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The Phosphate-Free Detergents II

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Introduction

In February 1971 R.C.S.I. Bulletin #111 (W) gave analyses of seven brands of phosphate-free (non-phosphate) detergents. Since that time other reports have been published (2,3) concerning the contents and cleaning effectiveness of non-phosphate detergents. Where comparisons can be made, the agreement between reports is quite good. A review of the importance of phosphate removal from detergents and of the nature of substitutes for phosphates has been published recently in Science (4).

Summary

Analyses of pH values and buffering capacity (alkalinity) are reported for 27 formulations of phosphate-free (non-phosphate) detergents. Four (15%) of the formulations have lower values of pH and alkalinity than typical phosphate-based detergents. Seven (26%) of the formulations have pH values less than or equal to the upper limit reported for phosphate-based detergents (10.6) when dissolved in distilled water at a concentration of 0.15%. These detergents are judged to be not substantially more hazardous to the user than present phosphate-based detergents. A total of 12 (44%) of the non-phosphate formulations have pH values less than or equal to 10.6 when dissolved in Rochester tap water. Of the remaining formulations, 11 (41%) have substantially higher pH values (11.0 or above) and alkalinities than phosphate-based detergents.

The environmental consequences of a total switch to non-phosphate detergents is discussed. It is concluded that no environmental harm is predicted from the alkalinity or silicate content of the non-phosphate detergents we have tested.

pH Value and Personal Safety

pH is the measure of the degree of alkalinity or acidity of solutions. Alkaline (or basic) solutions have pH values higher than neutral water, 7.00 at 25°C (77°F). The scale is logarithmic, which means that the effective concentration of base in a solution with a pH of 11.0 is ten times that of a solution with a pH of 10.0.

*Assistance in measurement of pH values was provided by the following students in Chemistry 124 at the University of Rochester: Linda Landon, Chris Lind and Allan Pinas.

In R.C.S.I. Bulletin #111 (W) it was stated that certain but not all phosphate-free detergents have high pH values and that adequate care should be taken to prevent skin irritation and fabric deterioration. On March 8, 1971 the FDA seized shipments of Ecolo-G and Bohack detergents in Landover, Md. and Queens, N.Y. These seizures were made under the authorization of the Hazardous Substances Act since these formulations were judged by the FDA to be hazardous and no warning labels appeared on the detergent boxes. FDA tests showed that direct contact with these detergents could cause destruction of skin and eye tissues in mice and rats.

Because of the seizure of two non-phosphate detergents by the FDA, concern has been expressed about the safety of all such detergents. The primary purpose of this report is to provide information about the pH and alkalinity of more than a score of phosphate-free detergents which are currently on the market.

pH Values for Detergents

Most detergents have pH values above 9. High pH values are beneficial to cleaning action, since they help to emulsify oils. The action of builders (water softening agents) such as polyphosphates, carbonates, silicates or borates is assisted by high pH values. However, excessively high pH values can result in irritation or destruction of skin or other tissues which come in contact with the detergents. Excessive pH values can also contribute to fabric degradation or destruction of certain fabric dyes.

At the present time no limits have been established to define what constitutes a corrosive or noncorrosive laundry detergent formulation. We do not propose to establish standards here, but rather will compare pH values to those of phosphate-based detergents.

The pH values of phosphate-based detergents have been reported to be between 9.0 and 10.6 at normal washing concentrations (typically 0.15%) (3). We have found that Tide XK, the largest selling brand of detergent, has a pH value of 10.1 in distilled water and 9.8 in Rochester tap water. Seven other popular brands of phosphate-based laundry detergents have similar pH values.

The pH values of detergents in distilled water and tap water are as shown in Table I. A concentration of 0.15% by weight was used in all cases. This concentration is typical of phosphate-based detergents; recommended use levels for non-phosphate detergents vary from approximately 0.03% to 0.3%. The pH values of alkaline solutions generally increase with increasing concentration; for detergents for which the pH rises dramatically with increasing concentration, the pH value in distilled water is footnoted.

It can be seen from Table I that out of 27 formulations of non-phosphate detergents the pH values of 4 brands are less than that of Tide XK; these are either liquid formulations or fine-fabric detergents which do not contain substantial amounts of builders (water softeners). A total of 7 formulations (26%) have pH values less than or equal to 10.6 in distilled water, the reported maximum value for phosphate-based detergents. In Rochester tap water, 12 formulations (44%) have pH values less than or equal to 10.6. In general, those formulations having pH values between 10.0 and 10.6 have silicates or borates as the principal water softening agents.

- Table I
pH of Detergents in Water at 25°C

	Name	Date[a]	Type	pH, 0.15% Tap water[b]	pH, 0.15% Dist. water	Alkalinity[c] meq/g
1	Tide XK	3/71	Phos[d]	9.8	10.1	1.7
2	Average of 8 brands	4/71	"	9.7	10.1	
3	"Typical brands"	e	"		9-10.6[e]	
4	Instant Fels	3/71	Soap	10.2	10.6	2.4
5	Trend[f]	4/71	NP[g]	7.4	7.0	0.0
6	Concern Super Conc.	3/71	"	9.3	9.7	1.3
7	Phos-Free (liq.)	4/71	"	9.3	10.0	0.4
8	Concern (liq)[h]	10/70	"	9.4	9.7	0.4
9	Cold Water All (liq)[h]	10/70[i]	"	10.2	10.6	1.8
10	Unpolluter	3/71	"	10.4	10.6	2.9
11	Miracle White	2/71	"	10.4	10.6	3.9
12	Acme	3/71	"	10.4	10.6	3.9
13	Spring Clean	3/71	"	10.5	10.7	3.7
14	Red and White	5/71	"	10.5	10.7	4.6
15	Macy's Controlled Suds	2/71	"	10.5	10.8	6.4
16	Staff	3/71	"	10.6	10.8	6.9
17	Bio-D	2/71	"	10.7	10.8	7.0
18	Ecolo-G	4/71	"	10.7	10.9	9.4
19	Brillo	4/71	"	10.7	11.0	8.1
20	Sears	10/70	"	10.8	10.9	7.8
21	Dairi Brite	4/71	"	10.8	10.8	8.5
22	Lemon Low Suds No. 311	10/70	"	10.8	11.0	8.5
23	Topco	3/71	"	10.8	11.2[j]	5.4
24	Topco[h]	10/70	"	10.8	11.3[j]	8.6
25	A D G	2/71	"	10.9	11.0	4.9
26	Basic L	10/70	"	10.9	11.1[j]	8.8
27	Bestline B-70	2/71	"	10.9	11.2[j]	9.4
28	P F D	3/71	"	11.0	11.1[j]	9.0
29	Amway SA-8	2/71	"	11.0	11.2[j]	8.0
30	Ecolo-G[h]	10/70	"	11.1	11.2[j]	4.0
31	Ecolo-G[h]	2/71	"	11.6	11.6	8.7

a. Date of purchase
b. Rochester tap water; Hardness = 90 mg/l (5 grains/gal), Alkalinity = 90 mg/l, ph 7.6.
c. Alkalinity to pH 7 in milliequivalents per gram
d. Phosphate-based laundry detergent
e. From reference 3 ; 0.15%
f. Fine-fabric detergent
g. Nominally phosphate-free detergent
h. Discontinued formulation
i. A sample purchased in 3/71 was similar; contains NTA
j. pH of a 1% solution is greater by 0.4 units or more

Of the 27 formulations of non-phosphate detergents, 11 (44%) have pH values equal to or above 11.0. The highest pH value observed was for the formulation of Ecolo-G (no. 31 of Table I) which was seized by the FDA. This formulation utilized sodium metasilicate as the principal water softening agent; it has now been removed from the market and replaced by a revised formulation (No. 18 of Table I). The remaining formulations generally use sodium carbonate (washing soda) as the principal water softening agent.

Meaningful Measures of Alkalinity and Corrosiveness

The pH value is the most meaningful measure of hazard to skin or other tissues when the detergent is subsequently washed off. However, if the detergent is not washed off or if deep penetration of tissue occurs, then the alkaline materials in the detergent must be neutralized by the affected tissue. The most meaningful measure of corrosiveness under these conditions is the buffering power, or alkalinity. In Table I are shown the amounts of acid (in milliequivalents per gram) required to bring solutions of detergents neutrality, i.e. pH 7.

It can be seen that most non-phosphate detergents have higher alkalinity values than phosphate-based detergents. The four non-phosphate formulations of lowest pH value have alkalinities substantially less than Tide XK. The detergents having pH values between 10.0 and 10.6 generally have alkalinities slightly above to somewhat more than twice that of Tide XK. Thus, these detergents are not greatly more hazardous than phosphate-based detergents. However, the detergents with pH values equal to or above 11 have alkalinities typically five times higher than that of Tide XK. Thus for the most alkaline detergents not only is the pH much greater than that of phosphate-based detergents but also the alkalinity is many times greater. The precautions suggested previously (1) of avoiding direct skin contact and of rinsing clothing adequately may be necessary to avoid skin irritation and fabric degradation when using these formulations.

Environmental Consequences

Concern has been expressed about the effect of the high pH and high alkalinity of certain phosphate-free detergents on the quality of receiving waters. Recommended water quality standards (7) specify that the pH of receiving waters be maintained between 6.0 and 9.0. Most fish would be harmed if the pH of the water rose above approximately 9.0. Furthermore, the toxicity of any ammonia present would be increased if the pH were increased. New York State water quality standards (8) specify in almost all cases that the pH of receiving waters be maintained between 6.5 and 8.5.

It appears that municipal waste has adequate neutralizing capacity to cope with any additional alkalinity introduced by detergents. If every household switched to detergents of high alkalinity (8.7 meq/g) then the alkalinity of residential wastes would be increased by approximately 0.5 meq/l. Any increase in pH of the waste waters would tend to result in precipitation of carbonate, hydroxide and phosphate salts of hardness ions, which would act to reduce the alkalinity and pH. The hardness of Rochester tap water is approximately 2 meq/l and of local stream waters is generally above 5 meq/l, of which a significant portion would be available for reducing alkalinity. The available acidity (to pH 8.5) of the effluent of one activated sludge sewage treatment system in Brighton is about 0.6 meq/l, thus such a system could cope with any anticipated increase in alkalinity from detergents. Furthermore, if the pH of the water were increased, the carbon dioxide generated during secondary treatment would neutralize the excess alkalinity rather than being lost to the atmosphere as at present. Thus, as long as wash water is mixed with other residential waste, the higher alkalinity of certain phosphate-free detergents is of little environmental consequence. Indeed the alkalinity may even reduce the available phosphorus in wast waters.

Concern has also been expressed about the presence of larger amounts of silicates in certain non-phosphate detergents compared to phosphate-based detergents. Certain non-phosphate detergents contain as much as 21% sodium silicate (as Na_2SiO_3). Sodium silicate has been cited (5) as fatal to rainbow trout at concentrations above 256 mg/l. However, the reported toxic effect of sodium silicate is undoubtedly due to a change in pH value rather than any toxicity of silicates themselves, since natural concentrations of silicates in lakes are typically 10 mg/l as SiO_2 (20.3 mg/l as Na_2SiO_3) and sometimes considerably exceed 100 mg/l as SiO_2 (203 mg/l as Na_2SiO_3) (6). The amount of silicate introduced by the use of those non-phosphate detergents containing large amounts of silicates would not exceed the amount of phosphate presently introduced from detergents (typically 25 mg/l as PO_4 in municipal wastes). Thus, any conceivable increase in silicate in receiving waters from the use of non-phosphate detergents would be of negligible environmental consequence.

Methods

Samples of detergents were purchased between October 1970 and May 1971. In most cases a representative sample of detergent was transferred to a glass jar immediately upon opening of the box. The analyses reported here apply strictly only to the box which was purchased; however, the formulations purchased were presumably those generally available at the time of purchase. Formulations known to be discontinued are footnoted in Table I.

pH values were determined with a Corning Model 12 expanded scale pH meter using a triple-purpose glass electrode. The meter was calibrated vs. Coleman pH 10.05 certified buffer at 25°C. Solutions of detergents in distilled or tapwater were prepared at 25 ± 1.5°C and the pH was measured promptly. The temperature compensator was adjusted to the actual temperature of the solution. The correction for sodium ion error was negligible in all cases. Either 0.300 g samples of detergents or aliquots of 1% solutions prepared from 5.00 g samples of detergents were used to prepare the solutions.

Distilled water was boiled, then brought to 25°C just before use. Rochester tapwater was allowed to flow from the tap for several minutes before samples were taken. Water analyses were performed by standard methods (9).

pH values for 0.3% and 1% solutions of detergents were also measured. In some, but not all, cases the pH increased with increases in concentration; those detergents exhibiting dramatic increases as the concentration is increased are footnoted in Table I. A few measurements at 50°C (122°F) indicate that pH decreases by ca.0.4 units compared to that at 25°C. Because of the temperature dependence of the ion product of water, this corresponds to an increase by a factor of 2 to 3 in effective hydroxide concentration.

References

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(3) "Ecologic Detergents: Will the Bubble Burst?", Chemical Week, April 28, 1971, p. 10.

(4) A. L. Hammond, "Phosphate Replacements: Problems with the Washday Miracle", Science 172, April 23, 363 (1971).

(5) I. A. Eldib, Testimony on "Labeling and Advertising Requirements for Detergents", Federal Trade Commission hearings, April 27, 1971.

(6) J. C. Sutherland, Proceedings Twelfth Conference on Great Lakes Research, 1969, p. 357.

(7) "Water Quality Criteria", Federal Water Pollution Control Administration, Washington, D.C., April 1, 1968, p. 32.

(8) "Classifications and Standards Governing the Quality and Purity of Waters of New York State", Part 701, Title 6, Official Compilation of Codes, Rules and Regulations, New York State Department of Environmental Conservation, 1968.

(9) "Standard Methods for Examination of Water and Waste Water", 12th ed., Public Health Association, New York, 1965.

End Note:

Since science is a continuous activity, conclusions must be made with some reservations. As this bulletin was being prepared for distribution, information was received from professional colleagues which prompted the writing of this addition.

Extensive calculations have been made to determine the amount of silicate which would be added to a lake such as Erie by complete substitution of phosphate softeners. Together with known laboratory and field evidence, it could be predicted that such complete substitution could bring about a change in the numbers and kinds of diatoms (yellow-green algae with silica shells). Diatoms have sometimes caused taste and odor problems in drinking water; they have never produced the huge blooms of the blue-green algae nor the immense wash-ins of the green alga, Cladophora.

Four years ago, the nuisance of algae to drinking water supply was discussed with the man who headed Chicago's system for a generation. His conclusions have been published as a note to a professional paper which I wrote - the economic cost of correcting algae problems in water supply is minor.

For some time it has also been suspected that an increase in sodium was bad for the lakes. Dr. Luigi Provasoli of Haskins Laboratory at Yale University has been a leader in this inquiry, but he is not an alarmist. No "worse threat" than phosphate is predicted for sodium by any responsible scientist. In perspective, it must be remembered that a huge amount of sodium enters the water from street and highway salting (sodium chloride). Both the silicate and carbonate softeners used in some phosphate-free washing products contain sodium.

In due consideration of even the worst possible consequences of adding silicates or sodium, there is no reasonable argument against delaying removal of phosphates from detergents. Furthermore, there is no reason to expect - or tolerate - the long range use of large amounts of sodium carbonate and sodium silicate in washing products. Already, acceptable phosphate-free products which contain neither are on the market.

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Although the public had been given no hint, R.C.S.I. predicted in its current bulletins that NTA would be cleared for use in home laundry products. As the bulletins were in preparation, private word has come of clearance by Canada.

Herman S. Forest
Editor