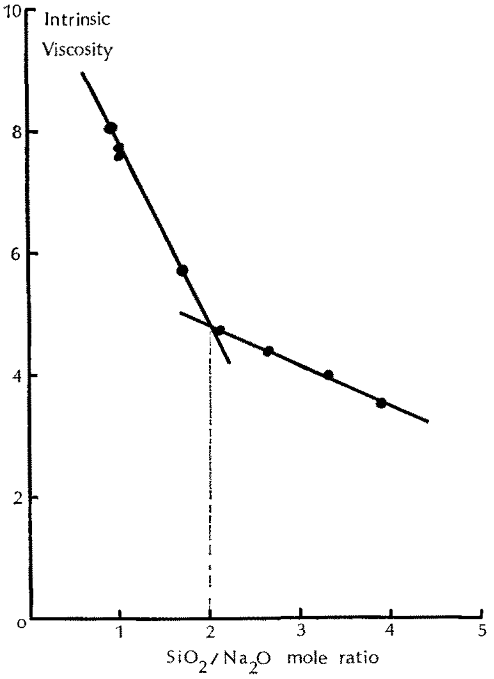

FIG. 2. Variation in silicate intrinsic viscosities with mole ratio.

Silicates of the entire ratio range can be of interest in cleaning formulations. Where hard metallic surfaces are to be cleaned, the preferred mole ratio is between 0.5 and 1 corresponding to ortho- or metasilicate. Most household detergents employ silicates in the 1.7 to 2.5 mole-ratio range.

Interactions in Solution

Combinations of silicate, phosphate, and surfactant are used so frequently in washing formulations that it is worthwhile to take a look at the interactions between these three components in solution. We have done this by means of measuring the critical micelle concentration of the surfactant in the presence of both silicates and phosphates and by studying silicate-phosphate solutions alone.

Fig. 3 shows the surface tensions owing to silicate with a 1.6 SiO_2/Na_2O weight-ratio and sodium tripolyphosphate. Neither one of these compounds alone affects the surface tension of the solution to any great extent; the surface tension of water is approximately retained. However, when combinations of silicate and phosphate are used, a small increase in surface tension is seen at low concentration up to about 1 weight percentage of solids. Above this concentration of solids there is an area where surface tension is lowered significantly in the presence of an equal or greater amount of phosphate relative to the silicate. Surface tensions in this region are poorly reproducible, a behavior typical of a surface that needs to be aged before reliable values can be obtained. Thus we can see that combinations of silicate and phosphate have considerable surface activity, and this surface activity is greater than each component alone would lend to the system.

Fig. 4 shows the effect of silicate-phosphate builder combinations on surfactant critical micelle concentration for an anionic surfactant. The 1.6 ratio silicate and the sodium tripolyphosphate have equivalent sodium concentrations for equal weights, and line 1 on Fig. 4 indicates that they are equivalent in depressing the critical micelle concentration of the detergent. With a combination of silicate and phosphate in equal amounts or with the silicate in excess, the

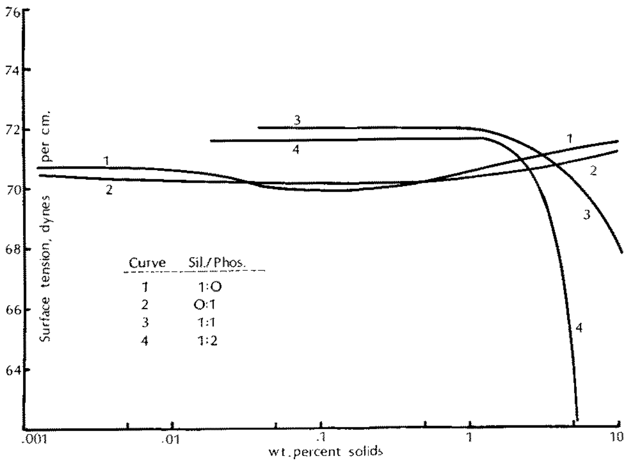

FIG. 3. Interactions between silicates and phosphates in solution.

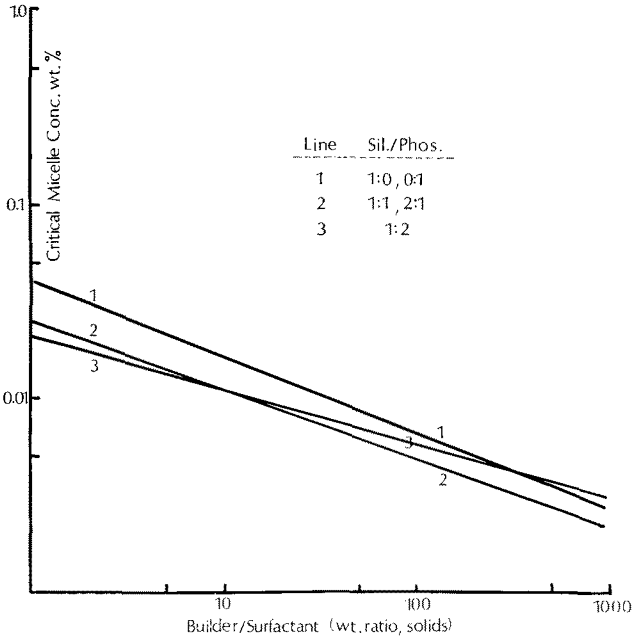

FIG. 4. Silicate-phosphate-surfactant interactions in solution.

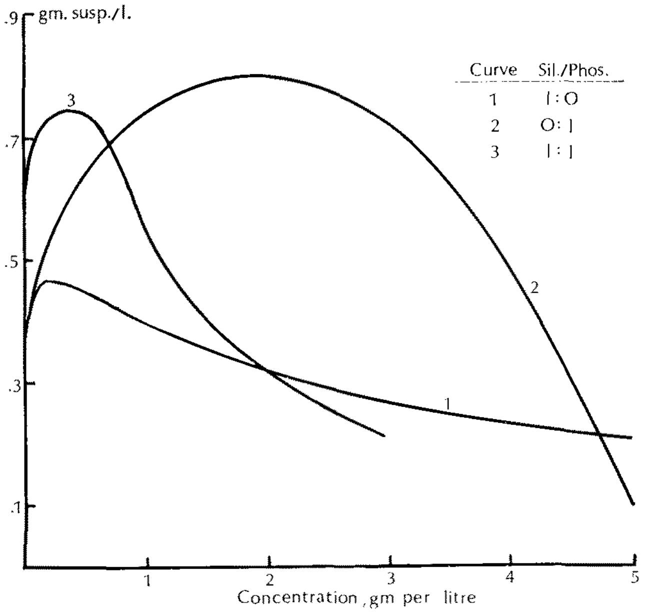

FIG. 5. Effect of silicate-phosphate interactions on suspending power.

critical micelle concentration is lowered beyond the value simply because of the sodium ion present, line 2 on Fig. 4. When the sodium tripolyphosphate is in excess, yet a different type of behavior is found, such that the critical micelle concentration is significantly lowered at low ratios of builder to surfactant and is raised at high ratios of builder to surfactant. The low area of builder-surfactant corresponds to the formulation of most household laundry compounds, and the combination of silicate and phosphate clearly gives a lower critical micelle concentration than either builder alone would. The high builder-surfactant ratios are used in the field of metal cleaning or mechanical dishwashing, and an excess of silicate over phosphate would give some advantage.

The enhanced surface activity from combinations of silicate and phosphate applies in the field of ore flotation as well as to suspension of polar soil in detergency. Thus Fig. 5 shows the data on the suspension of Ilmenite in water by combinations of silicate and phosphate. Although silicate alone shows its maximum activity at a low concentration, lower than that shown by the pyrophosphate, it is nevertheless true that the pyrophosphate is more efficient in suspending the Ilmenite. However, when combinations of phosphate and silicate are used, it can be seen that the total suspending efficiency is increased.

With the silicate-phosphate combinations the high suspending power of the phosphate is retained while the optimum concentration is lowered to the level represented by the silicate. This kind of synergistic effect is desirable in detergent builder formulations for the economical suspension of polar soils and the prevention of redeposition.

Reversion of Phosphates

Much has been published on the reversion of phosphates to lower-molecular-weight species and the effect of alkalies, acids, temperature, pH, etc. This type of work has recently been extended by comparing the reversion of phosphates in the presence of sodium silicates, sodium hydroxide, and water. In general, one can say that the base-catalyzed depolymerization of phosphates is more rapid at the lower pH than at high and that elevated temperatures cause more rapid rates of reversion. This kind of generalization is true in water systems with added base in the form of sodium hydroxide or any other simple alkali. The following results were obtained at a concentration of 10 g of sodium tripolyphosphate per 100 g of H_2O. The alkalies were added so as to obtain a ratio of Na_2O to STPP of 1:3.4.

Silicates have a definite, depressing tendency on the depolymerication of STPP, as shown in Table II.

As can be seen from the data above, in spite of the fact that the pH is being reduced from sodium hydroxide to metasilicate and to the 2.4 ratio sodium silicate, the depolymerization rate of the sodium tripolyphosphate decreases. As a comparison, the straight hydrolysis by water is given where the formation of ortho- and pyrophosphate is considerable and the pH change to 6.85 is almost two units lower after the hydrolysis than before, as the result of the formation of POH groups from the hydrolysis. The analytical results on the solutions after 16 hr are shown in Fig. 6; each of the three phosphates is analyzed in terms of relative P_2O_5 percentages. These results were obtained by column gradient elution chromatography, and the phosphate is finally determined as the hydrolyzed orthophosphate in the phosphomolybdate complex.

Hydration

The water from sodium silicate solutions may be used to hydrate anhydrous sodium tripolyphosphate and dry the mix by the heat of hydration. This is an alternative to spray-drying for the preparation of intimate mixtures of various components although the bulk density is bound to be greater.

TABLE II
Depolymerization of Sodium Tripolyphosphate[a]

Alkali used	pH after heating	% Reverted (corrected for STPP purity)
None	6.85	48.1
NaOH	13.20	52.4
Sod. metasilicate	12.90	44.6
2.4 Ratio sod. sil.	11.48	42.4

[a] Sample heated at 80C for 16 hr. Analysis of STPP: 94.75 STPP, 5.25% sodium pyrophosphate.

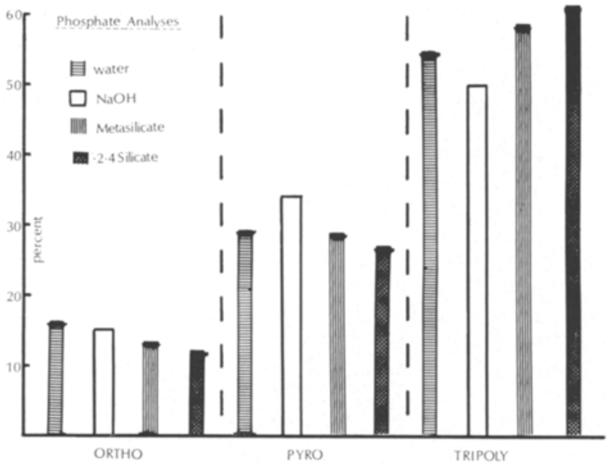

FIG. 6. Analyses of phosphate solutions after hydrolysis.

Type II sodium tripolyphosphate, anhydrous, in conjunction with a liquid silicate will yield formulations of dry, granular washing compounds on apparatus as simple as a ribbon blender. A typical formulation might be made up as follows: 40% anhydrous Na_2SO_4; 10 to 15% of a nonionic surfactant; up to 10% of a silicate of a 2 SiO_2/Na_2O ratio or greater, at a concentration of approximately 60% water, 40% solids; 30% anhydrous sodium tripolyphosphate; and 12 to 15% of water added as such, CMC, brightener, etc.

The above can be mixed in a ribbon blender; a dry product is obtained in approximately 15 min of mixing. Such a product will, upon extensive storage under adverse conditions, develop not more than 1% insoluble matter, be readily soluble in water, and be intimately mixed.

The bulk density of a product made by simple ribbon blending, by using the heat generated internally by hydration, is approximately 55 lb per cu ft, which is, of course, very much higher than generally desired for consumer washing-compounds. The bulk density can be lowered considerably by the inclusion of low-density sodium carbonate in place of sodium sulfate, by changing the order of the addition of the components of the mixture, or by applying some external heat during the drying operation in order to remove excess water at a more rapid rate.

The nonionic surfactants have a tendency to desorb from the solid particles to form a separate liquid phase that may stain the carton upon storage or give pasty products. The separation of such surfactants may be reduced by either increasing the SiO_2/Na_2O ratio of the silicate from 2.0 to 2.4 or by increasing the total surface area available, for example, by using a low-density sodium carbonate in place of high-density ingredients. Substitution of about one-third of the nonionic by an anionic surfactant is effective in reducing desorption.

Reaction with Trimetaphosphate

A recent paper by Horikawa et al. reported in detail upon the conversion of sodium trimetaphosphate to tripolyphosphate by using sodium silicate as the source of alkali. This reaction proceeds exothermally and spontaneously at room temperature. Conversion to the tripolyphosphate is complete with only a trace of pyrophosphate being formed and no lower-molecular-weight phosphates.

This reaction proceeds smoothly to completion, when the starting ratio of the silicate is below 1.5, to give a product that is dry to the touch and granular (Table III). When the reaction was carried out with sodium hydroxide, a light yellow product was obtained while a white product was obtained by use of sodium silicate. It was found that the addition of sodium hydroxide to sodium tripolyphosphate would lead to a light yellow color as well. After air-drying, the granulated product contains 20 to 25% water, the tripolyphosphate is completely hydrated, and the remaining water is associated with the silicate, the ratio of which has been raised by the consumption of Na_2O to convert the trimetaphosphate. The silicate-phosphate mixture, which is the product of the reaction, dissolves readily in cold water with no insoluble matter remaining. The untamped bulk density of the product is 0.67 g/cc, which is desirable from the standpoint of automatic dishwashing compounds.

The final ratio of the sodium silicate in the reaction mixture may be varied by either adding sodium hydroxide to the silicate before the reaction is conducted or by using mixtures of sodium trimetaphosphate and sodium tripolyphosphate, anhydrous. Should a mixture of phosphates be used, the resulting product will contain completely hydrated sodium tripolyphosphate. The reaction rate may be judged from the temperature increase as the reaction proceeds, as shown in Fig. 7. The fastest reaction is obtained with sodium hydroxide, followed by sodium orthosilicate, then by sodium metasilicate-5 H_2O. With the 1.6 ratio silicate it can be seen that the reaction is relatively slow.

With this process the detergent manufacturer has a new approach to making an intimate, dry mix at low processing cost. The heat of reaction plus the heat of hydration dry the product but leave it high enough in water content to give good solubility. An intimately mixed formulation has considerable advantages over mechanical mixtures that may segregate or have poor appearance. Further, it is free from the caking that results from the water migration which takes place in mixtures of hydrates and anhydrous components.

Corrosion Prevention

When we consider the question of corrosion prevention by silicates, particularly on soft metal surfaces such as aluminum or zinc, we must contend with the dualistic nature of sodium silicate below and above a 2 ratio. The crystalloidal silicates, such as sodium metasilicate, are monomeric and highly alkaline, giving solutions of high pH almost equivalent to those obtained with sodium hydroxide. The hydroxyl ion is left free to react with soft metal surfaces with the evolution of hydrogen and the formation of the metal oxide. Silicates with a ratio greater than 2 are capable of protecting metal surfaces; the higher the ratio, the

TABLE III

Silicate used	SiO_2/Na_2O (wt) (starting)	SiO_2/Na_2O (wt) (final)	Phosphate conversion to tripoly	Appearance of product
Orthosilicate	0.50	1.98	99+%	White, dry
Na Metasilicate·5 H_2O	0.98	1.94	99+%	White, dry
Na Metasilicate·5 H_2O	0.98	2.40	99+%	White, dry
1.6 SiO_2/Na_2O	1.58	2.34	Incomplete	White, tacky
2.0 SiO_2/Na_2O	2.04	2.41	99+%	Tacky
2.4 SiO_2/Na_2O	2.37	2.63	99+%	Tacky
Orthosilicate + NaOH	0.25	0.50	99+%	White, dry
NaOH	......	......	99.5+%	L. yellow, dry

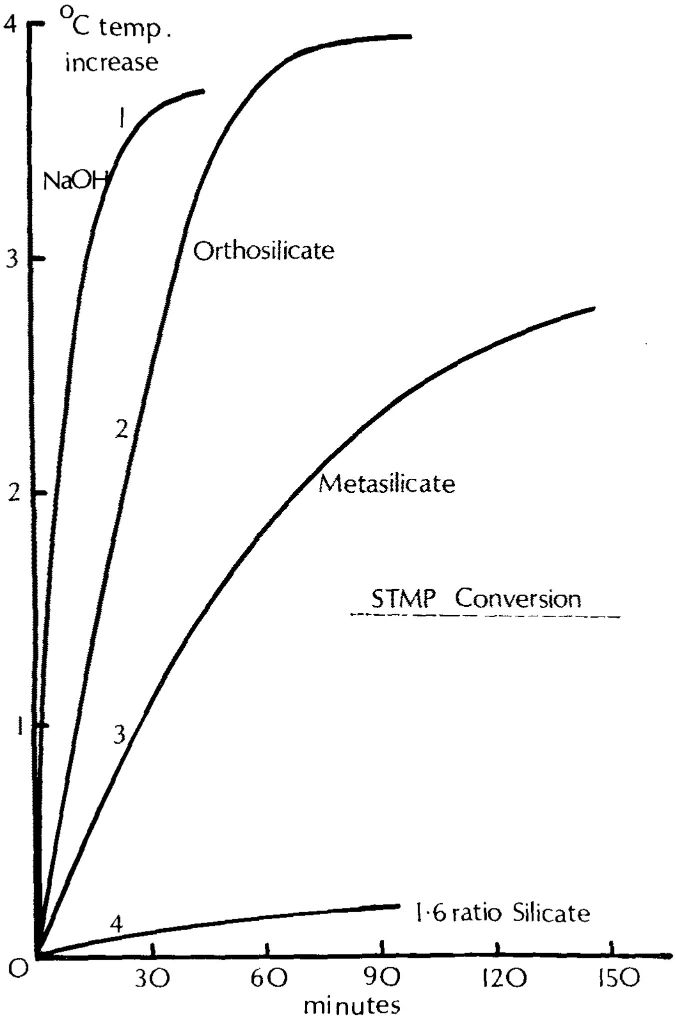

FIG. 7. Conversion of sodium trimetaphosphate to sodium tripolyphosphate.

better the protection in spite of the high pH levels attained. In this case, one is dealing with the chemisorption of negatively charged silicate micelles or high polymer colloidal particles on the surface of the metal, which thereby shield the metal from the hydroxyl ion present in solution. The bond formed between the metal and the silicate varies in strength, depending upon the metal. Aluminum will, for example, form a surface alumino-silicate which is highly stable and will give long-term protection. Iron or steel surfaces however will not react to form surface silicates to any significant extent, and the chemisorbed layer may be desorbed slowly. In such cases the solution must always contain sufficient silicate to ensure that the adsorbed micelles continue to shield the metal surface.

To state generally that the alkalinity of metasilicate solutions will react with metal surfaces is not telling the entire story. In a formulation containing a large proportion of phosphate, sodium sulfate, and other ingredients, the effective ratio of the sodium silicates is likely to rise. The phosphates are acidic with respect to sodium silicate and will therefore tend to raise molecular weight while neutral salts have a coacervating effect on the silicate. The net result is that a metasilicate may behave in such a system as though it had a ratio greater than 2 and therefore be capable of giving protection for soft metals.

Attack on porcelain glazes by highly alkaline solutions is well known if the hydroxyl ions are not shielded. Here again, the use of higher ratio silicates can prevent any significant etching. Nevertheless it is possible to use crystalloidal, low-ratio silicates in automatic dishwashing compounds, provided that the formulation also contains other salts so that partial neutralization or coacervation, with the resulting effective increase in ratio, will take place. The use of silicates with ratios above 2 is recommended to prevent glaze attack on fine chinaware.

Corrosion prevention by silicates is used to good effect by the detergent manufacturer. In today's washers most surfaces that come in contact with the cleaning formulation are resistant to corrosion, but the plant equipment often is susceptible to attack. Phosphates are bad actors in this respect because of their ability to sequester meetal ions, thereby providing a fresh surface for corrosive attack by other chemicals present. The silicate chemisorbed on metals provides an interface that protects the underlying metal from sequestration.

The protective oxide films that form on metal surfaces are sequestered by phosphate in solution unless steps are taken to stabilize these films. Silicates are effective in stabilizing the oxide films by the formation of complex surface silicates or by the chemisorption of silicate anions of high molecular weight. An example of the kind of protection that may be obtained is shown in Fig. 8, showing the results of corrosion tests that were done on aluminum and zinc by using concentrations of phosphate and silicate which are representative of spray-dryer feed slurries. The 2.4 ratio sodium silicate leaves the panels essentially unchanged except for a light protective film on the surface. But the two phosphates etch and pit the zinc rather badly and attack on the aluminum is extensive, though without pitting. Inclusion of silicate into the phosphate solutions results in aluminum panels that are practically unaffected while the zinc panels have only a light etch similar to that observed with the sodium silicate alone. None of the pitting and extensive dissolution of the zinc that took place with phosphates alone can be seen.

Insolubles

The formation of silica insolubles in heavy-duty detergent formulations results primarily from storage conditions. We have found that the absorption of water vapor and CO_2 from the air results in increased insoluble content with time. The absorption of CO_2 results in a somewhat lower pH so that the polymeriza-

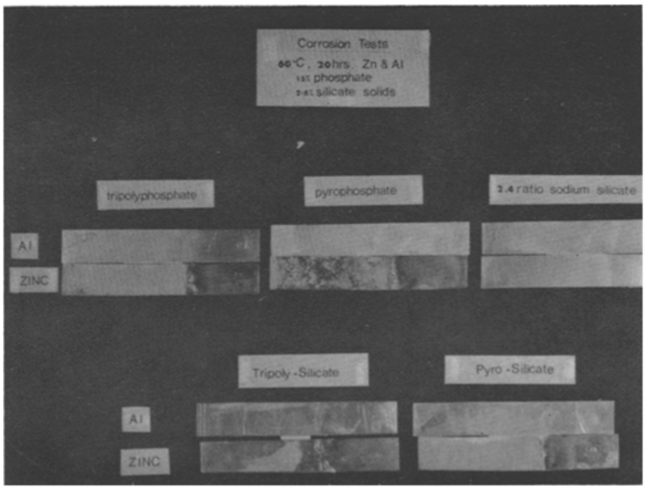

FIG. 8. Corrosion tests, Zn and Al, in the presence of silicates and phosphates.

tion of silicates may take place and a certain amount of SiO_2 is deposited. The absorption of water provides the ion migration that is necessary for this type of reaction to occur. Thus a detergent formulation can be made that has large amounts of sodium carbonate in it and yet has a low insolubles content even after long-time storage. The insolubles content in such a formulation increases only if water vapor is allowed to enter the package.

The most effective means to combat the formation of insolubles is to provide a package that is impermeable to water vapor. Such packages are in use today and are expected to become practical for heavy-duty detergent packaging. Another method of preventing insolubles is to include larger amounts of silicates in the formulation. By doing this, a high pH is maintained in spite of the fact that CO_2 absorption is taking place or alkali is being consumed by phosphate reversion. It can be shown that, for many months of storage, the relative amount of insolubles is less as the silicate content of the formulation is increased.

Much of the optical effect that has been termed attack on porcelain glaze has actually been found recently to be a question of surface filming. Three different kinds of film have been recognized, two of them owing to hard-water conditions and consisting of precipitates of calcium phosphate, when the compound contains large amounts of phosphate, and of calcium carbonate when the amount of phosphate present is low. The third type of film that occurs in soft water is attributed to the deposition of a film of silica which appears when the ratio of the silicate is too high or when too high a concentration of neutral salts is present, thus causing coacervation on the porcelain surface. This last type of filming can be avoided by using low ratio silicates, such as metasilicate, and avoiding neutral salts with anions of high-charge density, such as sulfate.

Discussion

Soluble alkali metal silicates are complex chemical systems. Their solutions may contain monomers, dimers, or higher-molecular-weight polymers. All of these are in a dynamic equilibrium, depending upon such factors as temperature, dilution, presence of salts, and the chemical composition of the silicate itself. This flexible behavior leads to many useful properties in detergency as well as in other fields. There are synergistic effects between silicates and phosphates, between silicates and detergent micelles in the presence of phosphates; the chemical behavior of polymeric phosphates may be modified by the presence of silicate. Also, silicates may prevent corrosion or reduce it, depending upon the total formulation. With some bleaches, such as isocyanuric acid, the presence of sodium silicate prevents undesirable decomposition reactions, but a proper choice of silicate particles is necessary to conserve available chlorine.

The reason that silicates continue to prove useful in the field of detergency is quite apparent from the data. In the washing of fabrics, the alkalinity provided by silicates, along with their buffering action, optimizes the detergency of the entire system without deleterious effects on the optical brighteners. The cleaning of hard surfaces may be broken down into two principal areas, dishwashing and metal cleaning. In metal cleaning it is important, for safety reasons, that no foam be built up in the electro-cleaning process; therefore it is undesirable to have large amounts of surfactant, but the high alkalinity of the silicates provides the detergency needed as well as electrical conductivity. In the formulations for automatic dishwashers, foam is also undesirable as a result of machine limitations and rinsability. Furthermore, the types of soil found on dishes are generally saponifiable, with the result that low-ratio silicates are much in demand in this field. So silicates are used in relatively large amounts in hard-surface cleaning because of the limitations of the machines, the absence of stable foams, and the advantages pertaining to a high, buffered alkalinity.

The hand dishwashing compounds for household use however do not generally employ silicates. This is not because the silicates would not do a fine cleaning job but rather because of the effect of alkalinity on human skin. Thus it is necessary to arrive at a total system that will result in a good cleaning job, preventing undesirable reactions from taking place, such as attacks on porcelain glaze, taking into account the limitations of the machines used in cleaning and the safety precautions relative to foam or to interactions with skin. All this must be done while providing an attractive, free-flowing material in a package that will be convenient to use as well as appropriate to the physical and chemical changes that may take place on storage, such as caking and development of insolubles.

The benefits to be derived from the inclusion of silicate in cleaning formulations not only involve the cleaning job at hand but also the ease of processing the formulation in the plant. There is much evidence which has been accumulated over the years that silicates prevent corrosion of plant equipment and result in slurries which may be spray-dried more readily by their inclusion. So, from the manufacturing point of view, it is also desirable to include silicates in formulations in order more easily to be able to supply the type of product needed in the field.

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