PHOSPHATE AND SILICA CONTENTS OF SOME COMMERCIAL BAR DETERGENTS

Susan E. Guitarte
Zenaida L. Ochotorena, Ph.D.

Introduction

Detergents are known to contain phosphorus in the form of phosphate. The phosphate in detergents functions as water softener and as an aid in its cleansing action.

Although the use of phosphate in detergents is highly effective, phosphate contributes to water pollution,This is known as the "eutrophication" problem (Gordon, 1973; Layman, 1984; E. Britannica, 1981). In eutrophication there is massive growth of algae "algal bloom" resulting in the depletion of oxygen necessary to sustain aquatic life. Since there is not enough supply of oxygen, fishes and plants die causing a continuous buildup of deposits of organic matter at the bottom of the lake, stream, spring or creek hastening the aging process of that body of water. Likewise in eutrophication the oxygen depletion of the water may shift water condition from those favoring aerobic activity to those that support anaerobic activity. The products under anaerobic decomposition are badsmelling and toxic (Micua, 1983).

Because of environmental consideration, the composition of detergents underwent rapid changes through the years. In 1970, the Federal Water Quality Administration of the United States called for the immediate reduction of phosphate levels in detergent formulation. At present, six States ban the use of phosphate in home laundry detergents and all the other States limit the phosphate content to an equivalent of 8.7% in automatic dishwashing detergents. Canada has placed a federal limit of 2.2 per cent in household detergents

Most countries in Europe have resorted to phosphate limitation dependig upon such factors as water hardness (allowable limits are higher for harder-water areas). West Germany has set a maximum amount of phosphates in detergents with scheduled reductions such as: for water of 0 to 7 degrees German hardness, the equivalent of 0 to 126 grains in the US and for soft water a decrease to a maximum phosphorus content of 0.7g to 0.5g per liter. In Italy, the government introduced a phosphate limit in March 1982; in the Netherlands a voluntary reduction by the industry was done in two stages, the latter stage of which went into effect on January 1, 1983; Switzerland legislated in 1977 to limit phosphate content. The first stage went into effect October 1, 1982 and the second stage, January 1, 1983; in Norway a limit of 12 percent sodium tripolyphosphate was set with a total ban on phosphate builders for automatic dishwashing detergents. Phosphate reductions are currently under discussion in Austria, but no decisions have yet been reached, and in Finland, a gentleman's agreement between industry and government to limit the phosphate content to the equivalent of 7 percent phosphorus has been forged.

In Japan, detergent makers decided upon total reformulation and as a result, within only two years more than 90 percent of the detergents produced and sold in Japan are phosphate-free and are built instead with zeolites (Layman, 1984).

In the Philippines today, detergent bars are in great demand. They are heavily used in laundry as well as in dish-washing. Every day detergent wastes are dumped into our lakes, streams, springs, and creeks. Because of the problems they pose to the environment, the researchers were prompted to look into the phosphate content of bar detergents.

It was, therefore, the purpose of this study to quantitatively determine the percentage content of phosphorus in some popular brands of detergent bars. Such information will assist us and our policy makers to determine whether there is a need to impose controls in the manufacture and use of bar detergents.

Experimental Procedures

Samples Used

Five brand names of commonly available bar detergents were randomly chosen for this study. These were Superwheel, Happy, Mr. Clean, Ajax and Solarwhite.

Instrument

A Pye Unicam Sp 6-450 UV/Vis Spectrophotometer was used in all measurements of absorbances.

Determination of Phosphorus (APHA, 1980)

Since phosphate was being determined, the glasswares were thoroughly washed with Perla soap bar, rinsed with hot diluted hydrochloric acid and then with distilled water.

a) Digestion Procedure (Sulfuric-Nitric Acid Digestion)

Weigh into the kjeldahl flask about 0.01 g sample (accurately weighed). Add one (1) ml of concentrated H_2SO_4 and five (5) concentrated HNO_3 and digest until the solution becomes colorless and the HNO_3 removed.

Cool the solution and add approximately twenty (20) ml of distilled water. To the resulting solution add 0.05 ml (1.0 drop) phenolphthalein indicator. Then, neutralize the solution with 1 N NA H until a faint pink tinge is produced. Transfer the neutralized solution filtering if necessary to remove particular materials or turbidity, into a 100-ml volumetric flask adding Filtrate washing to the flask, and adjust the sample volume to 100 ml with distilled water.

Determination of phosphorus by Colometric Method should be carried out immediately.

b) Colorimetric Determination (Molybdenum Blue Reaction)

To the digested sample solution, add four (4) ml of the molybdate reagent mixing it thoroughly after each addition. Since the rate of color development on the intensity of color depends on the temperature of the final solution, i.e., each ^{o} increase produces about 1 percent increase in color, samples and reagents are held within $2^{o}C$ of one another. The room temperature is held constant at $24^{o} - 26^{o}C$.

After the addition of the molybdate reagent, add 0.5 ml (10 drops) of the $SnC1_2$ reagent. After ten (10) minutes but before twelve (12) minutes, measure the absorbance against the blank of reagents and distilled water at a wavelength of 690 mm. Maintain the same time interval for all determinations including the standard since the color at first develops progressively and later fades.

The phosphate concentration should be determined from a calibration curve prepared by taking known phosphate standards through the same procedure used for the sample.

c) Preparation of Calibration Curve

A calibration curve is prepared by using a suitable volume of standard phosphate solution, $K_2HPO_4 . 3H_20$.

The standard solutions are carried out through the same procedure used for the sample. Equal timing and conditions, both in the digestion and in the color measurements are maintained. All analyses are performed at a room temperature between $24^{o} - 26^{o}C$.

d) Calculation

By chemical factor, gm/ml $K_2HPO_4 . 3H_20$ is converted to gm/ml phosphate.

In constructing the best straight line, the least square method is employed.

By gravimetric factor, % phosphate is converted to % $Na_5P_30_{10}$ and % phosphorus.

$$\% \text{ phosphate} \times \frac{\text{Molecular wt. } Na_5P_3O_{10}}{3 \text{ Molecular wt. } PO\text{-}^3\!/\!_4} = \% \; Na_5P_3O_{10}$$

$$\% \text{ phosphate} \times \frac{\text{Molecular wt. P}}{\text{Molecular wt } PO\text{-}^3\!/\!_4} = \% \; P$$

Determination of Silica (Hamilton, 1964)

About 0.70 gram of each sample is weighed into a porcelain crucible. The sample in the crucible is ignited slowly in a muffle furnace to about 1000°C and kept at this temperature for five (5) minutes.

The crucible is cooled and the content is carefully transferred to a 250-ml beaker. Ten (10) ml of water is added and the crucible is cleaned with small portions (totalling 10 ml) of 12 N HC1, adding the acid to the contents of the beaker. The mixture is stirred and warmed until solvent action ceases. It is then evaporated on a low temperature electric hot plate to complete dryness. Then it is heated in a drying oven at 105°C for one hour.

Add five (5) ml of 12 N HC1 to the residue and then with twenty five (25) ml of water, and heat from five (5) to ten (10) minutes. The silica is filtered on an ashless filter paper, washed twice with 2 N HC1 and then with hot water until free from chlorides. Evaporate the filtrate to dryness. Dry it in an oven and treat with HC1 as before. Then filter and wash it in order to recover the small amount of silica that invariably escapes the first treatment.

Ignite the combined residue on a constant weight porcelain crucible at 1000°C.

Calculation

$$\% \; SiO_2 = \frac{\text{Weight of } SiO_2}{\text{Weight of sample used}} \times 100$$

By gravimetric factor, % SiO_2 was converted to % Na_2SiO_3 and % Na_2SiO_7

$$\% \; Na_2SiO_3 = \% \; SiO_2 \times \frac{\text{Molecular wt } Na_2SiO_3}{\text{Molecular wt } SiO_2}$$

$$\% \; Na_2Si_3O_7 = \% \; SiO_2 \times \frac{\text{Molecular wt } Na_2Si_3O_7}{3 \text{ Molecular wt } SiO_2}$$

Reagents

All reagents used were of the Analytical grade and used without further purification.

a) Strong Acid Solution

300 ml concentrated Sulfuric acid (H_2SO_4) is slowly added to about 600 ml distilled water. When cooled, 4.0 ml concentrated Nitric acid (HNO_3) is added and the solution diluted to 1 liter.

b) Ammonium Molybdate Reagent

25 grams $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ are dissolved in 175 ml distilled water. 280 ml concentrated Sulfuric acid (H_2SO_4) to 400 ml distilled water. Cool the solution, add molybdate solution and dilute the resulting solution to 1 liter.

c) Stannous Chloride Reagent

Dissolve 2.5 grams of fresh $SnCl_2, 2H_2O$ in 100 ml glycerol. Then heat in a water bath and stir with a glassrod to hasten dissolution. This reagent is stable and requires neither preservatives nor special storage.

Results and Discussion

Silica Content

Sodium silicate is the most commonly used corrosion inhibitor in automatic dishwater detergents. It is added to protect appliances, china and metal surfaces against abrasion and corrosion. Zeolites which are alumino-silicate of Sodium, Potassium, Calcium, and Barium are likewise common constituents of present day detergents. These are used as substitutes for phosphates or added as builders.

The amount of sodium silicate in detergents is now being monitored. The developed countries all over the world have set an allowable range of silicon as Na_2SiO_3 in the different detergent formulations as given in Table 1.

Results of the silica analysis presented in Table 2 show that bar detergents available in our supermarkets have silica content as Na_2SiO_3 ranging from 3.5 to 13.0%.

Comparing these values with the 3-8% Na_2SiO_3 of the world formulation requirement for detergent laundry bars, it is shown that bar detergents Superwheel, Happy and Mr. Clean are within this range but bar detergents Ajax and Solarwhite whose Na_2SiO_3 contents are 9.7% and 13.0%, respectively, are beyond the world formulation requirement. However, comparing these results with theNa_2SiO_3 range set by other countries (Table 1), only bar detergent Solarwhite was beyond the range accepted in South America, the Middle East and Africa in their heavy-duty powder detergents of 5%-12%.

Table 1. Accepted % Sodium Silicate (Na_2SiO_3) in Detergent Formulation Around the World*

Countries	Na_2SiO_3 Range %
US (heavy-duty powder)	5 – 10
Canada (heavy-duty powder)	5 – 10
Australia (heavy-duty powder)	5 – 10
South America (heavy-duty powder)	5 – 12
Middle East (heavy-duty powder)	5 – 12
Africa (heavy-duty powder)	5 – 12
Europe (heavy-duty powder)	0 – 9
Europe (light-duty powder)	0 – 8
Japan	–
World Formulation for detergent laundry bars	3 – 8

* Layman, P.L., 1984

Table 2. Silica Content of Some Commercial Bar Detergents

Bar Detergent Samples	Average Silica SiO_2	Silica as % Na_2SiO_3	Silica as % $Na_2Si_3O_7$
Superwheel	3.5	7.1	4.7
Happy	3.8	7.7	5.1
Mr. Clean	1.8	3.5	2.3
Ajax	4.8	9.7	6.4
Solarwhite	6.4	13.0	8.6

Phosphate Content

The results obtained in the determination of phosphate in the commercial bar detergent measured by colorimetric method are shown in Table 3.

Table 3. Phosphate Content of Some Commercial Bar Detergents

Bar Detergent	Average Phosphate Content % PO ¾-	Conversion as P Content % P	Conversion as NaTPP % $Na_5P_30_{10}$
Superwheel	1.19	0.39	1.54
Happy	14.72	4.80	19.00
Mr. Clean	0.70	0.23	0.90
Ajax	3.06	1.0	3.95
Solarwhite	1.62	0.53	2.09

Table 4. Phosphate Content of Some of the Common Powder Detergents Manufactured in the Philippines (Micua, 1983).

Laundry Detergents	Percent Phosphate % PO_4	onversion as % $Na_5p_30_{10}$
FAB	34.8	44.9
CHEER	36.3	46.9
BREEZE	37.2	48.0
RINSO	41.0	52.9
DRIVE	47.4	61.2
TIDE	49.8	69.3

**Researchers' conversion of % PO_4 to % $Na_5p_30_{10}$

Table 5. Accepted % NaTPP ($Na_5P_3O_{10}$) in DETERGENT FORMULATION AROUND THE WORLD (Layman, 1984)

Countries	% NaTPP Range
US (heavy-duty powder)	25 – 35
Canada (heavy-duty powder)	25 – 35
Australia (heavy-duty powder)	25 – 35
South America (heavy-duty powder)	70 – 30
Middle East (heavy-duty powder)	20 – 30
Africa (heavy-duty powder)	20 – 30
Europe (heavy-duty powder)	20 – 35
Europe (light-duty powder)	10 – 40
Japan (heavy-duty powder)	0 – 15
World Formulation for Detergent laundry bars	–

As shown in this table, Happy bar detergent had the highest phosphate content of 14.72 percent, while Mr. Clean had the lowest phosphate content of 0.70 percent These values, compared with the phosphate content of some of the common powder detergents manufactured here in the Philippines and shown in Table 4, were relatively very low. The highest phosphate-containing bar detergent, Happy (14.72%) was less than half the phosphate content of the lowest phosphate-containing powder detergent, FAB (34.8%).

The phosphate content of the bar detergents converted to NaTPP content shown in Table 3, indicated that these values are lower than the accepted % NaTPP of heavy-duty powder Detergent Formulations of US, Canada, Australia, South America, Middle East, Africa and Europe, as shown in Table 5. Although the NaTPP content of Happy was found higher than the accepted value in Japan for heavy-duty powder detergent this was still found within the accepted value for light-duty powder detergents in Europe.

In the analysis of commercial sodium alkyl aryl sulfonate detergent (A. Chem., 1955), the NaTPP content range from 5.4% – 46.5%. The NaTPP contained in bar detergents were found.

Summary and Conclusion

The silica content of bar detergents studied have a silica content as Na_2SiO_3 ranging from 3.5 to 13.0 percent.

The Na_2SiO_3 content of the bar detergent studied were within the world formulation requirement for detergent laundry bars of 3-8 percent Na_2SiO_3 except Ajax and Solarwhite whose Na_2SiO_3 contents were 9.7 percent and 13.0 percent, respectively.

The bar detergent with the highest phosphate content was Happy (14.72%) and the lowest, Mr. Clean (0.70%).

All the phosphate or NaTPP contents of the bar detergents studied were very much lower than the phosphate contents of some of the common powder detergents manufactured in this country, and below the accepted % NaTPP for detergent formulation of heavy-duty detergent powders in U.S., Canada, Australia, South America, Middle East, Africa, and Europe.

The NaTPP contents of the bar detergents studied were within the accepted value required in the detergent formulation of light-duty powder detergents in Europe and even for heavy-duty powders in Japan.

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