SESSION III

Ingredients — Technology and Function

Total Hardness Ions in Laundry Washing Solutions

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ABSTRACT

A study was made of 1,600 actual washing solutions, and an estimate was made of the contribution of soils and fabrics to the total hardness. The amount of total hardness in the washing solution was appreciably higher than that present in the tap water. It was shown that the major source of the added hardness was that absorbed on fabrics during the previous wash/rinse operation. A significant amount was also contributed by the soil present on the fabrics being washed. Knowledge of the amount of hardness present in washing solutions is an obviously important factor in formulating detergents for optimal cleaning performance. The total amount of hardness present in Japanese washing solutions is, on average, more than double that present in tap water, largely because of the widespread practice of multi-load washing. By combining actual wash solution hardness data and product usage levels, it is possible to calculate the percentage of washloads that will be adequately sequestered, as a function of builder level. At the current average P_2O_5 level present in Japanese laundry granules (10% P_2O_5), only about 15% of the total number of washloads is adequately sequestered at recommended product usage. By contrast, at 20% P_2O_5 in product (the pre-1974 maximum builder level, now no longer allowed because of environmental concerns), about 85% of all loads were believed to be adequately sequestered. This comparison highlights the necessity of providing adequate replacement builders for phosphate and/or of appropriately reformulating the surfactant system to maintain the detergent performance characteristics at a satisfactorily high level.

BACKGROUND

The contribution of detergent builders to the washing of clothes is well established. In fact, essentially all of the leading brands of heavy duty laundry products for more than 25 years have contained some form of polyphosphate as a major component. The most common polyphosphate used is sodium tripolyphosphate, although pyrophosphate has also been used to some extent. Specific benefits that polyphosphate provides to the cleaning process have been discussed in several recent publications (1-3). One of the most important functions of the polyphosphate builder is the chelation, or sequestration, of hardness ions which are present in the washing solution. The chelation of these ions is important because the free Ca^{++} or Mg^{++} ions can: (a) react with fatty acids from the soil to form insoluble soaps which are extremely difficult to remove from fabrics, (b) react with anionic surfactants to form relatively insoluble salts which are ineffective in the detergent process, (c) cause flocculation of clay soils, and (d) form relatively insoluble salts with carbonate, which can deposit on fabrics and destroy their natural softness. Further, polyphosphates help to suspend soils that are washed from the fabrics and prevent their redeposition, i.e., prevent dingy fabrics. The amount of polyphosphate needed for good cleaning performance is directly related to the amount of hardness present in the washing solution; specifically, sufficient polyphosphate must be provided in the product formulation so that at least an equimolar ratio of phosphate to total hardness is present in the washing solution at actual usage conditions (4,5). The effect of phosphate (sodium tripolyphosphate) level on detergency performance is illustrated in Figure 1 (2).

The primary sources of these "hardness" ions are: (a) tap (or service) water, (b) components of soils on the fabrics being washed, and (c) ions occluded in the fabrics from previous wash/rinse operations. The total hardness present during the washing operation is, therefore, always higher than the tap water hardness. Since many Japanese housewives wash more than one load of fabric in a single washing solution, the contribution of soil/fabric to total hardness may be large relative to service water hardness.

The purpose of this paper is to present results of a study in which over 1,600 actual washing solutions were examined and analyzed for total hardness. An estimate of the contribution of soils and fabrics to the total hardness present is made. Results of actual phosphate levels present in these same wash solutions are also presented. A brief discussion of these results in relation to phosphate level in products is included, along with some references to potential substitute materials for phosphate.

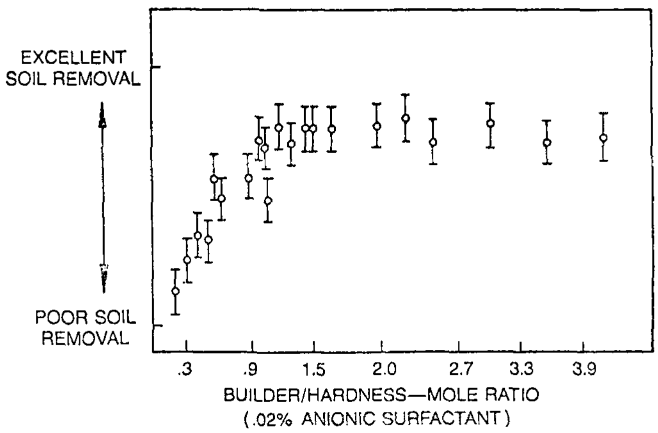

FIG. 1. Soil removal – collars and cuffs.

TABLE I

Number of Samples Analyzed

Sampling date	Number of housewives	Tap water	1st Load solution	2nd Load solution	3rd Load solution
Study I					
Aug.-Sept. 1974	Osaka (192)	192	190	135	---
	Tokyo (172)	120	172	124	---
Study II					
February 1975	Osaka (122)	13[a]	122	73	---
	Tokyo (112)	112	110	76	---
Study III					
May 1976	Osaka (106)	---	106	106	106
	Tokyo (95)	---	95	95	93
Total		437	795	609	199

[a]Approximately 1/10 of total samples were analyzed.

TABLE II

Distribution of Total Hardness Results (in parts per million as $CaCO_3$)

	Tap water		1st Load solution		2nd Load solution		3rd Load solution	
	Tokyo	Osaka	Tokyo	Osaka	Tokyo	Osaka	Tokyo	Osaka
Study I								
Mean	58.4	37.3	86.1	65.0	103.7	80.8	---	---
Median	58.2	37.7	78.7	61.6	99.3	80.4	---	---
Std. dev. of mean	1.78	1.01	4.12	2.46	3.69	2.98	---	---
Study II								
Mean	65.0	39.4	92.4	86.1	107.7	98.1	---	---
Median	66.4	41.0	90.5	77.2	103.7	94.8	---	---
Std. dev. of mean	1.44	---	2.57	3.94	4.54	5.77	---	---
Study III								
Mean	---	---	102.4	86.6	120.7	107.3	128.4	116.9
Median	---	---	97.6	83.9	114.7	104.4	121.5	113.0
Std. dev. of mean	---	---	4.16	2.96	5.97	3.63	6.35	4.89
Overall (weighted) mean	50.3		83.9		101.7		122.3	

TABLE III

(Study I Only)

	Tap water		1st Load solution		2nd Load solution	
	Tokyo	Osaka	Tokyo	Osaka	Tokyo	Osaka
Fe in ppm						
Mean	.047	.034	.344	.328	.683	.511
Median	---	---	.280	.240	.400	.400
Std. dev. of mean	.008	.008	.033	.030	.113	.050
Mole ratio Ca/Mg						
Mean	3.31	4.24	3.26	4.31	3.18	4.14
Median	2.90	4.30	2.80	4.30	2.90	4.10
Std. dev. of mean	.184	.112	.146	.133	.165	.136

EXPERIMENTAL PROCEDURES

Tap water and wash solution samples were collected from a number of Japanese housewives in Tokyo and Osaka on three separate occasions. These samples were analyzed by atomic absorption (6) for Ca, Mg, and P_2O_5 (samples from the first study were also analyzed for Fe). The housewives were instructed to take the tap water sample at the washing machine area before the addition of detergent product or soiled fabrics. The washing solution samples were collected at the end of the washing process before draining the wash solution or adding a new batch of soiled fabric. In cases where housewives washed a second load of fabrics in the same detergent solution, samples of wash water at the end of the second load were also obtained (third load solution samples were also collected for the final study). The number of samples analyzed for each study is shown in Table I.

EXPERIMENTAL RESULTS

Wash Solution Hardness

The distribution of total hardness for each set of samples was calculated as shown in Table II. The Fe results and Ca/Mg mole ratio for samples from Study I are shown in Table III.

The mean values of tap water hardness as measured in Studies I and II are in good agreement with the published Waterworks Association data for these cities in 1974 (7) (Tokyo = 67 ppm, Osaka = 40.4 ppm as $CaCO_3$). The combined distribution of measured Ca^{++}/Mg^{++} hardness

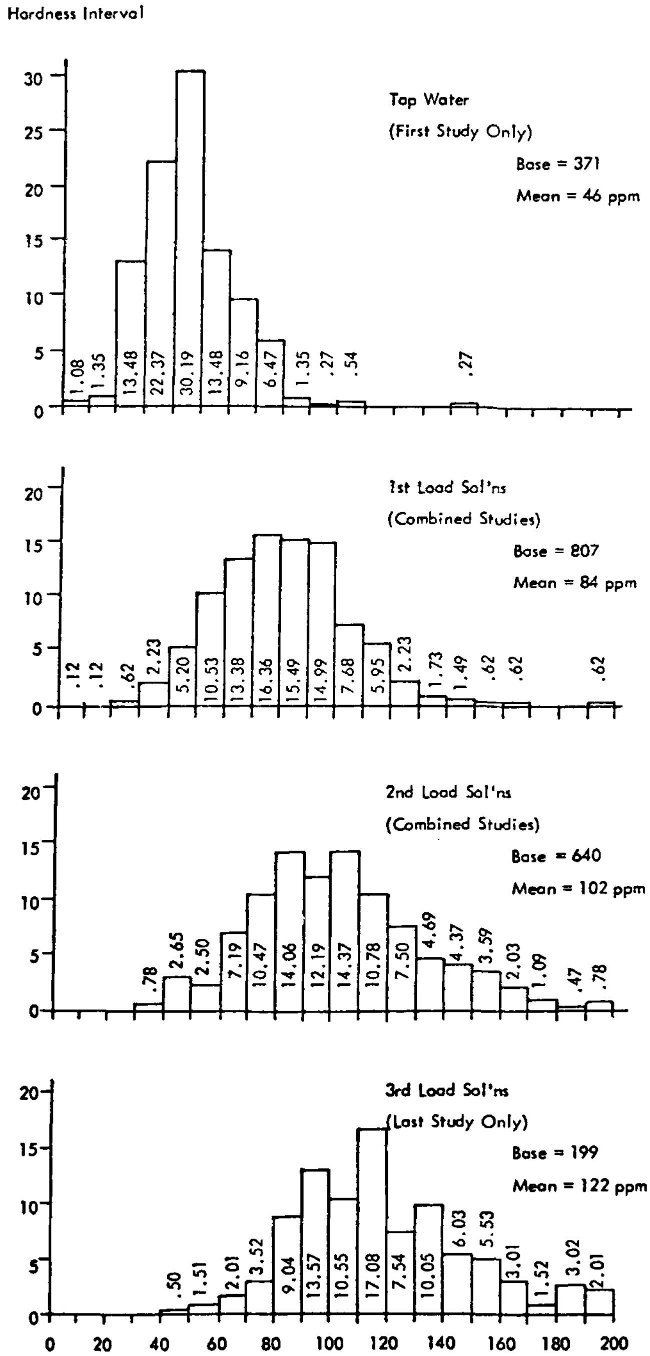

FIG. 2. Wash solution hardness (increase with fabric load).

levels in these cities is also a reasonable representation of the hardness in major Japanese cities.

The Fe levels in tap water are relatively low in both of the cities sampled. The increased Fe levels in first and second load solution indicate that some Fe is present as a soil component. The total levels of Fe present are sufficiently low relative to the Ca/Mg levels to be ignored in the calculation of total hardness.

The mole ratio of Ca/Mg (as calculated for Study I only) is slightly different between the two cities but does not change significantly in the wash solution; i.e., the Ca/Mg ratio from soils and fabrics is about the same as that in tap water.

The combined data from the three studies for tap water and each washload solution are plotted in Figure 2. This illustrates the increase in total hardness from the soil-fabric load. The increase in total hardness for each fabric load washed is significant; i.e., ca. 67% increase for first loads,

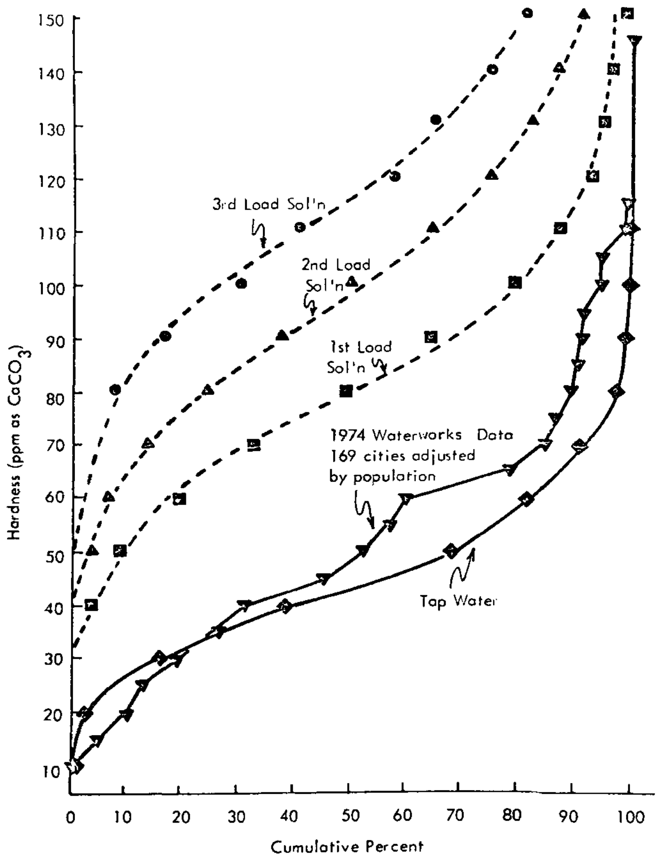

FIG. 3. Wash solution hardness (three studies combined).

102% for second loads, and 143% for third loads (relative to the initial tap water hardness). For further illustration, these same hardness data are plotted as cumulative percentages of samples in Figure 3. This shows the distribution of hardness from these studies vs. a weighted distribution (by population) of hardness from 169 cities as reported in the Waterworks Statistics (population data from April 1974 census). These two cities represent only a slightly lower tap water hardness level than the national published data.

The data in Table II also indicate that the average and median total hardnesses in wash solutions from Studies II and III were appreciably higher than those from Study I. This may be related to seasonal variations in soil levels or to changes in product usages and washing habits.

Data published by the Lion Home Science Institute in 1971 (8) show that wash solutions are commonly used to wash more than one load of fabric. The specific data are:

One load only	24.9%
Two loads	41.7%
Three loads	33.0%
More than three	.4%

Data obtained in the present studies are in good agreement with the above, showing the following percentage of solutions being used for washing one load only:

Study I	28.5%
Study II	26.1%
Study III	24.9%

Fabric Contribution to Total Hardness

The two possible sources of the extra hardness in these wash solutions are: the soil on the fabrics that are being washed and hardness ions that are occluded on the fabric from previous wash/rinse operations. The nature and amount of soil present in a realistic washload is highly

TABLE IV

Mole Ratio Phosphate/Hardness (STPP/$CaCO_3$)

	1st Load solution		2nd Load solution		3rd Load solution	
	Tokyo	Osaka	Tokyo	Osaka	Tokyo	Osaka
Study I						
Mean	1.26	1.67	1.06	1.37	---	---
Median	1.00	1.4	.85	1.10	---	---
Std. dev. of mean	.091	.117	.085	.11	---	---
Study II						
Mean	1.07	1.36	0.89	1.07	---	---
Median	.93	1.16	0.88	0.87	---	---
Std. dev. of mean	.088	.111	.059	.087	---	---
Study III						
Mean	1.10	1.21	0.97	0.99	0.98	1.00
Median	.92	1.02	0.83	0.89	0.79	0.86
Std. dev. of mean	.080	.094	.069	.068	.080	.074

TABLE V

Percentage of Samples with Less than 1 Mole Phosphate/Mole Hardness

	1st Load solution	2nd Load solution	3rd Load solution
Study I	38	51	---
Study II	46	59	---
Study III	53	64	65

variable from one time to another and therefore difficult to measure precisely. However, the quantity introduced from previous wash/rinse operations can be measured in a specific case by repeated washing of a clean fabric load in which no soil components are present. Such an experiment was run under the following controlled conditions.

Wash/rinse temperature	20 C
Time	10 min wash 10 min overflow rinse
Water hardness (tap)	77 ppm (3/1 Ca/Mg, molar)
Fabric load	1.2 kg Poly/cotton shirts Cotton towels (terry) Cotton T-shirts Nylon swatches Polyester swatches
Detergent product usage	40 g/30 liters (typical Japanese HDS with 11% P_2O_5)

The fabrics were washed and rinsed repeatedly (without intermediate soiling), and wash solution samples were taken after cycles 6, 7, and 8 and analyzed for total hardness. The experiment was replicated six times. The average increase in hardness was 24 ppm as $CaCO_3$ (i.e., from 77 to 101) with a standard deviation of about 4 ppm. This value would be expected to vary somewhat with conditions, such as tap water hardness, amount and composition of fabric load, etc. However, the results do suggest that a large portion (estimated at 70%) of the hardness increase measured in our Tokyo/Osaka study on actual wash solutions is derived from the previous rinse process and is therefore independent of actual soil load. The reason this occurs is that carboxyls on fabrics function as ion exchange substrates. This has been documented in other studies (9).

Phosphate in Solution (Phosphate/Hardness Ratio)

The wash solutions from each of these studies were also analyzed for P_2O_5 level. The molar ratio of phosphate to total hardness (based on P_2O_5 and Ca/Mg analysis on each sample) was calculated. These results give a distribution of phosphate/hardness ratios at three different time periods during which the phosphate levels in many detergent products were being reduced (from an average of about 12.5% to 10% P_2O_5). The mean and median phosphate/hardness ratios for each study, by city, are shown in Table IV. The percentage of wash solutions containing less than one mole of phosphate per mole of hardness is shown in Table V. The results suggest that the number of wash solutions with insufficient phosphate has increased importantly during the period of time between the first and last study.

In each of these studies, the housewives were asked to identify the brand of detergent product used at the time of sampling. From the P_2O_5 analysis on each housewife's washing solution and from the P_2O_5 level of the brand used, it was possible to calculate the amount of product used by each housewife. This showed that the average product usage, for regular density products, was about 30% greater than the recommended amount (40 g/30 liters) in the first study and about 60% greater than recommended in the third study based on first load solutions only. (Estimation of actual product usage for second and third load solutions is more complex since some housewives add extra product for these wash solutions.) This increase in average product usage suggests that at least some housewives have increased usage to compensate for decreased phosphate levels in product.

Implication for Product Design

The data on total water hardness are particularly useful in considering the design of detergent products and the appropriate recommended usage for that product. To illustrate, assume the recommended usage to be 40 g/30 liters (refer to Fig. 3 for percent of washloads vs. measured total hardness). For any specific phosphate level in product, the equivalent level of hardness which is completely sequestered by that amount of phosphate can be calculated by the following equation:

$$\text{ppm hardness equivalent} = \%\ P_2O_5 \text{ in product} \times \frac{40\text{ g}}{30\text{ liters}} \times 10^3 \frac{\text{mole wt } CaCO_3}{\text{mole wt phosphate} \times \%\ P_2O_5 \text{ in phosphate}}$$

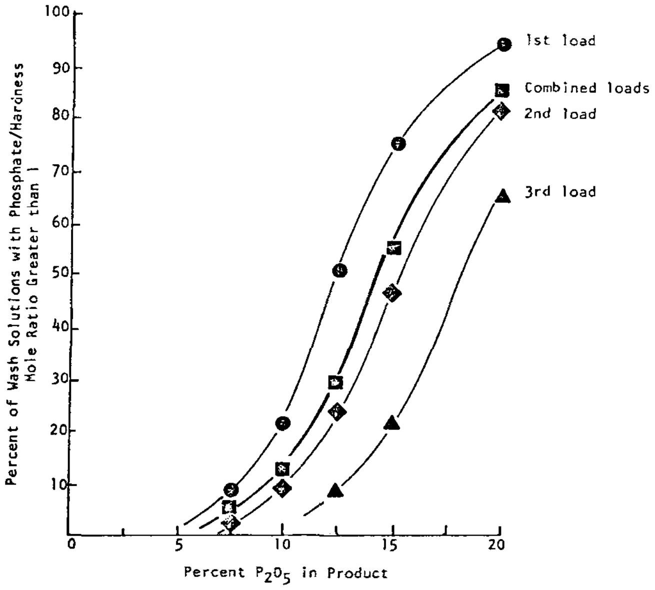

FIG. 4. Estimated percentage of washloads with mole phosphate/hardness greater than 1 as a function of phosphate level in product. Calculated as sodium tripolyphosphate and 40 g product per 30 liters washing solution assumed.

Entering Figure 3 at a specific hardness level, moving across to the hardness distribution line, and then down to the horizontal axis, gives an estimate of the number of washloads with a mole ratio of phosphate/hardness greater than one; i.e., sufficient builder for good detergency performance. Repeating this procedure for several phosphate levels yields a curve which illustrates the number of washloads expected to contain sufficient builder as a function of P_2O_5 level in product. Such a set of curves is constructed in Figure 4 showing first, second, and third load estimates at 40 g/30 liters recommended usage. For example, a product designed to provide sufficient sequestering builder for 50% of the first load wash solution, would require about 12.5% P_2O_5 (using tripolyphosphate as the P_2O_5 source). The plots for second and third load solutions assume no additional product is added. The estimates of product usage in these studies, based on the P_2O_5 analysis, show that some housewives do add some extra product with additional fabric loads; however, the quantities added are not sufficient to compensate for the added hardness. This is illustrated by the data in Table IV which show the builder/hardness mole ratio decreases across washloads. This same approach can be used to calculate equivalent levels of other sequestering builder materials – for example, an equivalent amount of NTA can be calculated by substituting the molecular weight of NTA for phosphate and the percent P_2O_5 in the equation.

Builder materials that function by mechanisms other than sequestration must be handled differently. As a specific example, the water insoluble alkali metal aluminosilicates remove calcium ions from solution by ion exchange, and their calcium binding capacity is highly dependent on the duration of the wash process, the pH, and temperature of the washing solution, the particle size of the silicates, and the concentration (1). Calculations of equivalent levels of these materials can be done if ion exchange capacity of the specific material at the specific condition of use is known. However, since the aluminosilicates are effective essentially on calcium ions only, they are generally used in combination with other builder materials. The overall equivalence calculations are then considerably more complex.

These considerations of "effective" builder level are relevant only to one, though basic, function of a detergent builder; i.e., the capacity to remove alkaline earth ions from the washing solution, the fabric, and the soil. However, the overall contribution of a specific builder material to total detergency is also a function of other solution effects; e.g., alkalinity contribution, effect on the surfactant action, soil suspending properties, etc. Further, detergent builders differ widely in the strength of hardness binding (3). Thus, detergency performance is only partially determined by the builder capacity, and the selection of surfactants, alkalinity source, etc., are also factors to consider in the design of product and in the level of a specific builder material required.

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