Environment Canada

The Effect of Detergent Phosphate Levels on the Cleaning Process

P. D. Goulden

TECHNICAL BULLETIN NO. 70
(Reprints Dr. Canada)

CANADA CENTRE FOR INLAND WATERS
BURLINGTON, ONTARIO, 1972

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Contents

Illustrations

Tables

Abstract

The determination of the cleaning performance of detergents containing 32%, 48% and 64% sodium tripolyphosphate (STPP) is described. The tests were carried out jointly with Ontario Research Foundation in 1970. The cleaning was measured under different conditions of detergent usage and water hardness. Artificially and naturally soiled fabrics were washed in a domestic washing machine.

It was found that phosphate level is critical below a mole ratio STPP:$CaCO_3$ of 0.3:1 but that above this ratio the other ingredients in a detergent formulation have as significant an effect on cleaning performance.

Résumé

Ce rapport décrit la détermination de la capacité de nettoyage des détergents contenant 32%, 48% et 64% de tripolyphosphate de sodium (STPP). Lors des essais qui ont été entrepris en 1970 conjointement avec la Fondation de Recherche de l'Ontario, la capacité de nettoyage a été mesurée pour différents détergents sous des conditions aussi différentes d'usage et de dureté de l'eau. Des tissus, artificiellement et naturellement souillés ont été lavés à la machine. Le résultat fut que le taux de phosphate semble critique au-dessous d'un rapport molaire STPP: $CaCO_3$ de 0.3:1. Cependant dépassé ce taux, les autres ingrédients faisant partie de la composition du détergent possèdent un effet important sur la capacité de nettoyage.

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INTRODUCTION

Concern for the eutrophication caused by nutrients entering the receiving waters has resulted in a restriction on the level of phosphorus in detergents in Canada. While there is a wealth of information on the effect of phosphorus on eutrophication, there is no clear picture in the literature of the effect of phosphate level on the performance of detergents. The "classical" hypothesis on the use of sodium tripolyphosphate (STPP) and other detergent builders is that they are required to sequester the water hardness cations on at least a mole to mole basis (Pollard, 1966).

However, after studying the data on the performance of detergents, e.g., the evaluation reported in *Canadian Consumer* (Anon., 1969), it is clear that an "acceptable" performance can be obtained with much less than a mole to mole ratio of STPP to water hardness.

This report describes a pilot study made in 1970 of the effect of three phosphate levels on the cleaning performance of a laundry detergent. Different conditions of water hardness and detergent usage were maintained.

Procedures for evaluating cleaning performance in the laboratory have been described in the literature (Rutrowski, 1967). It is known that the detergents industry uses these procedures for preliminary screening only, and that it considers results obtained by using very sophisticated techniques and naturally soiled fabrics as the only significant data. However, the use of these techniques requires large resources in equipment and people. Consequently, the testing laboratories and the Consumer Association take a compromise position, i.e., to wash artificially soiled fabrics in a domestic washing machine under various conditions (Anon., 1969).

For the tests described in this report different artificially- and naturally-soiled fabrics were used. All were washed in a domestic washing machine. The tests were designed to: (a) cover a ratio of STPP to hardness ranging from 0.2:1 to 2.8:1 on a molar basis; (b) apply a "normal" range of a detergent's usage and formulation; (c) provide an assessment of the effect of phosphate level; (d) determine the precision of such tests.

All the experiments were designed in joint discussion with Water Quality Division (W.Q.D.) and Ontario Research Foundation (O.R.F.) personnel. The preparation of the detergent formulations and the analysis of the data was carried out in the laboratories of W.Q.D. The procurement of the fabrics, the washing, and the measurements were carried out by O.R.F.

EXPERIMENTAL

Materials

(a) Fabrics - the following fabrics were used in the tests:

Fabric 1. All cotton fabric EMPA 112. They were soiled with cocoa-sweetened milk mixture which represents a type of pigment-fat soil that often occurs on table linen.

Fabric 2. Polyester/cotton (65/35) fabric with durable-press finish, Soil Cloth No. 26 (specification 51S-47 U.S. Bureau of Ships); soiled with a mixture containing ethyl cellulose, lampblack, hydrogenated vegetable oil, mineral oil, corn starch, oleic acid.

Fabric 3. Spun, nylon fabric soiled with same mixture as fabric 2.

Fabric 4. Spun, acrylic fabric soiled with the same mixture as fabric 2.

Fabric 5. Spun, polyester fabric soiled with the same mixture as fabric 2.

Fabric 6. Naturally-soiled polyester/cotton pillowcases. These were obtained by subjecting new pillowcases to a sufficient period of actual use to produce a well-soiled condition. (Through the courtesy of the hospital personnel, the pillowcases were placed in continuous service for a period of three weeks at the Lakeshore Psychiatric Hospital.)

(b) Detergents

"OMO", a detergent made by Lever Brothers, was purchased in a local grocery store. Portions of "OMO" were weighed into plastic bags. Into each of the plastic bags was weighed a combination of sodium sulphate and sodium tripolyphosphate to yield three sets of mixed detergents containing 32%, 48%, and 64%, respectively, sodium tripolyphosphate by weight. In each of these three sets of detergents, the levels of the ingredients other than the sodium sulphate – sodium tripolyphosphate, e.g., surfactant, silicate, suds boosters, optical brightness, etc., were the same. The surfactant level in the mixed detergents was approximately 13%. Three sets of mixed detergent bags were prepared, each containing 50-g, 100-g, and 150-g product to correspond to a domestic usage of $^1/_2$, 1 and $1\,^1/_2$ cups, respectively. (In the washing test, the contents of one bag could be added to the washing machine to give the desired formulation and usage.)

(c) Water

The local water supply had a hardness of approximately 9.9 grains per imperial gallon (equivalent to 141 ppm $CaCO_3$). To obtain the water of 7 grain hardness, the local water was diluted with distilled water; to obtain water of 11 and 15 grain hardness, calcium chloride and magnesium sulphate in the ratio of 3:1 expressed as $CaCO_3$ equivalent were added to the water. (The 3:1 ratio is very close to the ratio of calcium to magnesium hardness in the local water.)

Equipment

All washings were carried out in "Kenmore" Model-600 machine. This washer had a water capacity of approximately 14 imperial gallons. The reflectance readings were made on a Zeiss Elropho Photometer.

Procedure

(a) Sample Preparation

To a piece of carrier fabric – undyed cotton broadcloth, 30 in x 30 in – were stapled 4 in x 4 in swatches of five artificially-soiled fabrics and one 4 in x 4 in swatch of the naturally soiled fabric. In addition, two 4 in x 4 in pieces of undyed cotton/polyester fabrics were attached for determination of soil redeposition. For each of the test conditions, (3 water hardness x 3 phosphate contents x 3 detergent usages) four replicate determinations were made. One of the control, undyed swatches was removed after the first replicate and attached to the specimens in the

Table 1. Percentage reflectance improvement of the five artificially-soiled fabrics.

Treatment No.	Product usage g/load	Water hardness gr/gal	STPP	Percentage reflectance improvement of fabric 1	2	3	4	5	Average five fabrics	Corrected reflectance improvement
1	50	15	32	5.1	14.4	15.1	17.1	13.3	13.0	12.9
2			48	7.4	21.1	18.7	29.6	26.1	20.6	20.6
3			64	9.1	24.7	17.7	27.5	27.2	21.2	22.1
4		11	32	8.0	20.5	28.2	24.1	23.6	20.9	20.6
5			48	11.4	23.9	25.1	36.1	23.0	23.9	24.1
6			64	13.7	20.2	18.1	29.2	21.6	20.9	21.6
7		7	32	10.3	31.6	21.9	28.7	26.5	23.8	24.6
8			48	13.4	22.6	27.4	27.5	21.2	22.4	22.8
9			64	19.5	14.8	32.1	29.1	9.1	20.9	21.4
10	100	15	32	12.6	24.9	31.9	27.2	25.7	24.5	24.8
11			48	13.3	22.7	42.4	28.1	13.9	24.1	23.6
12			64	16.3	20.6	43.2	27.8	19.8	25.5	25.1
13		11	32	12.4	24.8	41.6	31.8	24.1	26.9	26.3
14			48	17.1	19.4	42.8	36.9	15.2	26.3	25.8
15			64	19.0	23.2	44.9	29.6	18.5	27.0	27.1
16		7	32	12.9	23.7	40.9	29.2	20.4	25.4	25.1
17			48	17.2	21.7	42.5	30.0	17.8	26.3	25.8
18			64	17.9	20.7	45.1	32.6	17.5	26.8	27.1
19	150	15	32	13.8	24.6	45.5	27.0	24.7	27.1	26.8
20			48	17.1	23.6	43.3	29.2	22.0	27.0	27.1
21			64	16.2	24.2	45.9	28.2	23.8	27.7	27.6
22		11	32	16.7	23.0	44.9	35.3	24.3	28.8	28.5
23			48	15.7	20.7	44.5	32.4	22.1	27.1	26.6
24			64	15.3	24.2	44.8	27.8	18.5	26.1	27.1
25		7	32	16.9	24.2	41.1	29.0	23.0	26.8	27.1
26			48	16.5	26.7	45.3	31.2	22.9	28.5	28.3
27			64	17.7	24.8	47.3	35.6	24.5	30.0	29.8

Table 2. Percentage reflectance readings of artificially-soiled fabrics after wash.

Initial percentage reflectance – Fabric 1 36.8
– Fabric 2 19.7
– Fabric 3 19.3
– Fabric 4 27.0
– Fabric 5 19.1

Fabric No.	Usage g/load	STPP %	Percentage reflectance readings, water hardness (grains $CaCO_3$ per gallon) 7				11				15			
1	50	32	48.3	47.5	45.7	47.0	50.1	43.7	42.3	43.2	41.9	40.0	43.2	42.4
		48	49.2	50.6	50.6	50.3	49.1	45.4	49.8	48.4	43.6	44.4	44.4	44.4
		64	55.9	57.2	56.7	55.4	47.0	50.9	52.0	52.2	45.8	46.7	45.5	45.9
	100	32	48.5	49.5	49.2	51.5	52.5	48.2	46.9	49.3	50.4	48.5	50.8	47.8
		48	52.7	55.9	54.8	52.7	52.3	57.1	54.0	52.3	48.1	52.4	46.8	53.2
		64	54.5	55.8	55.0	53.4	53.9	55.2	56.0	58.2	52.7	54.0	52.9	52.8
	150	32	53.3	55.0	51.9	54.9	52.8	53.4	54.4	53.7	52.1	49.1	51.4	59.7
		48	55.3	54.1	51.4	52.5	51.8	50.8	53.4	54.0	54.3	57.4	52.8	51.2
		64	54.0	54.5	54.4	55.4	48.4	55.7	52.7	53.8	53.1	51.7	52.7	54.6
2	50	32	55.4	52.1	47.8	49.9	39.6	41.6	38.7	40.9	35.6	32.5	36.6	31.9
		48	44.3	38.8	42.8	43.2	43.3	44.7	47.0	39.5	39.8	41.2	39.8	42.6
		64	33.8	34.7	36.0	33.7	37.2	37.9	42.5	42.0	43.9	44.3	45.3	44.0
	100	32	42.1	43.2	44.5	44.0	48.3	45.9	39.5	44.3	47.6	48.6	38.6	43.8
		48	42.5	43.0	40.9	39.3	42.4	36.1	40.9	37.2	45.7	41.0	39.6	43.4
		64	40.2	39.2	41.3	41.2	43.5	42.6	42.2	43.4	41.2	39.1	42.2	38.8
	150	32	45.0	45.5	40.9	44.4	43.2	43.3	42.3	41.9	40.2	46.7	43.7	46.6
		48	49.1	42.5	46.8	47.4	40.4	40.3	40.9	40.1	43.9	42.5	44.9	42.0
		64	41.6	46.2	43.6	46.6	45.0	47.4	40.4	42.9	41.9	43.4	44.7	45.8
3	50	32	32.8	50.6	43.8	37.7	54.9	45.2	42.0	47.8	38.8	27.5	44.8	26.7
		48	54.5	50.7	44.5	37.4	52.0	43.8	52.0	29.8	49.3	30.4	38.4	33.9
		64	49.1	54.0	54.2	48.4	38.0	36.9	36.9	38.8	35.7	37.6	38.0	36.9
	100	32	57.5	61.9	59.9	61.7	65.4	59.2	58.4	60.6	47.7	54.8	44.1	58.1
		48	60.2	62.1	63.5	61.4	60.4	63.8	64.2	59.8	57.5	63.0	64.2	62.3
		64	59.1	65.8	65.4	67.2	67.1	63.7	60.3	65.7	60.9	61.9	63.7	63.7
	150	32	60.9	63.5	55.7	61.7	64.8	61.3	65.6	65.1	64.9	66.4	64.4	63.6
		48	64.9	65.0	63.5	65.0	64.5	63.5	61.8	65.5	64.0	63.4	60.8	62.3
		64	65.9	66.6	67.8	66.0	63.5	66.9	62.7	63.4	65.4	64.9	66.2	64.4
4	50	32	56.7	53.5	57.3	55.5	55.9	50.1	45.6	52.8	45.4	45.6	44.2	41.1
		48	53.0	54.8	53.4	56.7	64.3	65.5	62.2	63.2	58.4	56.3	54.6	57.1
		64	55.2	54.9	58.5	55.7	55.8	55.7	56.7	56.7	52.4	56.6	54.4	54.5
	100	32	55.8	56.1	56.3	56.8	60.6	58.4	57.7	58.6	57.5	55.6	50.0	53.9
		48	59.3	59.3	56.2	53.2	64.1	63.9	65.4	62.4	54.4	54.9	55.0	56.2
		64	55.6	60.4	69.0	63.6	55.4	59.0	53.8	58.1	52.4	53.6	56.7	56.5
	150	32	56.3	59.2	53.4	55.1	61.5	60.3	64.9	62.5	53.8	53.6	53.9	54.9
		48	58.5	58.8	58.1	57.4	63.7	64.3	54.0	55.7	56.3	57.0	56.2	55.3
		64	66.0	62.4	61.3	60.8	49.1	54.4	53.5	62.3	53.9	54.6	58.3	54.1
5	50	32	44.7	47.2	43.6	46.8	44.2	43.4	38.0	45.1	34.4	33.2	33.8	28.4
		48	45.0	39.5	39.6	37.3	41.5	42.9	41.9	42.0	44.7	46.8	43.9	45.4
		64	29.3	26.4	29.3	27.8	38.0	41.9	42.9	40.1	44.6	46.8	47.4	46.6
	100	32	34.9	39.6	42.3	41.1	47.9	42.8	39.0	43.1	49.3	44.9	39.4	45.8
		48	47.2	40.7	31.3	28.4	28.9	36.3	28.9	43.0	29.2	37.6	34.1	31.2
		64	36.1	40.2	36.6	33.5	34.4	40.6	32.6	42.7	39.3	35.3	38.9	42.2
	150	32	38.4	44.2	44.9	41.1	46.7	39.8	47.4	39.7	41.7	50.8	42.2	40.4
		48	41.7	43.0	39.0	44.4	39.7	40.2	39.9	44.8	37.5	39.9	50.0	37.0
		64	46.7	38.6	45.3	44.0	34.4	40.6	32.6	42.7	46.4	39.4	43.9	42.1

subsequent washes in order to obtain the cumulative effect of soil redeposition in four washes.

(b) Washing Procedure

The carrier cloth was placed in the machine with sufficient undyed cotton fabric to make a 6 lb load. The wash was carried out using water of 140°F and at the "regular" cycle, i.e., agitation at a speed of 70 cycles per minute with the detergent solution for 14 minutes followed by a combined rinse and spin, then a final rinse and spin. Local water of about 9.9 grain hardness was used for the rinse in all treatments. The swatches were ironed dry for the reflectance measurements.

(c) Measurement of Cleaning

Reflectance readings were made on the original soiled and on the laundered swatches at four different locations on each swatch. The readings were made by using the Zeiss Elropho Photometer, with an incandescent light source and a narrow band filter of 570 nm wave length. This eliminated the effects due to optical brighteners.

RESULTS AND DISCUSSION

Cleaning

The reflectance readings of the five artificially-soiled fabrics for each of the wash conditions are shown in Table 2. The results shown are the percentage reflectance readings: these represent the amount of light of the chosen wavelength band reflected from the fabric, expressed as a percentage of the amount of light reflected from a standard magnesium-oxide block, under the same conditions of illumination. Hence the soiled fabric has a low reflectance reading. The reflectance reading increased as the fabric is washed. A measure of cleaning is the difference between the percentage reflectance before and after washing. This difference is designated as the percentage reflectance improvement. The results giving percentage reflectance improvement for the 5 artificially-soiled fabrics are shown in Table 1. Each value represents the average result of the four replicate washes.

Confidence Limits

From the results shown in Table 2 and Table 1 it is clear that there are large differences in the percentage

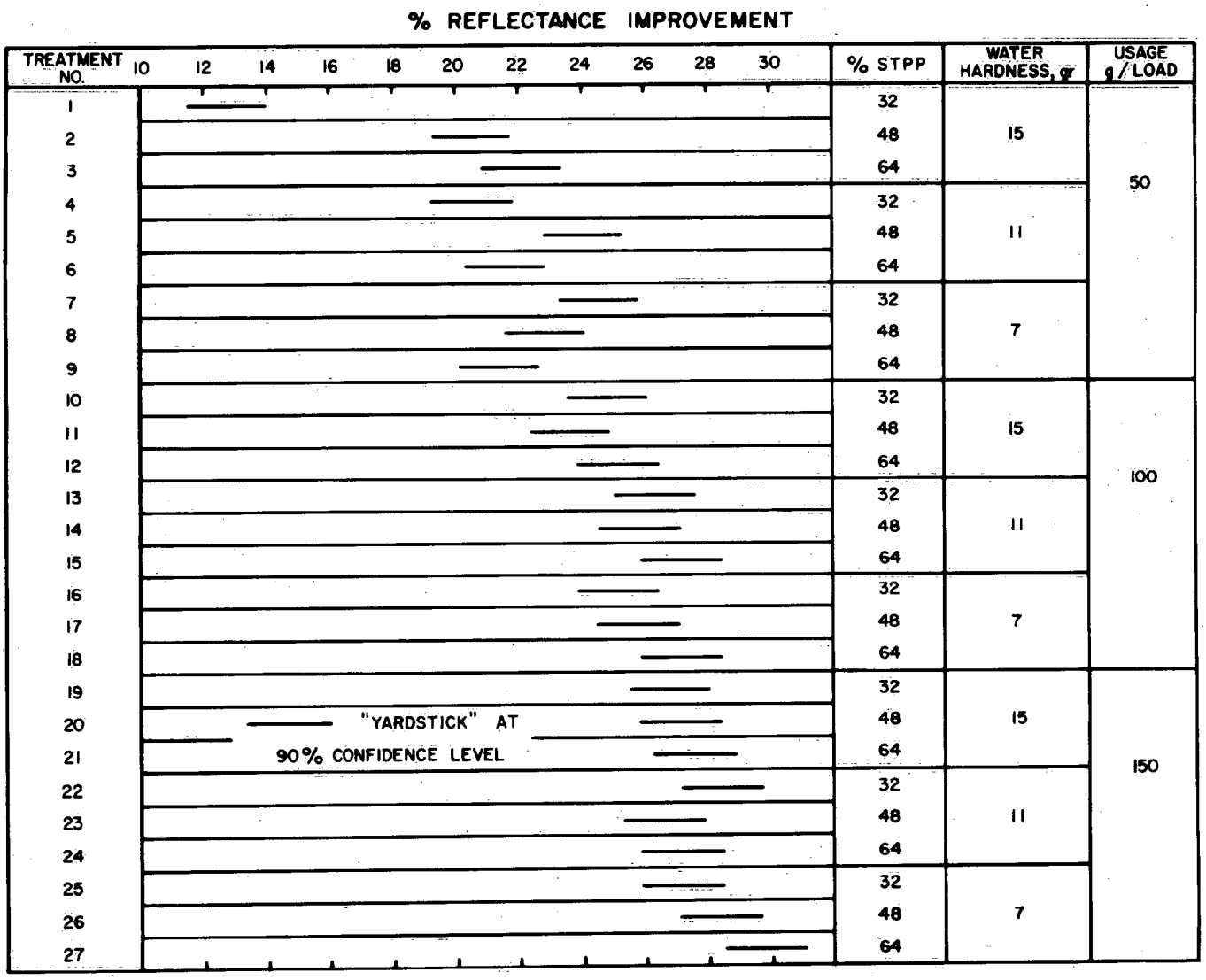

Figure 1. Percentage reflectance improvement of the twenty-seven treatments.

reflectance improvement between the different fabrics. The purpose of the tests was to obtain a measure of the overall cleaning for each comparison of water hardness, product usage, and formulation. In order to be able to combine the results for the different fabrics, the following statistical treatment was given: the mean reflectance improvement for each fabric under all conditions was calculated and the reflectance improvement for each treatment of this fabric was then converted to a fraction of the mean reflectance. An analysis of variance was then carried out using these fractions.

The results showed that the coefficient of variation for the determinations of the reflectance improvement in a single wash for a single fabric is 30%. Hence for the mean reflectance improvement representing the 5 fabrics, with 4 washes each, the confidence interval or "yardstick" at 90% confidence level is 11.5% or 2.7 reflectance units. Essentially, the same size yardstick was obtained by taking some of the treatments in pairs and using the washing results on the same fabrics as paired observations for the determination of the standard error of the mean difference. Analysis of the data given in the *Canadian Consumer* evaluation yields the same order of precision.

Using the calculations from the average reflectance improvement for each fabric, the overall reflectance improvement in each treatment was calculated. This "corrected" reflectance improvement is shown in the last column of Table 1 and is used in the following discussion.

Factors Affecting Cleaning

The reflectance improvement for each treatment is shown in Figure 1 where the ratio of product usage to water hardness increases from left to right. Reflectance

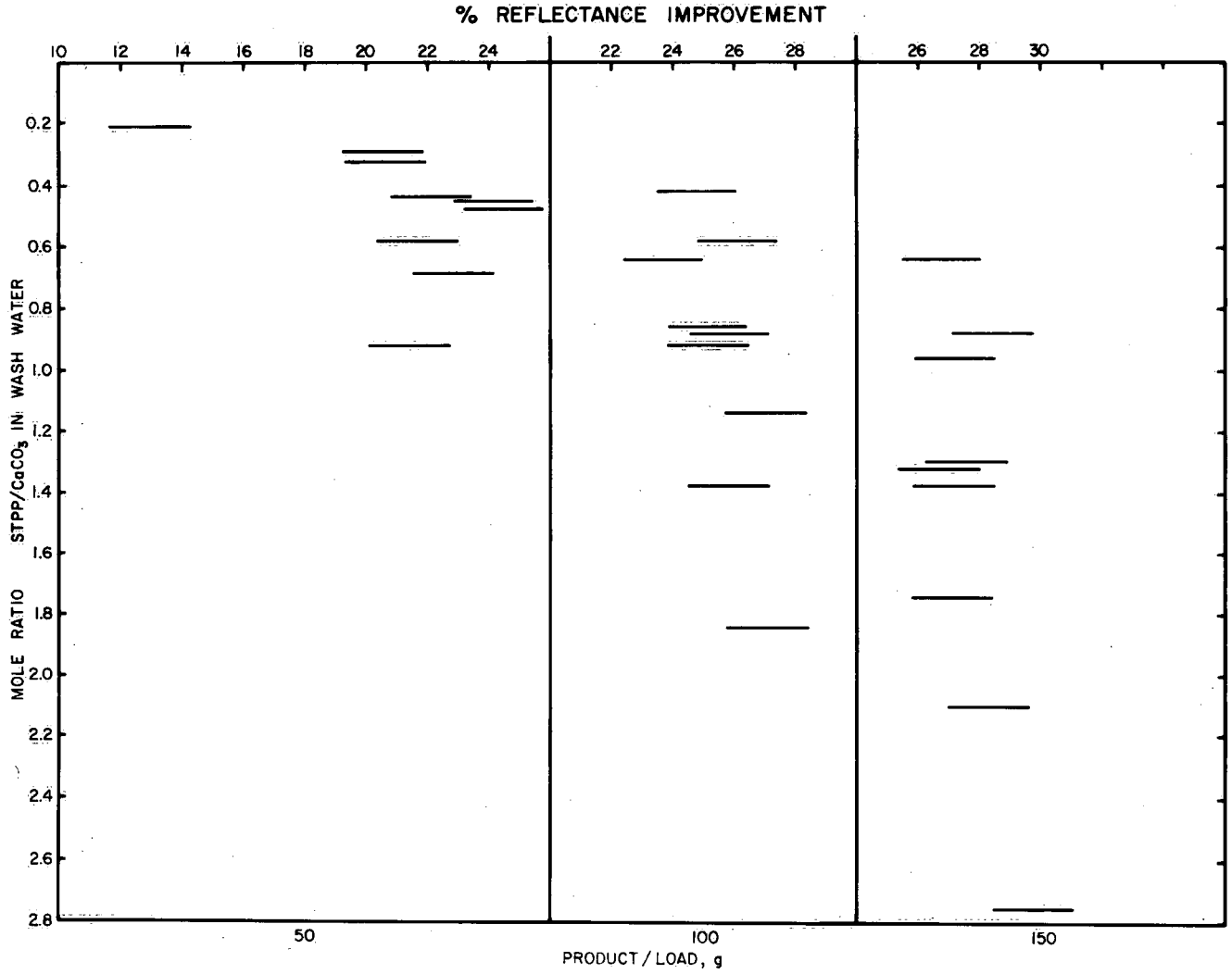

Figure 2. Ratio STPP/$CaCO_3$ vs. percentage reflectance improvement.

improvement versus the mole ratio of STPP to water hardness is shown in Figure 2.

It is clear that at low phosphate level, low product usage, and hard water there is a serious loss of performance; but above a mole ratio of about 0.3:1, STPP:$CaCO_3$ tripolyphosphate is no magic ingredient. There is as much significant improvement in performance by increasing the other ingredients in the detergent as by increasing the phosphate.

The study was designed so that there was an overlap of phosphate levels between the three product usages, e.g.,

50-g product at 64% STPP gives equivalent STPP to 100-g product at 32% STPP

100-g product at 48% STPP gives equivalent STPP to 150-g product at 32% STPP

100-g product at 64% STPP gives equivalent STPP to 150-g product at 47% STPP

Apart from the extreme conditions in treatment no. 1 (50g, i.e., $^1/_2$ cup usage, 32% STPP, 11 grain water hardness) it is seen from Figure 2 that, within one product usage, phosphate level has very little effect on cleaning and that there is no correlation between equal phosphate use at different product usages, although as a generalization, it appears that more phosphate gives directionally better performance. A manufacturer striving for ultimate cleaning performance in a product will probably use high phosphate levels but reduction of the phosphate levels will not lead to disastrous results except under extreme conditions.

The percentage reflectance improvement by itself does not have much meaning unless it can be related to what a user will see. It seems fairly well accepted that a difference of two reflectance units (and possibly one in extreme cases) can be detected by the human eye if the cloth is white and clean (Anon., 1969). On dark cloth, a difference of three units is scarcely noticeable to the eye. Hence the "yardstick" of the overall measurements of 2.7 reflectance units which was obtained in the study is approximately equivalent to the differences visible to the human eye.

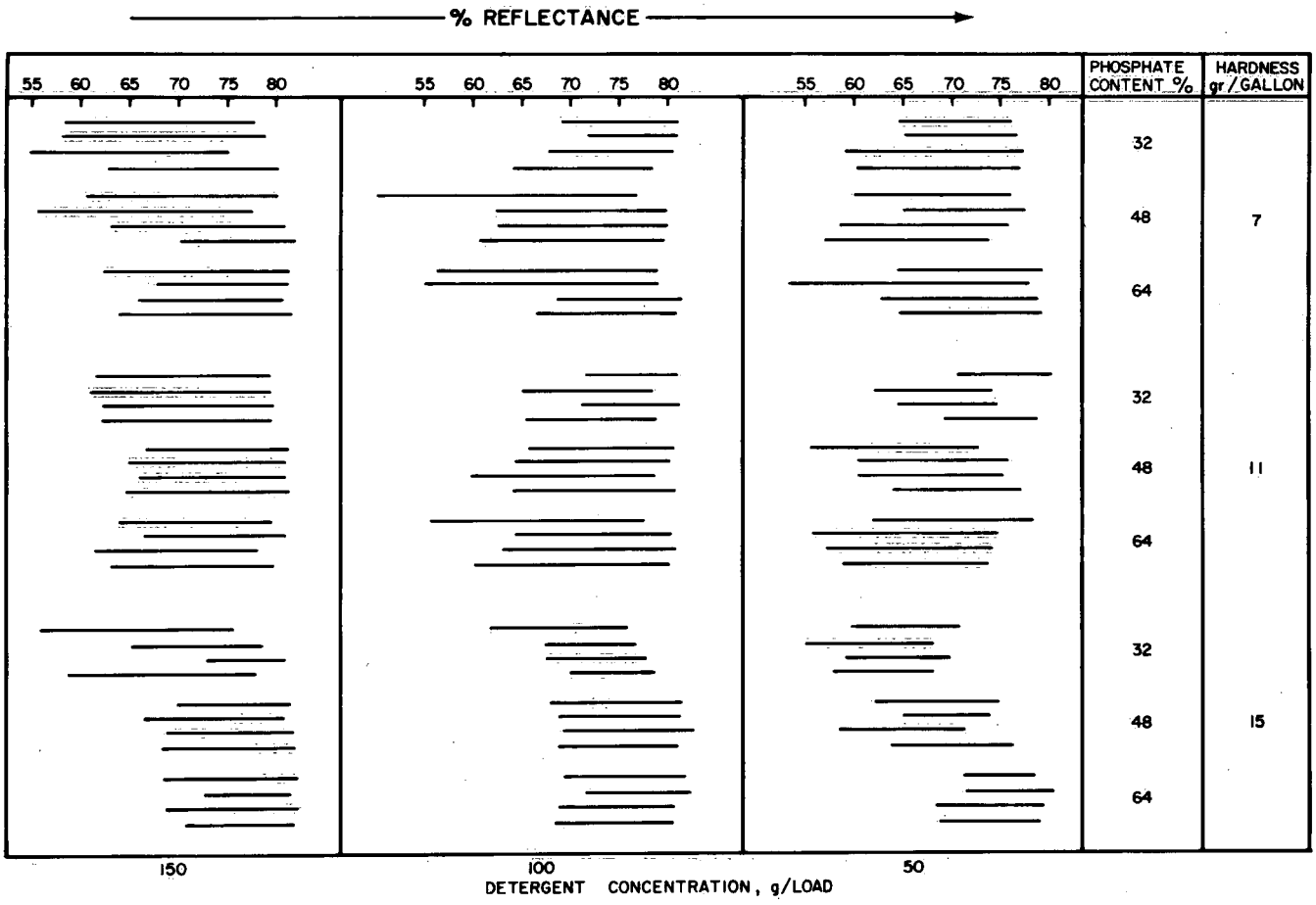

Figure 3. Cotton/Dacron naturally-soiled fabric: improvement in percentage reflectance after laundering of quadruplicate samples.

It should be noted that the 50-g usage corresponds to a usage of about $^1/_2$ cup of detergent having a density of 0.4 g cm^{-3}. There are many detergents which have a lower density, and some which have a higher density than this. Obviously the density of the detergent partly determines the usage when measurement is made on a volume basis. The use of artificially-soiled clothes for the washing test does not add to the wash water the hardness that is brought into the wash on a load of naturally-soiled clothes. This is believed to be equivalent to about 4 grain hardness in the wash water.

Soil Redeposition

Two actions can take place during detergency; soil removal and soil redeposition. The detergent removes soil from the cloth and, in the case of particulate material, it must hold it in suspension in the water and prevent it from redepositing on the cloth. The overall cleaning measurement is a measure of how well both or either of these functions are carried out. To determine if redeposition is taking place, clean clothes are used in the washing process and their reflectance measured before and after. In the present study the soil redeposition was measured in each wash separately and for the accumulation of the four replicate washes in each treatment. The results of these measurements show that there was essentially no soil redeposition in any of the treatments.

Naturally-Soiled Clothes

The naturally-soiled clothes had a variety of soil levels before the wash. Because of this variability, mathematical treatment of the results is very difficult. The results are shown graphically in Figure 3 where the bottom of each bar represents the reflectance before the wash and the top of each bar represents the reflectance after the wash. The results are in agreement with the results obtained by washing the artificially-soiled fabrics.

REFERENCES

Anon., 1969. Synthetic laundry detergents. Canadian Consumer, 7, (3), 99-105.

Pollard, R.J., 1966. Amino-acid chelating agents in detergent applications, soap and chemical specialties, 42, (9), 58-62 and 130-135.

Rutrowski, B.J., 1967. A realistic soil cloth and test procedure for detergent evaluation. J.A.O.C.S., 44, 103-106.