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The Importance of Raw Material Selection in Detergent Manufacture

INTRODUCTION

Today's detergent market has placed strict demands on the quality and specifications of raw materials for detergents. Detergents have evolved to include significant variations in composition, physical form, and dosage. For each product type there are, both, a well-defined manufacturing process and a list of raw material specifications that must be met. In consumer products, for example, the advent of compact or ultra detergents have placed emphasis on processes that produce concentrated and relatively dense products that deliver acceptable performance at low dosage under normal use conditions. The advent of products like this often requires raw materials that complement the manufacturing process and facilitate the production of the finished product with the desired properties.

The suppliers of raw materials have developed grades of the standard ingredients with variations intended to meet the requirements of the finished product and the manufacturing process. The following parameters are always considered in selecting a grade of an ingredient for detergent manufacture:

<u>Assay</u>. Usually high assay is preferred for better quality and for extending the shelf life of the finished product.

<u>Density and Particle Size Distribution</u>. Product segregation and flow properties are in part determined by the density and particle size distribution of the solid ingredients, which also play a role in the absorptivity of surfactants.

<u>Friability</u>. The tendency of a solid material to crumble or be easily pulverized is referred as friability. This property may impact the particle size distribution in the finished product and affect product segregation and flow properties. Friability is an important consideration during product processing and shipment.

<u>Hydration Characteristics</u>. Water is present in most detergent products, including detergents in powder form. Often, a solid ingredient will bind some of that water to form hydrates. The rate of hydration and the stability of the resulting hydrated species affect the caking and flow properties of powder detergents and the processability and stability of liquid products.

<u>Chemical Stability</u>. Detergent ingredients must be compatible with each other and must be stable enough to withstand the manufacturing process. This is especially critical in liquid detergents and in powder detergents containing bleach, enzymes, or a high alkalinity.

The selection of raw materials for detergent manufacture is illustrated by our experience as a long term supplier of detergent ingredients. The properties and use recommendation for the various types of phosphates, carbonates, and oxygen bleaches we supply are discussed in the sections that follow.

PHOSPHATES

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Phosphate salts are used as builders in detergents, where they provide water softening, alkalinity, and soil suspension and dispersion. They are also excellent processing aids during detergent manufacture, providing benefits like absorption of nonionic surfactants and the binding of free water. There is a broad selection of phosphate chemicals for use in detergents and other related applications. Table-1 shows a list of these compounds together with their major applications.

The most commonly used phosphates for detergent applications are sodium and potassium salts of pyrophosphate and tripolyphosphate. Some of the chemical properties of these compounds are listed on Table-2. All these salts give solutions of alkaline pH and are effective in chelating both calcium and magnesium ions in water. The potassium salts are significantly more soluble in water than the sodium salts and are preferred for many liquid detergent applications. Sodium tripolyphosphate (STPP) is by far the most important phosphate for detergent applications. Some of the detergent benefits derived from STPP include:

Hardness Control,
Alkalinity & Buffering,
Soil Dispersion & Peptization,
Processing Aid for Powder Manufacturing (absorbs surfactants and binds moisture), and
Control of Rheology and Stability of Liquid Detergents.

STPP Physical Form

In selecting a grade of STPP for a particular application there are several parameters to choose from. Among these: granularity (powder or granular grades of various densities), crystalline phase (Phase-I, Phase-II, or hexahydrate forms), and moisture content (dried or moisturized). Understanding these parameters is important because they control the behavior of STPP in the presence of water during detergent manufacture and in the finished product.

Anhydrous STPP crystals can have one of two crystalline structures, referred as either Phase-I or Phase-II crystals (1). Phase-II crystals have a more stable structure than Phase-I crystals. As a result, when Phase-II STPP is placed in contact with water it hydrates at a slow rate and forms relatively large crystals of the hydrated salt, $STPP\bullet 6H_2O$, Figure-1. The Phase-I form of STPP, on the other hand, hydrates relatively fast to provide a large quantity of small hexahydrate crystals (2). The presence of a small level of $STPP\bullet 6H_2O$ seed crystals (which can be achieved by pre-moisturizing STPP with as little as 0.5% water) will accelerate STPP hydration and make the Phase-II form behave somewhat similar to Phase-I material (3). Commercial STPP is always a combination of Phase-I and Phase-II STPP with or without moisture added. Any STPP with more than about 10% Phase-I crystals is usually referred as Phase-I STPP in the trade.

The importance of the phase and moisture content of STPP is clearly illustrated in the case of detergents in slurry form. Table-3 shows the initial viscosities measured in a home laundry detergent slurry containing 15% STPP. When STPP of very low Phase-I content is used, an unstable slurry with relatively low viscosity is obtained. Here, hydration of STPP occurs relatively slow with less water being bound during processing. The few hexahydrate crystals that eventually form are large in size and are difficult to suspend in the slurry. On the other hand, when STPP of high Phase-I content is used, a homogeneous and stable product of high viscosity is obtained. In this case, STPP hydrated quickly during processing to provide a large number of small hexahydrate crystals. Hydration of STPP into solid particles of $STPP\bullet 6H_2O$ results in the binding of a significant quantity of water (i.e. up to about 29 g of water for every 100 g of STPP). This fact alone would result in an increase in the viscosity of the slurry system. Viscosity is also directly proportional to the quantity of particles in the system, which in this case are mainly crystals of $STPP\bullet 6H_2O$.

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If the low Phase-I STPP is pre-moisturized (1.8% water in the example in Table-3), the slurry obtained is somewhat similar to that obtained using high Phase-I STPP. This effect is further demonstrated by measuring the viscosity of a dishwash slurry containing 25% STPP as a function of time, Figure-2. The system using moisturized STPP gives a slurry of relatively high viscosity, which does not change much on aging. On the other hand, the slurry made using the dry STPP starts out with a very low viscosity before thickening days later. As discussed before, the effect of pre-moisturizing STPP is the formation of seed crystals of STPP•$6H_2O$, which helps promote hydration of the remainder of the STPP when it comes in contact with water.

The effect of moisture and phase content of STPP on the stability of slurries is illustrated in the formulation of automatic dishwash slurries containing 25% STPP, Figure-3. The slurries were formulated using STPP of varying Phase-I and moisture content. They were then monitored for physical stability, which was taken as the number of days they remained smooth and homogeneous before separating into two or more distinctive phases. By using STPP of relatively high Phase-I content and having at least 0.5% moisture added, the stability of the slurry is maximized, Figure-3.

STPP Selection

Table-4 lists the most common grades of STPP in terms of their densities. Most of these grades are available as either the Phase-I or the Phase-II crystalline form. In the agglomeration of HLD powders, the density of granular STPP has an impact on the density of the finished product and is also related to the maximum amount of nonionic surfactant that can be added and still obtain a dry, free-flowing powder. Light density granular STPP has a density of about 0.5 g/cc and is able to absorb almost 25 g of nonionic surfactant per 100 g of phosphate. On the other hand, dense granular STPP (with a density of 1.0 g/cc), has an absorptivity of just 11 g of nonionic surfactant per 100 g of phosphate. The ability of STPP granules to hold surfactants is associated with the presence of microscopic pores on the STPP particles.

The type of STPP recommended for each granular detergent application is summarized on Table-5. In traditional home laundry powder manufacturing, most of the ingredients are mixed in a crutcher to provide a slurry that is then dried in a spray tower to yield a granular product of relatively low density. This manufacturing method requires ingredients that will hydrate fast into a slurry that is smooth and has the proper viscosity for easy pumping. The ingredients must be chemically stable to the conditions found in the crutcher and in the spray tower, and yield a finished product that is acceptable in terms of density, solubility, flowability, and other pre-defined physical properties. In this application, moisturized sodium tripolyphosphate (STPP) powder of Phase-I crystalline structure is preferred. It hydrates quickly and yields a smooth slurry that, upon drying, produces a detergent bead which is crisp and free-flowing and does not tend to cake upon storage.

Dry Neutralization could be used for the manufacture of regular or ultra laundry detergents (4). In this method, the acid form of an anionic surfactant is sprayed directly onto an alkaline powder where it is neutralized and absorbed together with any excess water. The alkaline powder usually consists of sodium phosphates and/or sodium carbonate. Compared to spray drying, this method reduces manufacturing costs and provides product with improved appearance. Powder STPP is the most effective grade of STPP for this application. It can be used in combination with granular STPP in applications where nonionic surfactants are also part of the formulation.

In many processes for the manufacture of ultra or compact home laundry powders, a small portion of the product is still spray dried, but the bulk of the production may involve agglomerating liquid components (i.e. nonionic surfactants, liquid silicates) with the powders (i.e. phosphates, zeolites, carbonates, and the spray dried component). Post addition may also be part of this process. The physical properties of the solid ingredients are especially critical during the agglomeration step. Phase-I STPP is again preferred for this application. The selection of STPP granularity is based on the best compromise between the need for high density and high absorptivity.

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Automatic dishwash powders rely mainly on agglomeration technology. Many of the requirements discussed for the manufacturing of ultra home laundry powders also apply here. The absorptivity of nonionic surfactants, however, is not as important, since their level in these products is usually very small. One of the main considerations is the uptake of water from the agglomerating agent, usually liquid sodium silicate. The selection of STPP is mainly based on its capacity to hydrate quickly, to retain enough water without caking or lumping, and to form a finished product that dissolves easily. Phase-I STPP, in powder or granular form and containing a small amount of added moisture, is usually selected for this application.

Detergents in slurry form can be formulated for laundry, dishwashing, and industrial and institutional applications. In these products, most of the inorganic salts are dispersed in an aqueous solution of surfactants and other ingredients. This process incorporates many of the same raw material requirements found in the crutcher step of traditional (spray dried) home laundry powder manufacturing. Again, the ingredients must be stable, hydrate quickly, and yield a smooth slurry. In this case, however, the slurries must have long-term stability in terms of composition, rheology, and physical appearance. Phase-I STPP with a small level of moisture is preferred for this application: it hydrates quickly into micron-size crystals during the manufacturing process.

Products in gel or liquid form require ingredients that remain dissolved and stable in the finished detergent. Potassium salts of phosphate are ideal for this application because of their high solubility. Potassium tripolyphosphate and potassium pyrophosphate are used throughout. Sodium salts of these ingredients can be used as long as other sources of potassium ions (i.e. potassium hydroxide, or potassium carbonate) are included in the formulations.

SODIUM CARBONATE

Like phosphates, sodium carbonate is a multifunctional detergent ingredient. It has many of the detergent attributes discussed before for STPP: hardness control (which in this case occurs by precipitation rather than by complexation of calcium and magnesium ions), source of alkalinity, filler, carrier, and agglomeration aid for powders. In traditional spray dried detergents, sodium carbonate functions mainly as a filler, alkalinity source, and as a builder. In spray drying plus post addition manufacturing technology, sodium carbonate provides alkalinity and acts as a builder and carrier for liquid ingredients. The same attributes are important for dry blending technology and in agglomeration technology, but in the latter case it also acts as an agglomeration aid.

There are several grades of sodium carbonate commercially available. These are defined according to the density of the granular products: fine powder, very light density granular, light density granular, medium density granular, dense granular, and extra-dense granular. The absorptivity of the various grades is associated with the density of the products and the size of the microscopic pores on the granular particles, Table-6. The absorptivity numbers range from 23% nonionic surfactant for very light density granular to 8% nonionic surfactant for extra-dense granular sodium carbonate. For any given application, a compromise must be made in terms of product density and absorptivity, as was the case with phosphates. The light grade of sodium carbonate (density = 48 lb/ft^3) works well in most applications. This material has a high nonionic surfactant absorptivity, and hydrates and dissolves quickly in water.

OXYGEN BLEACHES

The three most important oxygen bleaches for detergent applications are sodium perborate monohydrate, sodium perborate tetrahydrate, and sodium carbonate peroxide. These compounds are important in the formulation of color-safe bleach detergents for laundry, and bleach formulations where reactivity with enzymes or other

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ingredients needs to be minimized. The major detergent benefits of oxygen-based bleach ingredients are in assisting stain removal, whiteness maintenance, and the control of spots and film on glasses in dishwash applications.

Table-7 summarizes the major attributes for each kind of bleach ingredient available from FMC. Of the two sodium perborates, the tetrahydrate has the lowest active oxygen content, and also the highest density. Stabilized sodium carbonate peroxide is sodium carbonate containing hydrogen peroxide in place of water of hydration. This particular grade has been coated with a proprietary technology to make it stable in detergent formulations (5). It has an active oxygen content of 11.5% and a density of 60 pounds per cubic foot, which is higher than either of the two perborate products. It is possible to prepare sodium carbonate peroxide with active oxygen higher than 11.5%, but that may compromise its stability and flow characteristics.

The oxygen bleach compounds discussed here are suitable for most powder detergent applications. Post addition is recommended during processing to preserve stability. It is also important to eliminate or minimize the level of free water and the presence of some heavy metals to avoid decomposition.

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