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Phosphates and Detergents in Water Pollution

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In the last year detergents and the phosphates in detergents have attracted much attention. It is claimed that they are causing water pollution. A movement is underway to encourage consumers to use detergents with no phosphate or a low percentage of phosphate, and many lists have been published giving the phosphate content of detergents. The major detergent manufacturers have stated that their goal is to replace the phosphate in detergents. Some no-phosphate detergents are presently on the market.

Why Eliminate Phosphates from Detergents?

When phosphorus and other nutrients accumulate in waterways, the water is fertilized. This process of fertilization is called eutrophication. The process is a natural one but it is speeded up by the activities of man as we contribute waste to the water. Eutrophication is good until we have too much — and then we confuse eutrophication with pollution.

Algae grow well in the eutrophic or fertilized water. After algae die, they may wash ashore, decay, and cause odor. They may also sink to the bottom as they die; in that case the decay process uses up oxygen that had been dissolved in the water. Then the fish die. Now the phosphates did not kill the fish, neither did the other nutrients nor the algae. The fish died from a lack of oxygen, which was one of the consequences of the eutrophication of water.

Detergent Functions and Ingredients

What do we expect detergents to do? For satisfactory cleaning, detergents should:

Wet the surface to be cleaned

Wet the soil to be removed

Emulsify the oily soil

Remove the soil

Keep the soil suspended

The first four functions are important for all cleaning. The last is less important for light cleaning — where there is a minimum of soil — or for hand dishwashing. But keeping the soil suspended is very important in laundering.

What is in a box of laundry detergent to accomplish these five functions and others? The box contains a carefully formulated, complex mixture. Until recently a general formula or recipe might have been about as follows. About 20 percent of the contents of the box was made up of a surface active agent. The polyphosphates plus other alkaline salts made up approximately 35 to 50 percent of detergent in the box. Sodium carboxymethylcellulose (CMC) was present to help suspend soil; less than 1 percent was used. A corrosion inhibitor to protect the metal parts of the washer was included; the silicates, about 5 percent, were used for this purpose. About 0.1 percent fluorescent dye was included to improve the whiteness and brightness of the laundered fabrics. Sodium sulfate, a by-product of the manufacture of many surface active agents, also was usually present. In addition, coloring matter, perfume, or bleach might have been present.

The surface active agent or *surfactant* is particularly useful in wetting both the cloth and the soil and in removing soil. And it is because it serves those functions that the surfactant is present. Users are particularly aware of its presence because solutions of most surfactants will foam. If the surfactant does not decompose readily, it will be transported with other wastes into the natural waterways and will remain there to cause foam.

Hard vs. Soft Detergents

In the early 1960's there were many complaints about foam on lakes and streams. After much research, surfactants were made that did an equally good job of cleaning but degraded or decomposed rather easily through the action of bacteria in sewage treatment plants and septic tanks. Before mid-1965, all the important manufacturers of detergents replaced the hard-to-degrade surfactants with soft,

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biodegradable materials. The changeover was done with very little fanfare, but it was done.

A New Pollution Problem

The pollution problem discussed in present times is not related to the surfactant. A new problem exists.

Phosphates, particularly from detergents, have been blamed for the excessive growth of algae in the waterways. About two billion pounds of phosphates are used annually in the detergent industry. That is a lot of phosphate, and much of this ends up eventually in the waterways. You can imagine, then, that there is plenty of phosphate from detergents to help the algae grow. Additional phosphorus comes from human waste, industrial waste, and the runoff from agricultural land.

The main chemical element in algae is carbon, but there are 15 or 20 other elements, including phosphorus. **One hypothesis states that the way to control the growth of algae is to control the amount of phosphorus present. Another hypothesis states that algae can be controlled by controlling the amount of carbon or carbon dioxide present.** Experimental evidence is available to support each of these hypotheses. It is likely that phosphorus is the limiting element in some natural waters and carbon in others. More research is needed before we will know which hypothesis is correct for each particular situation.

For the moment let us assume that it would be good to reduce the amount of phosphorus getting into our waterways. On that assumption, what choices do we have? An obvious, seemingly simple one is to remove phosphates from detergents. Another solution is to remove phosphates, no matter what the source, from waste water. Let's talk about the second choice first.

Solution — Better Waste Treatment

The technology is available to remove phosphates in waste treatment plants. Much of our sewage, however, enters the waterways without adequate treatment. Some domestic wastes go untreated into rivers and lakes; some wastes are subjected to primary treatment only; a growing number of disposal plants add secondary treatment; and a few plants provide tertiary treatment. Primary treatment, in its simplest form, allows solid materials to settle out and involves no other treatment except chlorination. In secondary treatment, bacteria act on the solid wastes to decompose them. Tertiary treatment usually involves chemical treatment and further filtering and perhaps other treatment of the effluent.

Phosphates can be removed by treating them with lime to form insoluble materials. Addition of aluminum or iron salts helps the insoluble phosphates to settle out. Phosphate removal can occur in any of the three treatment steps.

If we really wish to slow down the eutrophication process, we should be working for better community waste treatment facilities. More adequate waste treatment would decrease both the carbon (and carbon dioxide) and the phosphorus entering the waterways. We would be much less concerned then about whether phosphorus or carbon was the limiting factor. **Many people believe that better waste treatment is the best long-term answer.**

Phosphates in Detergents

Let us return, however, to the suggestion that phosphates be eliminated from detergents. Several detergent manufacturers have said that this is their goal; others have already removed the phosphates.

Why are phosphates present in detergents? They serve the following functions:

- Soften water by sequestering hardness ions
- Increase the efficiency of the surface active agent
- Furnish necessary alkalinity for cleaning and provide resistance to change in alkalinity during washing
- Reduce redeposition of dirt by keeping the dirt particles in suspension
- Emulsify oily and greasy soils

Because the phosphates serve these important functions, either substitutes for the phosphates must be found, or the clothes will not be washed as well.

It has been suggested that perhaps the percentage of phosphate in the box could be reduced without replacing the phosphates with a substitute. If only slightly less phosphate was present, the cleaning could be reduced considerably. To compensate for the reduced phosphate in the box, consumers would likely use more detergent, and thus more phosphate, to accomplish the cleaning desired.

Substitutes for Phosphates

A very promising substitute for the phosphates in terms of cleaning has been identified. It is the sodium salt of nitrilotriacetate, better known as NTA. NTA is a good water softener and can also function to suspend soil. It was being considered as a component of detergents as long ago as 1967. When NTA became available in sufficient quantity and at a low enough price, it was substituted to some extent for phosphates in detergents.

Complete substitution did not occur for three reasons:

- Not enough NTA was produced for complete substitution. Additional manufacturing plants were being built to increase the supply but were not completed.
- NTA absorbs moisture. If NTA completely replaced the phosphates, the detergent would lump in the box.
- Use of NTA was a very recent development; no one knew what long-term effects large quantities of NTA would have on the environment.

Late in 1970, enough data had been accumulated to indicate possible hazards from massive, long-term use of NTA. Even though NTA functioned satisfactorily in the cleaning process as a substitute for phosphates, it was not without question as far as the environment was concerned. Because of the questions raised, NTA will not be used in detergents unless further testing gives evidence that it is safe in the environment.

Two other substitutes for phosphates are being used. These are carbonates and silicates. Although they serve some of the functions of the phosphates such as increasing the alkalinity and acting as buffers, the carbonates and silicates are much less effective than the phosphates in controlling hardness and suspending soil. As a result it is difficult for detergents in which carbonates or silicates have replaced the phosphates to clean heavy soil as well as we expect them to. Detergents containing a high percentage of silicate are highly alkaline. They should be stored out of reach of children and should be used with care.

No doubt research on substitutes will continue and perhaps other materials will be found.

Soap and Washing Soda

Many people have suggested that we abandon synthetic detergents and return to soap. Soap is a good cleaning agent — as long as it is used in soft water. The water must remain soft even after clothes and soil are added if the soap is to be a good replacement for the present detergents. Soap is even relatively good in suspending soil and therefore does not require phosphates for that purpose.

About one-third of the households in the U.S.A. have naturally soft water; fewer than 10 percent of the households have ion exchange water softeners. To use soap effectively, the rest of us would have to buy softeners, and some families will choose that solution so that they can use soap. If we all tried to switch to soap, we would soon discover that there is not enough fat to make the soap required.

Washing soda has been suggested as a water softener to use with soap. Washing soda is an alkaline material that can act as a precipitating water softener. It was widely used as a water softener by homemakers until about a generation ago when more effective water softeners were discovered and made available and when synthetic detergents began to replace soap. Some community water supply systems use washing soda, or its equivalent, to remove calcium and magnesium ions and thus to soften water.

For washing soda to be an effective water softener, the precipitate that forms must be removed by filtration or by some other method. This step usually is not included when the water is softened at home. As a result, the precipitate can continue to furnish calcium and magnesium ions.

When soap is added to the water for cleaning, the equilibrium between calcium ions in solution and those tied to the precipitate is upset; therefore, soap can steal calcium ions away from the precipitate. The calcium ions stolen by the soap react to form soap curd — and then the problem is the same as it was before the water was softened with washing soda.

Soap Curd and Automatic Washers

Soap was used by homemakers before we had synthetic detergents. Weren't the problems with soap curd the same then? Or why are the problems greater now?

When wringers are used to remove water from clothes, a flood of water is squeezed out of the cloth and travels over the surface of the cloth. This flood of water flushes soap curd off the surface of the cloth and returns the curd to the water.

In automatic washers, water is removed from the clothes during the spin step by centrifugal force. During spinning, the water is forced through the clothes and the clothes act as a filter to trap the soap curd.

Therefore, although we could tolerate some soap curd when we used wringer washers, it causes much greater problems now that we have automatic washers.

Differences in Phosphate Content of Detergents

Many lists of detergents showing phosphate content have been published. When the lists began appearing in the spring of 1970, they were a fairly unsophisticated lot. One homemaker wrote that from school-age children, the garden club, etc., she had collected seven lists — all different. Originally, mild detergents, heavy-duty ones, enzyme presoaks, and machine dishwashing agents were all mixed together in one list. Some of the testing was rather casual. No attempt was made to identify the specific phosphate compound reported. Recent lists are more sophisticated in that they classify the detergents by type and name the phosphate reported.

Real differences in phosphate content for a specific brand of detergent may now exist for either or both of two reasons:

- Over a period of time the manufacturer may be trying new formulations. Lists based on samples collected at different times will show different percentages of phosphate.
- A manufacturer may substitute other components for part of the phosphate in detergents sold in areas where eutrophication is a problem and not substitute for the phosphates where eutrophication is not a problem. Samples of the same brand name of detergent obtained from different parts of the country may have different phosphate contents.

Phosphorus Compounds in Detergents

Several phosphate compounds are used in detergents. Other phosphates not actually contained in detergents are named in discussions of detergents (see trisodium orthophosphate and phosphorus pentoxide below).

- Sodium tripolyphosphate (STPP) is the most common phosphate found in heavy-duty detergents.
- Tetrasodium pyrophosphate (TSPP) is used in some heavy-duty powdered detergents.
- Tetrapotassium pyrophosphate (TKPP) is used in liquid detergents. Because the potassium salt

is more soluble than the sodium salt, it is chosen so that the product can be more concentrated.

• Trisodium orthophosphate, more commonly called trisodium phosphate (TSP), is used in some precipitating water softeners and is an ingredient in some powdered hard-surface cleaners such as paint cleaners. Trisodium phosphate usually is not included in laundry detergents, but it is the form in which the phosphate content is listed on detergent packages in some states.

• Chlorinated trisodium orthophosphate (C1TSP) is an ingredient in some of the scouring powders with bleach and may be an ingredient in mechanical dishwashing compounds.

• Phosphorus pentoxide is the form in which the Canadian law indicates the phosphorus content of detergents.

The phosphate content of detergents can be expressed properly in any one of these. See the adjacent column for conversion factors. It is important to know which phosphate is referred to when percentages are quoted. For example, in New York State a box of detergent actually containing 40 percent sodium triployphosphate (STPP) must be labeled as containing 53 percent trisodium phosphate (TSP). No additional phosphate is added to the box for sale in New York State; it is just that the law required labeling in terms of TSP instead of STPP, and a box with 40 percent STPP has as much phosphorus as one with 53 percent TSP. Likewise the Canadian law will limit phosphate content to 20 percent expressed as phosphorus pentoxide (P_2O_5); in terms of STPP this is about 35 percent which was about the lower limit of STPP in laundry detergents marketed in the U.S. before phosphates were considered to be pollutants.

Phosphates In Detergents

Abbreviation	Chemical Name	Chemical Formula	A[1]	B[2]
STPP	Sodium tripolyphosphate	$Na_5P_3O_{10}$	0.2526	3.9542
TSPP	Tetrasodium pyrophosphate	$Na_4P_2O_7$	0.2332	4.2872
TKPP	Tetrapotassium pyrophosphate	$K_4P_2O_7$	0.1937	5.1638
TSP	Trisodium orthophosphate	Na_3PO_4	0.1892	5.2862
C1TSP	Chlorinated trisodium orthophosphate	—	0.0813	12.3001
—	Phosphorus pentoxide	P_2O_5	0.4366	2.2903

[1]A Multiply phosphate concentration by number given to obtain concentration of phosphorus.

[2] B Multiply phosphorus concentration by number given to obtain concentration of phosphate.

Data in the first five rows obtained from:

Phosphates in Detergents and the Eutrophication of America's Waters, Twenty-Third Report by the Committee on Government Operations, Union Calendar Number 469, House Report Number 91-1004, April 1970.

Summary

In summary these points can be made:

• Eutrophication is a complex problem.

• Detergent phosphates added to waste water may contribute to cultural eutrophication.

• Phosphates in waste water can be removed by adequate waste treatment. Waste treatment facilities should be improved.

• Some substitutes for phosphates have questionable effects on the environment; some are less effective; other substitutes are being sought.

• New laws will be proposed and new lists will be prepared. Sound information must be used intelligently if either the laws or the lists are to be useful.

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James E. Kraus, Director

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