

Builders and Other Detergent Adjuvants for Water Washes

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THE PHENOMENAL GROWTH of synthetic detergents during the last decade has resulted, in great part, from the exploitation of the synergistic action existing between surfactants, builders, and other detergent adjuvants. At the present time the average heavy-duty built synthetic detergent for household



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use contains about 30-50% sodium tripolyphosphate, a chemical which has grown from an insignificant volume 10 years ago to about 1,200,000,000 lbs. per year present U. S. production.

In a typical heavy-duty built detergent there are usually about two parts of sodium tripolyphosphate and/or pyrophosphate to one part of organic active, from 5 to 10% (dry-weight basis) of sodium silicate, from 20 to 30% of soda-ash and/or sodium sulfate, (with some of the sodium sulfate often accompanying the alkylarylsulfonate active), and about 1% of sodium

carboxymethylcellulose. The phosphates are used in the formulation for their building action, the silicates primarily for their corrosion-inhibiting properties, the soda-ash as an alkaline buffer with some building action, the sulfate as a filler with slight building action, and the carboxymethylcellulose as an anti-redeposition agent. These various constituents will be discussed individually in this article, in which we shall try to clarify the functional role of the adjuvant and explain why the particular compounds now being used to fulfill this function are the best ones presently available.

Physical Chemistry of the Washing Process

Although there is no question but that the process of washing fabrics involves a number of phenomena which are related in an extremely complicated way and that these phenomena and their interrelations are not well understood, we shall try to present briefly our ideas concerning the physical chemistry of washing either fabrics or hard surfaces. The purpose of washing is obviously to remove soils, which we have arbitrarily classed in the four major categories given below:

- a) dirt, which is defined as particulate material that is usually inorganic and is very often extremely finely divided so as to exhibit colloidal properties;
- b) greasy soils, which are typified by hydrocarbons and fats (esters of glycerol and long-chain organic acids);
- c) stains, which include the wide variety of nonparticulate materials which give color even when present in very low concentration on the soiled object; and
- d) miscellaneous soils, which primarily include sticky substances and colorless liquids that evaporate to leave a residue.

The dirt on the soiled objects is held mechanically by surface irregularities to some extent. However a

major factor in binding dirt is an attraction between surfaces, which goes under the name of van der Waals' forces. This is a theoretically complicated dipole interaction which causes any extremely small uncharged particle to agglomerate with other small uncharged particles or to stick to an uncharged surface. Obviously, if colloidal particles bear charges of opposite sign or, if one kind is charged and the other kind is not, the attraction will be intensified and the tendency to agglomerate will be greatly reinforced. Likewise a charged particle will tend to stick to an uncharged surface and *vice versa*, and a charged particle will be very strongly attracted to a surface exhibiting an opposite charge. In addition, dirt particles can be held onto a soiled surface by sticky substances or by the surface tension of liquids, including liquid greases.

Greases, stains, and miscellaneous soils are usually sorbed onto the soiled surface. In most cases these soils are taken up as liquids through capillary action. In an essentially static system an oil cannot be replaced by water on a surface unless the interfacial tensions of the water phase are reduced by a surface-active agent.

The washing process whereby soils are removed consists basically of applying mechanical action to loosen the dirt particles and dried matter in the presence of water, which helps to float off the debris and acts, to some extent, as a dissolving and solvating agent. Greasy soils are hardly removed by washing in plain water, and natural waters also often contain impurities, such as calcium salts, which can react with soils to make them more difficult to remove. Therefore detergents are used. The detergent active is that substance which primarily acts to remove greasy soils. The other constituents in a built detergent assist in this and in the removal of dirty stains and the hydrophilic sticky or dried soils.

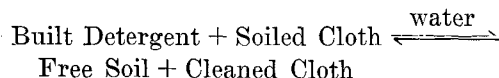
As is well-known, detergent actives belong to the chemical class consisting of moderately high molecular weight and highly polar molecules which exhibit the property of forming micelles in solution. Physicochemical investigations of anionic surfactants, including the soaps, have shown that there is little polymerization or agglomeration of the chain anions below a certain region of concentration called the critical micelle concentration (1). Below the critical micelle concentration, monomers and some dimers are present (2). In the critical micelle region there is a rapid agglomeration or polymerization to give the micelles, which have a degree of polymerization averaging around 60-80 (3). For anionics these micelles appear to be roughly spherical assemblages in which the hydrocarbon tails come together so that the polar groups (the ionized ends) face outward towards the aqueous continuous phase. Obviously hydrophobic (oleophilic) substances such as greases, oils, or particles having a greasy or oily surface are more at home in the center of a micelle than in the aqueous phase. Micelles can imbibe and hold a considerable amount of oleophilic substances so that the micelle volume may be increased as much as approximately two-fold (4).

Related to micelle formation is the ability of detergent actives to congregate at oil-water interfaces in such a manner that the polar (or ionized) end of the molecule is directed towards the aqueous phase and the hydrocarbon chain towards the oily phase. In the cleaning process, sorbed greasy soils become coated in this manner with an oriented film of surfactant. Then during washing the greasy soil rolls back at the edges so that emulsified droplets can disengage themselves from the sorbed oil mass, with the aid of mechanical action, and enter the aqueous phase. Obviously a substance which can be strongly sorbed on the surface in place of the soil will tend to accelerate this process and effectively push off the greasy soil (5, 6).

Substances other than detergent actives also tend to be strongly sorbed from aqueous media onto surfaces of other condensed phases (7, 8, 9). This is particularly true of highly charged ions, especially those ions which fall into the class of polyelectrolytes. Whereas the usual organic surface-active agent is strongly sorbed at oil-water interfaces, the highly charged ions are strongly sorbed at interfaces between water and insoluble materials exhibiting an ionic structure. Thus for aqueous media we can think of the idealized organic active as an oleophilic or hydrophobic surface-active agent, and an idealized builder as a hydrophilic or oleophobic surface-active agent! It is interesting to note that a number of surfaces, such as cellulose or wool, can sorb both ideal hydrophilic and oleophilic surface-active agents since these surfaces exhibit both polar and nonpolar properties due to their chemical structure. Indeed both wool and cotton surfaces are ionized to a small extent.

Grease-free inorganic particles are removed and dispersed by detergent builders which, in this case, play the role of the active. First, the phosphate is strongly sorbed on the surface of the dirt so as to give it a greatly increased negative charge. The charged particles then repel each other and are also repelled from the charged surface, which almost invariably bears a negative charge under washing conditions. The negatively charged dirt particles then leave the surface and go into the aqueous phase.

The crude picture of the detergency process thus far developed can be represented as



The influence of mechanical action on the particles of free soil may be compared to that of kinetic energy on a molecular scale (10, 11).

Freed soil must be dispersed and protected against flocculation. Cleaned cloth must be protected against the redeposition of dispersed soil. It is evident that the requirements imposed by these effects upon any one detergent constituent acting alone are severe.

Upon consideration of the variety of soils and fabrics normally encountered in the washing process, it is little wonder that the use of a large number of detergent additives having "synergistic" properties has gained widespread acceptance. In the over-all process it is difficult to assign a "pure" role to each constituent of a built detergent formulation; and indeed there is no more reason to separate the interrelated roles of the active, builder, anti-redeposition agent, etc. than there is to assign individual actions to each of the

numerous isomers making up a given commercial organic active. A kinetic approach to detergency, based on the absolute theory of reaction rates, might clarify the process in terms of variables which are a collective function of the molecules and molecule-ion involved.

The ability of inorganic salts to effect a degree of surface activity equivalent to much higher concentrations of salt-free surfactant manifests itself by the lowering of the critical micelle concentration, decreasing of interfacial tensions, increasing sorption or surfactant on substrates, etc. (12).

In addition to affording peak surfactancy at lower concentration levels, certain inorganic salts actually increase a surfactant's peak performance even at these reduced concentrations. This might be expected since certain inorganic ions have the ability to deflocculate and protect finely divided particulate soils or dispersed oily droplets to a greater extent than many organic surface-active agents through the preferential sorption of their anions as well as their pH control and buffering action (13). For effective building of a detergent formulation, the increasing charge density on the surface to be protected with increasing builder concentration must be balanced against the corresponding decrease of the effective range of the charges (14, 15). The pH as well as the buffering capacity of the added builder must be considered for acid soils since the surface charge of both amphoteric and neutral fibers has been shown to be pH dependent (16). Inasmuch as the concentration of added inorganic salts also determines the minimum concentration level of the organic surfactant for peak performance, as mentioned previously, it is obvious that a proper balance of components in a built detergent system becomes difficult to predetermine theoretically.

Although in the idealized and over-simplified presentation of detergent theory given thus far we have considered organic actives and inorganic builders as widely separate classes, real substances do not lie completely in one class or the other. Indeed these two classifications of hydrophilic and oleophilic surface-active agents merge into each other. Thus, for example, an anionic surfactant will negatively increase the *zeta* potential of inorganic substances, such as finely divided ferric oxide or clay particles. On the other hand, a polyphosphate will also do the same thing for droplets of Nujol. Thus there is a competing action between the sorption of the organic active, the builder, and the anti-redeposition agent which makes the interpretation of practical washing results in terms of scientific studies of carefully isolated phenomena difficult to carry out quantitatively. Indeed the competing equilibria of the practical case have hardly been even conceived by the theoretical investigator.

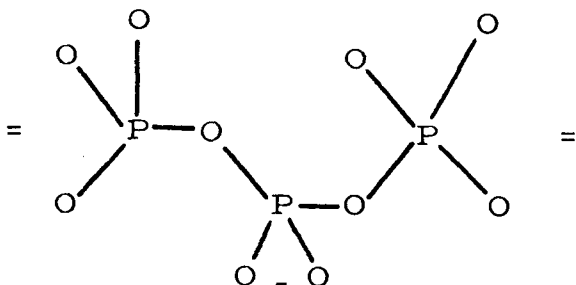
So far in this brief theoretical run-down, we have treated mainly soil removal and its dispersal. Prevention of soil redeposition is also an important consideration. In this case two major mechanisms must be considered. One of them is the strong sorption of a protective substance on the clean fabric so that no sites are available for the resorption of soil. Likewise any shift of the equilibrium between sorbed soil and solubilized soil towards the solubilized form will reduce redeposition. Sodium carboxymethylcellulose acts in both ways, with its unusually good efficacy with cotton being primarily attributable to sorption on the cloth (17, 18, 19). Phosphate builders have

an indirect way of preventing redeposition through complexing of cations, a process which will be discussed later in this paper. This particular builder effect is an example of the complicated interrelationships pertaining to the interpretation and basic understanding of detergency.

Phosphate Builders

In the order of importance the phosphates now being commercially utilized as builders are sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$; tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$; two vitreous sodium phosphates having average formulas approximating $\text{Na}_8\text{P}_6\text{O}_{19}$ and $\text{Na}_{16}\text{P}_{14}\text{O}_{43}$; and tetrapotassium pyrophosphate $\text{K}_4\text{P}_2\text{O}_7$, which is used in liquid detergents (20). Of all of these, sodium tripolyphosphate and tetrasodium pyrophosphate are, by far, the most important (21).

Structure and Preparation. The builders described are all members of the homologous series of chain phosphates. The structure (21) of the tripolyphosphate anion, a typical chain phosphate ion, is shown below:

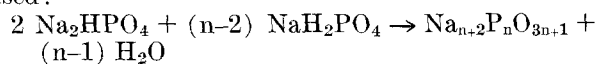


The tripolyphosphate is the third member of the chain-phosphate homologous series, the pyrophosphate is the second member. Only the first three and the extremely long members of the homologous series have been crystallized in the form of sodium salts. The sodium salts of intermediate members have been made as amorphous materials which belong to the chemical class of random reorganization polymers. Only two compositions out of the infinite series of amorphous sodium phosphates are made on a reasonably large commercial scale today. One of them exhibits a $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ mole ratio around 1.33 and is sold under such names as "sodium tetraphosphate," "SQ phosphate,"¹ and "Quadrafos."² This material consists of a mixture of variously sized straight-chain phosphates, with the average chain being based on 5-6 phosphorus atoms (22). The other sodium phosphate glass of commercial interest has a $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ mole ratio around 1.14 and also consists of a distribution of various sized chain phosphates. In this case the distribution is broader, with the average sized chain being based on 14 phosphorus atoms alternating with an equal number of oxygen atoms (22). This glass is called "hexametaphosphate," and it is sold under this misnomer and under the trade name of Calgon.³

Of interest to detergent manufacturers is the crystalline acidic form of pyrophosphate— $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, sodium acid pyrophosphate. It has a pH of *ca.* 4.2 as compared to the pH of *ca.* 10.2 for tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$. Both are identically good buffers, and mixtures of the two can be used to obtain a stable pH ranging from 4.2 to 10.2. Sodium acid pyrophosphate has also been used with sodium tri-

polyphosphate (pH = *ca.* 9.9) to lower the pH towards the neutral region.

The phosphate builders are prepared by thermally dehydrating orthophosphates (21). This dehydration, which is carried out in kilns run at temperatures in the neighborhood of 1,000°F., is briefly summarized by the following chemical equation in which the generic formula of the chain phosphates, $\text{Na}_{n+2}\text{P}_n\text{O}_{3n+1}$, is used:



where $2 \leq n < \infty$ and the $\text{NaH}_2\text{PO}_4 \cdot \text{Na}_2\text{HPO}_4$ double salt plus the excess of NaH_2PO_4 or Na_2HPO_4 are the reagents.

In addition to the homologous series of chain phosphates, there is a homologous series of ring phosphates which are also reasonably stable in aqueous solution. The ring phosphates however exhibit none of the useful properties of the chain phosphates (23). Indeed in many respects the ring phosphate anions are very similar to anions of the simple salts, such as the chloride ion. Branched phosphates are also known but are of little interest in detergency since they undergo rapid hydrolysis in aqueous solution (23). This hydrolysis is attributable to scission at the branching points, and it ceases when the branching points are eliminated from the structure through hydrolysis.

Builder Properties of the Chain Phosphates. As a family the chain phosphates are all first-rate detergent builders. For this family of chemical compounds the properties which play a role in detergency building are listed below:

- formation of soluble complexes with metal ions, including the calcium and magnesium ions of hard water and the sodium ions of the built detergent (24);
- dispersion, deflocculation, and peptizing of finely divided inorganic solids (25);
- electrolyte activity, including salting out and dissolubilization of organic substances in aqueous solution as well as the related action of lowering critical micelle concentration for organic actives (23);
- pH buffering, as effected by the smaller members of the homologous series of chain phosphates which thereby help to control pH and furnish hydroxyl ions (21, 23); and
- inhibition of nucleation of certain crystals, including calcium carbonate (23).

The water softening or sequestering action of the chain phosphates has great practical importance in washing processes since the efficacy of detergent actives is considerably diminished by the multiply charged cations of hard water. It is well known that soaps form insoluble calcium and magnesium salts called "soap curds" and that the washing ability of anionic detergent actives is diminished by increasing water hardness. Likewise a number of nonionic actives are found to be less effective detergents in hard than in soft water. The water-softening ability of the chain phosphates has been attributed to the formation of a chelate type of complex in which the calcium is very firmly bound (25). Although sodium is also complexed by the chain phosphates, calcium and the other multiply-charged metal ions are very much more strongly held by the phosphate than is the sodium. Thus the dissociation constant of the tripolyphosphato calcium complex (27) is about $10^{-6.5}$ as compared to the value of *ca.* $10^{-1.6}$ for the tripolyphosphato sodium complex—the 1:1 complex assumed in both cases (24).

The numerical values of these equilibrium constants show that in a wash water (24) the amount of free or uncomplexed calcium is vanishingly small.

¹ Registered trademark of the Monsanto Chemical Company.

² Registered trademark of the Rumford Chemical Works.

³ Registered trademark of Hagan Chemicals and Controls.

However, in spite of the small calcium concentration, it is still possible to form a calcium precipitate under such conditions if the solubility constant of the precipitate corresponds to a considerably larger negative power of 10 than the dissociation constant of the complex. In this case the chain phosphate then starts to play another role, that of peptizing the precipitate. This peptizing action will be discussed in more detail below.

In much of the technological literature concerning the water-softening ability of the phosphates, comparison of the efficacy of different phosphates is made on the basis of "calcium values" (24). Without a complete interpretation involving characterization of the precipitate and recognition of solution parameters, such as pH and ionic strength, the calcium values are generally quite uninterpretable and have very little theoretical or practical meaning for systems that are not identical in composition to the solution used in the test. Fortunately the recent scientific literature has some papers on phosphate complexing, which have been interpreted in a manner sufficiently sophisticated so that the results are generally meaningful.

Since the multiply-charged cations of hard water not only interact with organic actives so as to render them less efficacious but also precipitate, gel, or render less soluble a number of possible soil components, the complexing of calcium and magnesium by chain phosphates obviously plays an important role in detergent building. On the other hand, the complexing of sodium by the chain phosphates also contributes a minor part to the building process. Thus electrolytes are found to cause an increase in the amount of redeposition of soil (28, 29). Since 10% or more of the sodium in sodium tripolyphosphate at wash concentrations is bound as a tripolyphosphato sodium complex (30, 31), which reduces the average charge of the tripolyphosphate present, the electrolyte character of the sodium tripolyphosphate is abnormally small so that the resulting soil redeposition must be less than would have been expected for a completely ionized sodium tripolyphosphate. The formation of polyphosphato sodium complexes gives the polyphosphates a reserve fund of electrolyte character, which is only drawn upon when ionized sodium and/or tripolyphosphate are removed from the solution. Complexing tends to hold the electrolyte concentration constant so that electrolyte-sensitive properties do not vary erratically from one set of washing conditions to another.

The action of the chain phosphates in dispersing, deflocculating, or peptizing colloids is truly amazing. For example, the addition of a tiny pinch (0.05% on the weight of the dry solid) of, say, sodium tripolyphosphate to a ball of clay sufficiently firm to mold on a potter's wheel reduces the clay to a fluid having a consistency about the same as that of a creamed soup (Figure 1). This phenomenon is explained on the basis of sorption of the polyphosphate anions on the clay particles so as greatly to increase the negative *zeta* potential of the particles (25). This causes the negative particles strongly to repel each other and breaks down the "house-of-cards" structure responsible for the plasticity of the untreated clay (about 55% dry clay in water corresponds to optimum plasticity). This process of dispersing colloidal particles also occurs in systems in which the solids content is very low. Thus a few per cent of, say, manganese dioxide in water are readily removed by filtration

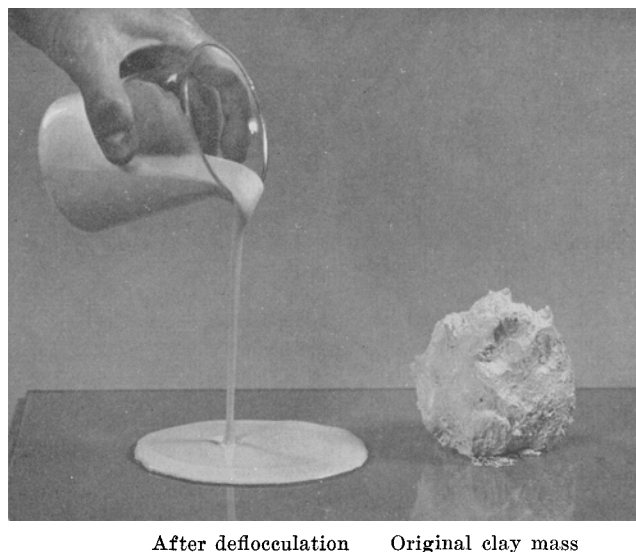


FIG. 1. Deflocculation of a kaolin mass (65% solids) by 0.05% sodium tripolyphosphate on the weight of the dry clay.

through ordinary filter paper whereas the addition of a fraction of a per cent of a chain phosphate to the water so peptizes the manganese dioxide that essentially none of it is removed in an identical filtration. Again the mechanism is sorption of the chain phosphate ion on the particles so as to increase the surface charge negatively.

Elimination of ring-around-the-bathtub by the use of a small amount of a chain phosphate in hard water is an example of the combination of the dispersing and complexing action of the phosphate. Although chain phosphates, such as sodium tripolyphosphate, will, through complexing action, completely dissolve the calcium salts of low molecular weight fatty acids, they are not sufficiently powerful complexing agents to dissolve the more insoluble calcium soaps, such as calcium stearate. However, no matter how insoluble the calcium soap, ring-around-the-bathtub is eliminated, and a good head of foam is produced by the presence of a chain phosphate. The complexing action of the phosphate releases sufficient free fatty acid anion to give a foam and do a proper washing job while whatever soap curd is present is well peptized and will not stick to either the bathtub wall or fabric surfaces. If the concentration of free fatty acid anion is reduced by skimming off the foam, the finely divided, completely suspended soap curd dissolves (rapidly, because of its large surface area) so as to replenish the dissolved active form of the soap.

The electrolyte function and pH buffering ability of the chain phosphates is important in practical detergency. Reduction of critical micelle concentrations and salting oleophilic substances out of the aqueous phase and into the micelles is typical of the helpful action of electrolytes in detergency. The buffering action of chain phosphates comes only from the ends of the chains where there is a weakly acidic replaceable hydrogen. 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 the glassy phosphates. The so-called "hexametaphosphate" has essentially no buffering action since there are only

two end-groups for every 14 phosphorus atoms. This means that, in "hexametaphosphate," there is one buffering function per seven phosphorus atoms as compared to one buffering function for each phosphorus in the pyrophosphate.

In the use of phosphates as water conditioners there is a very interesting phenomenon called "threshold treatment" (21), in which a very small amount of a chain phosphate—too small an amount to do appreciable complexing—prevents the formation of scale in pipes carrying hard water. Study of this phenomenon shows that the nucleation of crystallites of calcite (a form of calcium carbonate and the main constituent of pipe scale) is inhibited by chain phosphate anions sorbed on the surface of the nucleating crystals. Growth of crystals of substances other than calcite is also inhibited by the chain phosphates. Presumably this phenomenon may play some role in the washing process. It is obviously closely related to the dispersing, deflocculating, and peptizing action of the chain phosphates.

The tendency of various ions to affect the charge of surfaces in contact with solutions of the ions has received considerable attention by colloidal chemists. In classical colloid chemistry the efficacy of various simple anions has been related to each other in the Hofmeister or lyotropic series, in which the hydroxyl and orthophosphate ions are found to be strongly sorbed and hence highly efficacious, as compared to such ions as sulfate or those of the simple organic acids. When these simple anionic groupings are bonded together as in a polyelectrolyte, they are even more strongly sorbed. This is to be expected since sorption of neighboring units on a chain will hold a given unit close to the surface even though it becomes desorbed so that in this case it is effectively not desorbed after all. For example, the sodium tripolyphosphate anion, which consists of three PO_4 groups sharing oxygen atoms so as to make a straight chain, is a considerably stronger lyotropic agent than the orthophosphate anion which consists of a single PO_4 group. It is found that the negative *zeta* potential of oily droplets as well as of inorganic particles is increased by the adsorbed chain phosphate.

It is generally known that cations of high charge and/or high molecular weight tend to precipitate anions of high charge and/or high molecular weight (23). This effect plays a role in detergency with respect to both phosphate builders and anionic actives. Either of these anions (highly charged phosphates or high-molecular-weight anionic surfactants) will precipitate cationic actives or germicidal agents (usually quaternary ammonium salts, having at least one long-chain organic group attached to the nitrogen). This makes the cationics incompatible with the built detergent formulations. Interaction between proteins and the phosphate builders or the organic anionics may also play a role in soil removal. The practical effect of protein complexing and precipitation in detergency is worth some study from a fundamental viewpoint.

Other Properties of Chain Phosphates. There are a number of nonfunctional properties of chain phosphates which are of interest to detergent manufacturers. In the field of admixed detergents such properties as bulk density, dustiness, and sorption of liquid actives are important. These properties depend on the average particle size and the particle size distribution. In addition, the ability to sorb

liquid actives is also a function of the character of the individual particles. Some processing conditions lead to particles which have optimum sorbency.

Degradation of chain phosphates is a subject of considerable interest to the manufacturers of spray-dried detergents. It is now well understood that, at the temperatures and pH values corresponding to washing conditions, the degradation of chain phosphates is negligibly small (32, 33). Hydrolytic degradation of chain phosphates in aqueous solution is also inappreciable even during the spray-drying process. The hydrolytic degradation of chain phosphates in solution exhibits a first-order reaction rate which is extremely dependent upon temperature and pH. For the pyro- and tripolyphosphates a great deal is known about the kinetics of hydrolysis (32); and a rough picture is available concerning the hydrolysis of the longer chain-phosphate anions (33). As noted previously, the rate of hydrolysis in aqueous solution is quite slow. For typical wash-water conditions (corresponding to a pH of 9.5 at 110°F.), the half-life of sodium tripolyphosphate is 0.4-year whereas severe spray-drying conditions (high soluble salts content at pH 10 and 212°F.) corresponds to a half-life of 9 hrs. In either case the amount of degradation is obviously so small as to be of no practical interest. The shelf life of an alkaline, built liquid detergent is satisfactorily long as shown by the half-life of about 3–5 years for the tripolyphosphate ion at 80°F. and pH 10 in concentrated solution. By lowering the pH, the shelf life can be shortened to the danger-point. Thus, at 80°F. and a pH of 8, the half-life of the sodium tripolyphosphate ion in concentrated solution is reduced to about 1 yr. The hydrolysis of the pyrophosphate ion in solution is several-fold slower than that of the tripolyphosphate ion; hence pyrophosphates have been preferred over tripolyphosphates for liquid detergents in which the phosphate is all or nearly all dissolved.

In spite of the fact that dissolved tripolyphosphate does not degrade appreciably during the spray-drying process or the preceding crutching operations, appreciable build-up of pyro- and orthophosphate is sometimes observed. This is attributable to a degradation of the tripolyphosphate anion upon dehydration of its crystalline hexahydrate, $\text{Na}_3\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ (27). Sodium tripolyphosphate readily forms a hydrated crystal; but, once the water is incorporated into the crystal structure, it cannot easily be removed without causing scission of P–O–P linkages in the tripolyphosphate anion. This degradation because of crystal dehydration can be reduced and indeed practically eliminated by two approaches. One is to avoid hydrating the sodium tripolyphosphate in the first place, and the other consists of spray-drying in such a way that the hexahydrate crystals are not exposed to high temperature and low humidities for any length of time, thereby reducing the amount of dehydration. Through proper slurry formulation and dryer operation, tripolyphosphate degradation can be reduced to the point where there is essentially no orthophosphate and less than 10% of the phosphorus appears as pyrophosphate, with the remainder of the phosphorus in the form of the tripolyphosphate anion. It should be noted that the pyrophosphate ion does not undergo degradation upon dehydration of its crystalline decahydrate. The temperature of the reversible transition between the anhydrous pyrophosphate and its decahydrate occurs at 79.5°C. (23).

Potassium phosphates have received favorable consideration for use in liquid detergents because of their high solubility. Thus, for example, the solubility of tetrapotassium pyrophosphate is 187 g. of the anhydrous salt per hundred grams of water at 25°C. as compared to a solubility of 6.3 g. of anhydrous salt per 100 g. of water for the sodium analog.

Other Adjuvant Salts

Soda ash, Na_2CO_3 ; sodium sulfate, Na_2SO_4 ; trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot \text{ca } 12 \text{ H}_2\text{O} \cdot \text{ca } \frac{1}{4} \text{ NaOH}$; several sodium silicates, and occasionally borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$, are incorporated into built detergents. All of these compounds reduce the critical micelle concentration of actives and, except for the sodium sulfate, act as alkaline buffers.

Soda Ash. This is a very common ingredient in built detergents. It is probably the cheapest source of alkalinity available in handy form. The good sorbing properties of soda ash also make it a useful ingredient in both admixed and spray-dried detergents.

Sodium Sulfate. Sodium sulfate is present in most built detergents based on anionic actives since it is obtained during the neutralization step in the manufacture of the active. It is also added to some formulations. It has no buffering action and acts primarily as a filler contributing a small amount of building action because of its ionization to give an anion with a doubly negative charge.

Trisodium Phosphate. Trisodium phosphate is never used in spray-dried detergents but is occasionally employed as a builder in admixed detergents. It is a good source of alkalinity and exhibits some building properties; however, since it is an orthophosphate, its building action is considerably less than that of the chain phosphates. Trisodium phosphate has been used as a water softener for many years. It softens the water by precipitating insoluble calcium orthophosphates (primarily hydroxylapatite) (21, 23).

Sodium Silicates (34). Liquid silicates (often called di- and trisilicates) are used as corrosion inhibitors in spray-dried, heavy-duty built detergents (35, 36). These water glasses having $\text{SiO}_2/\text{Na}_2\text{O}$ ratios ranging from 2.0 to 3.3 are used to the amount of 5–9% on an anhydrous basis. Without protection by silicates the corrosion of aluminum immersed in a typical heavy-duty formulation will be in the range of 250–300 mils per five years (37). This corresponds to etching away to a depth of one-fourth inch or more on aluminum and die-cast metal during the life of a washing machine. However the 5–9% of silicate (anhydrous basis) will reduce this corrosion to a negligible 3–10 mils per five years. In addition to the liquid silicates, crystalline sodium orthosilicate, Na_4SiO_4 , and crystalline sodium metasilicate, Na_2SiO_3 , are also employed as adjuvants in admixed detergents and cleaning compounds. In this case the silicates are primarily employed as sources of alkali and as highly alkaline buffering agents. The silicates also exhibit some building action, being strongly sorbed on surfaces (36).

In all detergent formulas in which silicates are used there is a slow reaction between the sodium silicate and the carbonate of the air to form insoluble, hydrated silica and sodium carbonate. This hydrated silica is the main source of insoluble material in present-day built detergents. Because of this reaction the average box of heavy-duty built detergent on

the market shelf contains 1–2% by weight of insolubles ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$).

Sodium Borate. Borax has been used for many years as a builder for soaps. It is not used to any extent in spray-dried detergents and enjoys only a small market in the building of admixed detergents and industrial cleaning compounds. Probably the main reason it is still being used today is that grandfather found it satisfactory.

Miscellaneous Detergents

Anti-redeposition Agents. Although a number of chemicals are found to give satisfactory anti-redeposition activity, cost limits this field essentially to sodium carboxymethylcellulose, which is used in amounts of 0.5–1.5% on an active basis. (Sodium chloride from the preparative reaction may be a diluent of sodium carboxymethylcellulose.) In brief, sodium carboxymethylcellulose is made by reacting sodium cellulose with chloroacetic acid, then neutralizing. Proof of its efficacy is given by repeated wash tests on naturally soiled fabrics. After 30 to 40 washes there is about 40% less yellowing and greying when sodium carboxymethylcellulose is employed in a good heavy-duty formulation as compared to the same formulation without the anti-redeposition agent.

Polyvinyl pyrrolidone has been used to some extent as an anti-redeposition agent in specialty detergent products. The main reason for its use is that it can be readily incorporated into a liquid formulation.

Other Adjuvants. Optical brighteners, perfumes, fabric softeners, foam stabilizers, emollients, and anti-tarnishing agents are used in detergent formulations; however they will not be discussed in this paper.

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Optical Bleaches in Soaps and Detergents

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GERMAN TEXTILE CHEMIST named Kraiss (1) demonstrated in 1929 that incompletely bleached linen could be made to appear much whiter by immersing it in an aqueous solution of aesculin and drying. The solution of aesculin was colorless but was highly fluorescent. This experiment proved Kraiss' theory that whitening of linen can be brought about by fluorescent blue light compensating for the blue light absorbed by the yellow contaminants in linen. Aesculin is a glucoside and can be found in the bark of the horse chestnut tree. The optically effective part of the molecule is 6,7-dihydroxy coumarin. This coumarin has no affinity for cellulosic fibers and was mechanically deposited in the soaking operation. A simple wash or rinse removed it from the fabric. It therefore was of little commercial value.



F. G. Villaume

In 1937 Imperial Chemical Industries obtained a patent (2) in which the use of N,N'-diacyl derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid for treating textile fibers is described. The patent mentions that such treated materials fluoresce under ultraviolet radiation, but there is no mention of a whitening effect being observed. About this same time I. G. Farben investigated the use of colorless, ultraviolet-absorbing materials as protective agents against deterioration by light, particularly by incorporation in wrapping paper. Some of the compounds studied were N,N'-bis-triazinyl derivatives of diaminostilbene (3), but again no indication was given of their potential value as whitening agents for textiles.

It was soon observed however that some of these compounds had excellent affinity for cellulosic material and produced a whitening effect. Subsequently I. G. Farben started to market several of these products, but further development was interrupted by World War II. The first products of this type were Blancophor B and Blancophor R.

After World War II an intense effort developed in the United States to exploit products of this type, particularly in soaps and detergents used for laundering. Research programs were initiated by the major soap companies and several of the dyestuff

manufacturers. In September 1948 one of the major soap companies in the United States, Lever Brothers Company, announced that it had a whitening agent in its soap product. Five weeks later a second major soap company, The Procter and Gamble Company, made a similar announcement. Today it is difficult to find a soap or detergent recommended for washing cotton which does not contain an optical bleach.

Chemical Structure of Brighteners

What are optical bleaches (also referred to as brighteners, whitening agents, and fluorescent bleaches)? They can be classified as dyes if we define a dye as a substance that is able to affix itself to a textile fabric and influence the apparent color of the fabric. When material dyed with a nonfluorescent substance is placed in daylight or artificial white light, it will reflect part of the light striking it and will absorb part of it. The reflected light is perceived as color. The absorbed light is converted to longer wavelengths (infrared) and radiated as heat. With a brightener no significant visible light is absorbed. Rather, invisible ultraviolet energy is absorbed, converted to longer wavelengths, and emitted as visible blue light.

For a structure to be fluorescent, it seems that there must exist a conjugated double bond system as, for example, in the stilbene molecule (Figure 1). The stilbene nucleus is found in a number of the commercial brighteners. The electrons which hold the atoms together in a molecule are called bond or *sigma* electrons (4). Since the carbon atoms in the stilbene molecule need only three of their four valence electrons in the formation of *sigma* bonds, there remain free electrons in the molecule. These are the so-called *pi* electrons, the energy level of which can be changed easily by small forces such as light. In the lower diagram of Figure 1 the *pi* electrons are illustrated by asterisks and the *sigma* bonds by lines. Ultraviolet radiation can excite the *pi* electrons to a higher en-

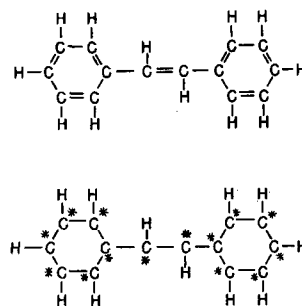


FIG. 1. Stilbene.