Behavior of Subsilicates With Soap

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ABSTRACT

The behavior of sodium subsilicates as soap builders in commercial laundry operations is discussed, with particular reference to the technically anhydrous product containing 2 mols of sodium oxide per 1 mol of silicon dioxide. A system for evaluating soap builders is suggested, and subsilicates are evaluated according to this system. The data presented indicate that the technically anhydrous 2:1 ratio sodium subsilicate is eminently suitable as a soap builder in commercial laundering.

BEHAVIOR of SUBSILICATES with SOAP

This paper is intended to be of interest to those who apply soaps in commercial laundry operations. It covers in a general way the behavior of subsilicates, particularly the 2:1 ratio sodium subsilicate, corresponding to the formula Na_4SiO_4,—as a soap builder in commercial laundry operations.

It is generally accepted that soap solutions operate most effectively as detergents when in the pH range of 10.0 to 11.6. In laundry operations there are substances present which are acidic with respect to this ideal pH range. These substances tend to lower the pH of the soap solutions. If the tendency is not counteracted by the addition of alkaline "builders," the sodium oxide content of part of the soap is used up in neutralizing these acidic substances. In this way, part of the soap is actually acting as a "builder" for the remainder of the soap. Obviously, soap is a very expensive builder, owing to its relatively high cost per unit of sodium oxide content.

The ideal laundry soap builder is considered to have the following properties:

1. It will dissolve and neutralize acid substances which would otherwise use up soap.
2. It will exert its buffer action strongly in the pH range between 10.0 and 11.6.
3. It will be a good detergent itself, thus adding to the detergency of the solution.
4. It will rinse from the clothes readily.
5. It will be in such form that it can be conveniently used. The builder must of course be compatible with soap.

An examination of the behavior of the 2:1 ratio sodium subsilicate in laundry operations, indicates that its properties conform extraordinarily well with those of the ideal builder, mentioned above.

I. Neutralization of Acid Substances

There are two classifications of substances encountered in commercial laundry operation, which are acidic with reference to the ideal pH range for soap performance. They are:

(1) the acidic soil in the clothes; and
(2) sodium bicarbonate in the water.

Christoffers[1] has shown quite clearly that the pH values of laundry detergent solutions are depressed upon contact with the laundry load, and that the sodium oxide contents of the solutions, available at pH levels between 10.0 and 11.6, are depleted.

He has made plant scale tests on several types of laundry loads, with subsilicate-soap formulas, and measured the absorption of the sodium oxide available at various pH levels. He has shown that the *total* sodium oxide content is not reduced by the acidic soil of the load, but that the sodium oxide available above a pH of 10.0 (i.e., at a level where it is of value in maintaining the soap solution at an effective range for good detergency) is reduced by an average of 71% for the various loads tested, representing an average absorption of 35.7 gms. of sodium oxide available at this level, per 100 lbs. of clothes washed.

The following table gives a summary of Christoffers' data:

TABLE A

Absorption of Alkali by Laundry Loads[1]

Load	Na_2O available over pH 10.0, absorbed per 100 lbs. of clothes	Percentage of the Na_2O available over pH of 10.0 which was absorbed	Na_2O available over pH 8.3 (phenolphthalein point) which was absorbed per 100 lbs. of clothes	Percentage of the Na_2O over pH 8.3 which was absorbed	pH level at which no Na_2O was absorbed by the soil
A	29.4 gms.	78.3%	22.4 gms.	48.3%	3.5 pH
B	37.9 gms.	59.2%	27.2 gms.	33.4%	5.5 pH
B[1]	30.2 gms	71.8%	18.3 gms.	32.6%	6.0 pH
C	37.1 gms.	75.0%	24.7 gms.	38.5%	5.0 pH
Avrg.	33.7 gms.	71.0%	23.1 gms.	38.2%	5.0 pH

Load A—539 lbs. netted white shirts, average soil, 44"x96" metal tray commercial wash wheel.

Load B—430 lbs. netted wet wash, moderate to heavy soil, 44"x120", metal tray commercial wash wheel.

Load B[1]—476 lbs. netted wet wash, moderate to heavy soil, 44"x120" metal tray commercial wash wheel.

Load C—550 lbs. netted wet wash, moderate to heavy soil, in 44"x120" commercial wash wheel.

In this work, the soap and alkali builder (composed principally of the 2:1 ratio sodium subsilicate) were added to the wash wheel prior to the addition of the load of clothes. pH vs. titration curves on the washing solutions were plotted and the clothes were then added. Curves were again made after the washing operation. These curves serve to show not only the total sodium oxide content of the solutions, but the sodium oxide available at any pH level. From these curves the sodium oxide available for use in soap building—that is, available above the pH of 10.0, was determined and the effect of the acidic soil in depleting this available sodium oxide content was readily shown, as given in the above table.

The second factor encountered in laundry operations, which tends to depress the pH of soap, is the sodium bicarbonate content of the water used. It is the general custom in commercial laundries to remove hardness from water by means of base exchange softeners. The calcium bicarbonate content of such water is converted to sodium bicarbonate, with the result that in some parts of the country, laundries are using water which, although it has zero hardness, contains as much as 500 parts per million of sodium bicarbonate, or even more.

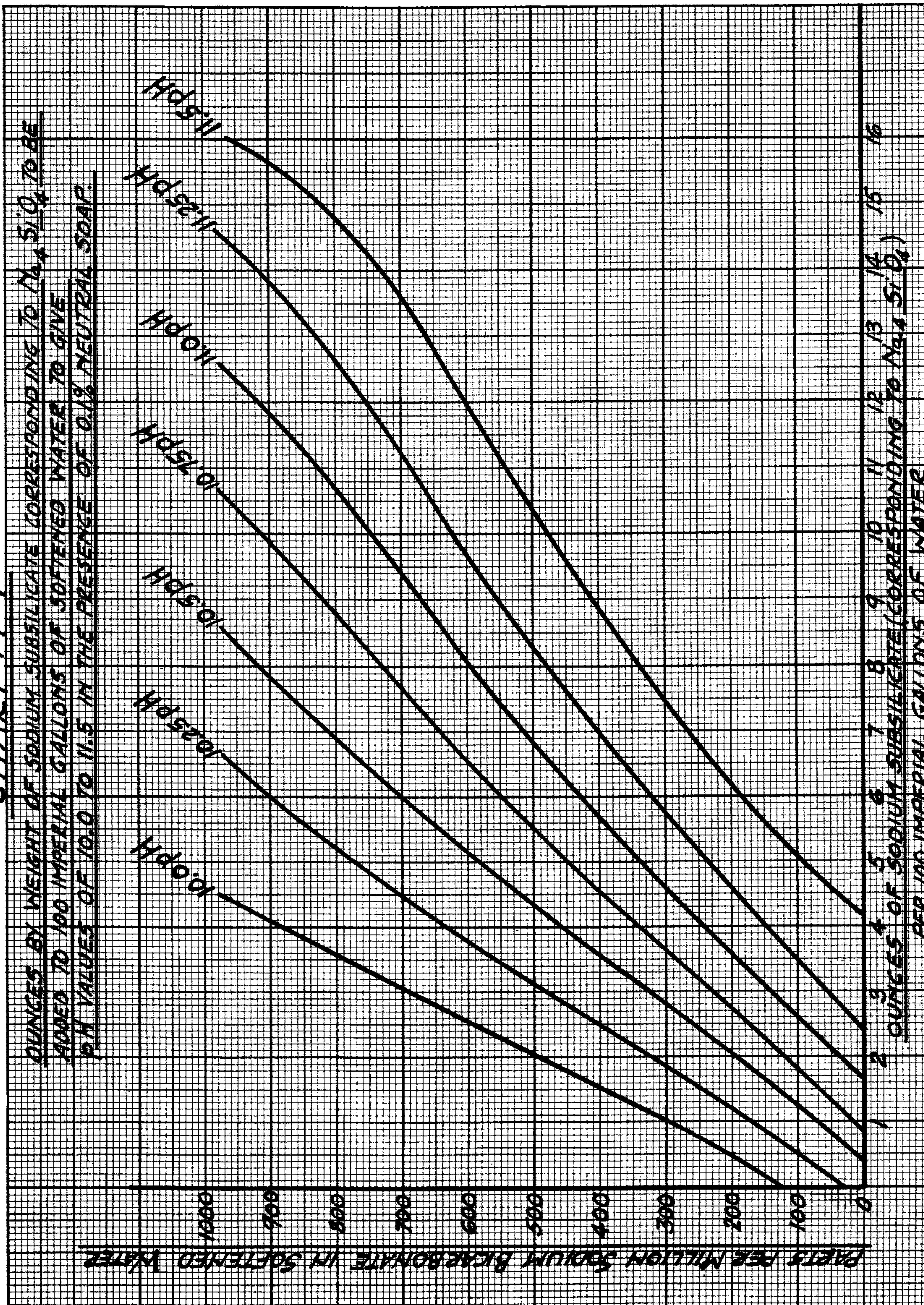


CHART No 1
OUNCES BY WEIGHT OF SODIUM SUBSILICATE CORRESPONDING TO Na_4SiO_4 TO BE
ADDED TO 100 IMPERIAL GALLONS OF SOFTENED WATER TO GIVE
pH VALUES OF 10.0 TO 11.5 IN THE PRESENCE OF 0.1% NEUTRAL SOAP.
11.5pH
11.25pH
11.0pH
10.75pH
10.5pH
10.25pH
10.0pH
0 100 200 300 400 500 600 700 800 900 1000
PARTS PER MILLION SODIUM BICARBONATE IN SOFTENED WATER
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
OUNCES OF SODIUM SUBSILICATE (CORRESPONDING TO Na_4SiO_4)
PER 100 IMPERIAL GALLONS OF WATER

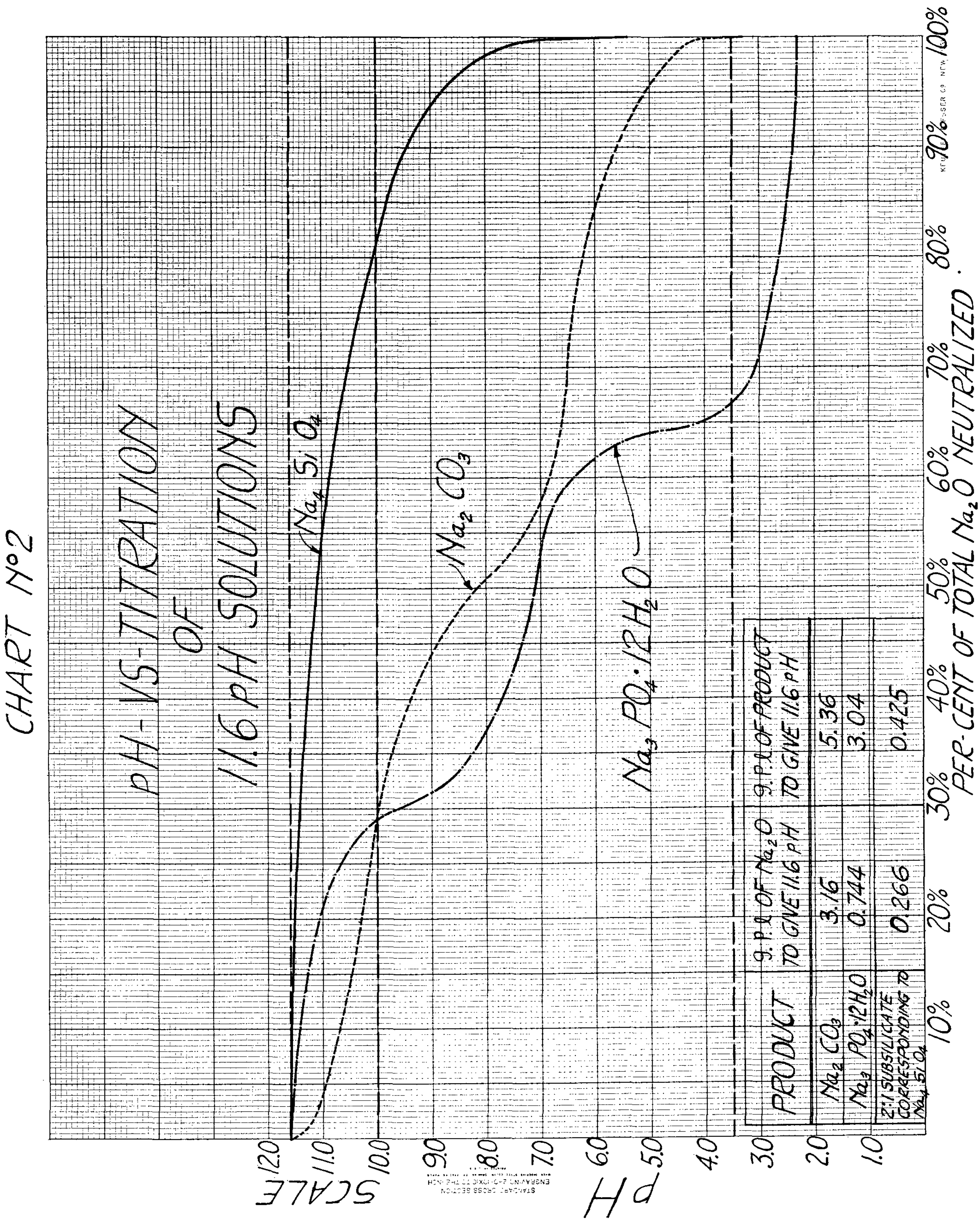


CHART No 2
PH-VS-TITRATION
OF
11.6 pH SOLUTIONS
Na_4SiO_4
Na_2CO_3
$Na_3PO_4 \cdot 12H_2O$
PRODUCT | g. P. L. OF Na_2O TO GIVE 11.6 pH | g. P. L. OF PRODUCT TO GIVE 11.6 pH
Na_2CO_3 | 3.16 | 5.36
$Na_3PO_4 \cdot 12H_2O$ | 0.744 | 3.04
2:1 SUBSILICATE CORRESPONDING TO Na_4SiO_4 | 0.266 | 0.425
PER-CENT OF TOTAL Na_2O NEUTRALIZED.
10% 20% 30% 40% 50% 60% 70% 80% 90% 100%
pH SCALE
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0

The effect of this sodium bicarbonate in depressing the pH of built soap solutions is shown by Bayley,[2] He has plotted curves showing the amount of soap builder (2:1 sodium subsilicate) which is necessary to attain various desired pH's within the ideal soap range, with varying amounts of sodium bicarbonate present. His work was done in solutions containing 0.1% neutral soap, so that it is representative of the actual conditions in the laundry. These curves are given in Chart I, and they show graphically the pronounced effect of the sodium bicarbonate present in the water, on the requirements for builder. For example, an increase in sodium bicarbonate content from 100 ppm. to 350 ppm. in the water, is shown to double the amount of builder necessary to attain a pH of 11.0.

The effect of sodium bicarbonate on alkali builder requirements was also shown by one of the authors.[3] This work showed that in order to maintain satisfactory suds levels and give first quality washing, water containing 1000 ppm. sodium bicarbonate required an average of 62.77 ozs. of the builder per 300 lbs. load, as against an average requirement of only 44.77 ozs. for the same size load, when only 250 ppm. sodium bicarbonate were present.

The effectiveness of various commercial soap builders in this important function of neutralizing the two above-mentioned classes of acidic substances which would otherwise use up soap, can be nicely measured from their pH titration curves, which indicate the percentage of sodium oxide available at any pH level. Since 10.0 is generally agreed upon as the bottom of the ideal pH level for soap solutions, the sodium oxide content available above a pH 10.0 is suggested as a measure of the value of the soap builder in this regard.

The following table shows these values for several alkalies which are accepted by the laundry industry as being safe for use as laundry soap builders.

TABLE B

Soap Builder	Percentage Na_2O Available Above pH 10.0*
Sodium Carbonate	11.7%
Modified Soda (corresp. to sesquicarbonate)	0%
Trisodium Phosphate, hydrated	9.0%
Sodium Metasilicate, hydrated	19.5%
Sodium Sesquisilicate, hydrated	29.2%
2 to 1 Sodium Subsilicate, technically anhydrous	46.92%

* (Tests made in solutions of such concentration as to furnish .04692% Na_2O available over pH of 10.0.)

The comparative values of the above products and the outstanding value of the 2:1 ratio sodium subsilicate have been confirmed by extensive observations in commercial laundries during the past four years.[4]

II. BUFFER ACTION in IDEAL pH RANGE

The second requirement of an ideal laundry soap builder, is that it must be buffered strongly in the pH range ideal for soap, (i.e., 10.0 to 11.6). Stated another way, this would mean that large proportions of its sodium oxide content must be available for neutralization at pH levels within this range. The predominant proportion of the sodium oxide in the 2:1 sodium subsilicate is available here. This is not true in the case of some of the other commonly used builders such as sodium carbonate and hydrated trisodium phosphate, for example.

Chart 2 shows pH vs. titration curves for 11.6 pH solutions of these three soap builders.

It will be noted that 29.5% of the total sodium oxide in the sodium carbonate solution is available in the range between 11.6 and 10.0. The corresponding figure for trisodium phosphate is 29.0%. With the 2:1 sodium subsilicate, however, 80.5% of the total sodium oxide is available in this ideal laundering range.

The matter may perhaps be shown even more strikingly by Charts 3 and 4. They are based on the values shown in Chart 2, but they show by the distribution of shaded areas, the percentage of total sodium oxide available at various pH levels—for each of the three builders. In each case the total shaded area is 1200 small squares, representing 100% of the total Na_2O in the solution. With sodium carbonate, 354 out of the 1200 shaded squares are between the levels of 10.0 and 11.6, illustrating that 29.5% of the total Na_2O in the solution is available for use before the pH drops to 10.0.

It is interesting to note in comparison that the 2:1 subsilicate solution furnishes that percentage (29.5%) of its sodium oxide with a change of less than .2 pH units, indicating the much greater buffering action of the 2:1 subsilicate, in that range.

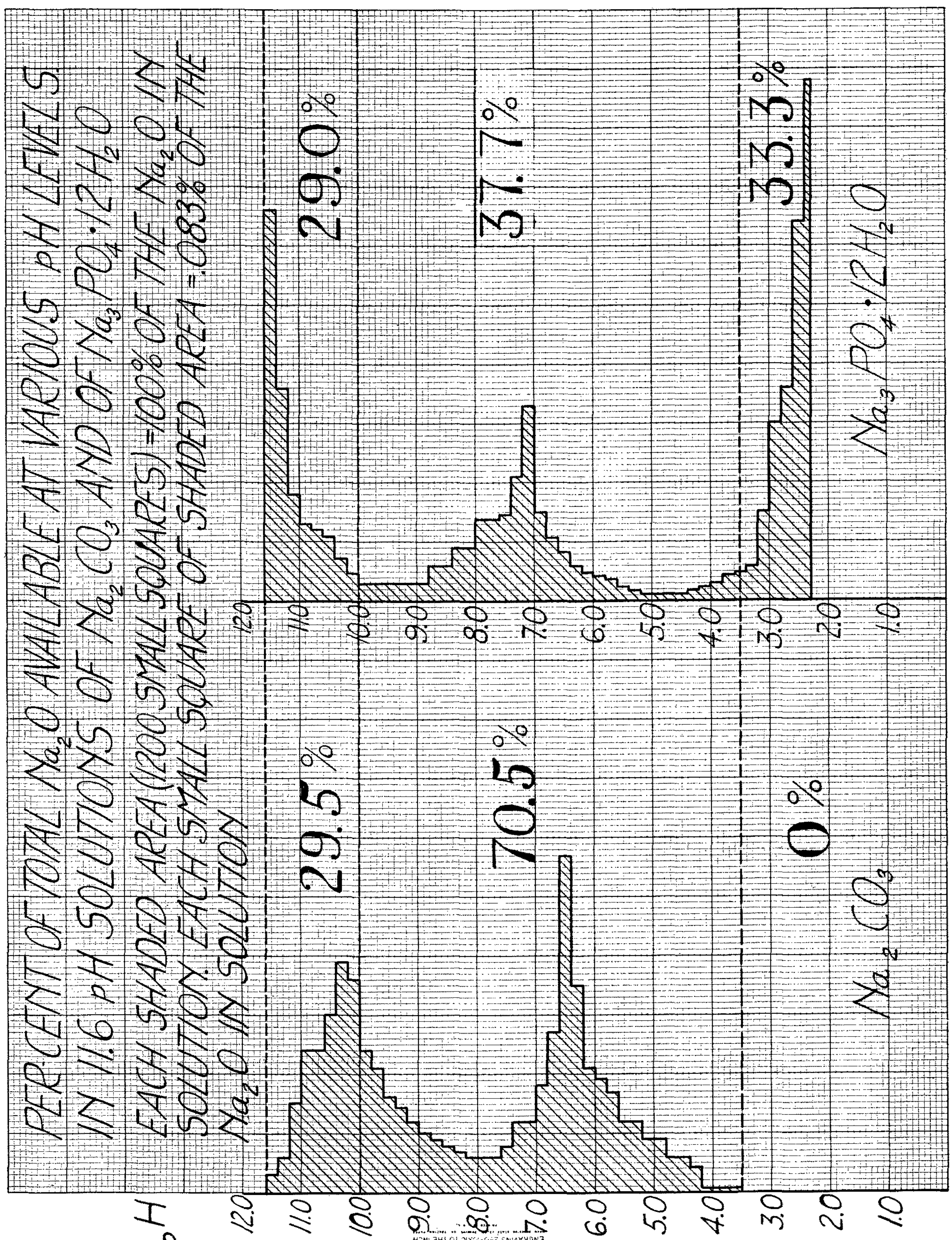
III. DETERGENT VALUE ADDED BY BUILDER

The third qualification of an ideal soap builder is that it be a good detergent in itself, so that it can add to the detergent effectiveness of the solution. All of the commercially available sodium subsilicates and especially the 2:1 ratio product, are outstanding on this point. As described by one of the authors in an earlier paper,[5] the subsilicate corresponding to the formula Na_4SiO_4 has been widely adopted for cleaning steel before tinning, and for many other heavy duty cleaning operations which are just as exacting. In most of these cases there is no soap or other detergent present, and it is the sodium subsilicate solution alone which acts as the detergent. The advantages of subsilicates over other alkaline salts, such as sodium carbonate, etc., as a lone detergent in solution, have been indicated in many industrial applications and confirmed by field reports[6] during the past several years; and although sodium subsilicates are used in laundry operations chiefly to support soap as the primary detergent, the inherent detergent properties of the subsilicates make them additionally desirable for this purpose.

IV. EASY RINSING

Since the purpose of laundering is to remove foreign matter from the clothes, the addition of other foreign substances in the washing process should be avoided whenever possible. Fortunately, the inert material which is added to the clothes when a soap builder like sodium carbonate is used presents no problem of removal other than that of extra rinsing. Rinsing is, however, a rather expensive procedure in the commercial laundry since it consumes not only valuable water, but valuable time of the operators as well.

As can be seen from Chart 2, the 2:1 ratio sodium subsilicate carries with it a very much smaller proportion of sodium oxide inert for detergent work, than do such builders as sodium carbonate and trisodium phosphate. In actual practice the 2:1 sodium subsilicate rinses out much more readily than such builders as sodium carbonate. A typical example of this is shown in a report[7] of tests made at the Royal Standard Laundry, Chiswick, London, summarized in Table C. This work shows that one rinsing operation could consistently be eliminated when the 2:1 subsilicate was substituted for the soda ash and metasilicate previously used, in a washing formula recommended by the British Launderers' Research Association.



PER CENT OF TOTAL Na_2O AVAILABLE AT VARIOUS pH LEVELS.
IN 11.6 pH SOLUTIONS OF Na_2CO_3 AND OF $Na_3PO_4 \cdot 12H_2O$
EACH SHADED AREA (1200 SMALL SQUARES) = 100% OF THE Na_2O IN SOLUTION. EACH SMALL SQUARE OF SHADED AREA = .083% OF THE Na_2O IN SOLUTION
29.0%
37.7%
33.3%
$Na_3PO_4 \cdot 12H_2O$
29.5%
70.5%
0%
Na_2CO_3
pH
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

CHART No 3

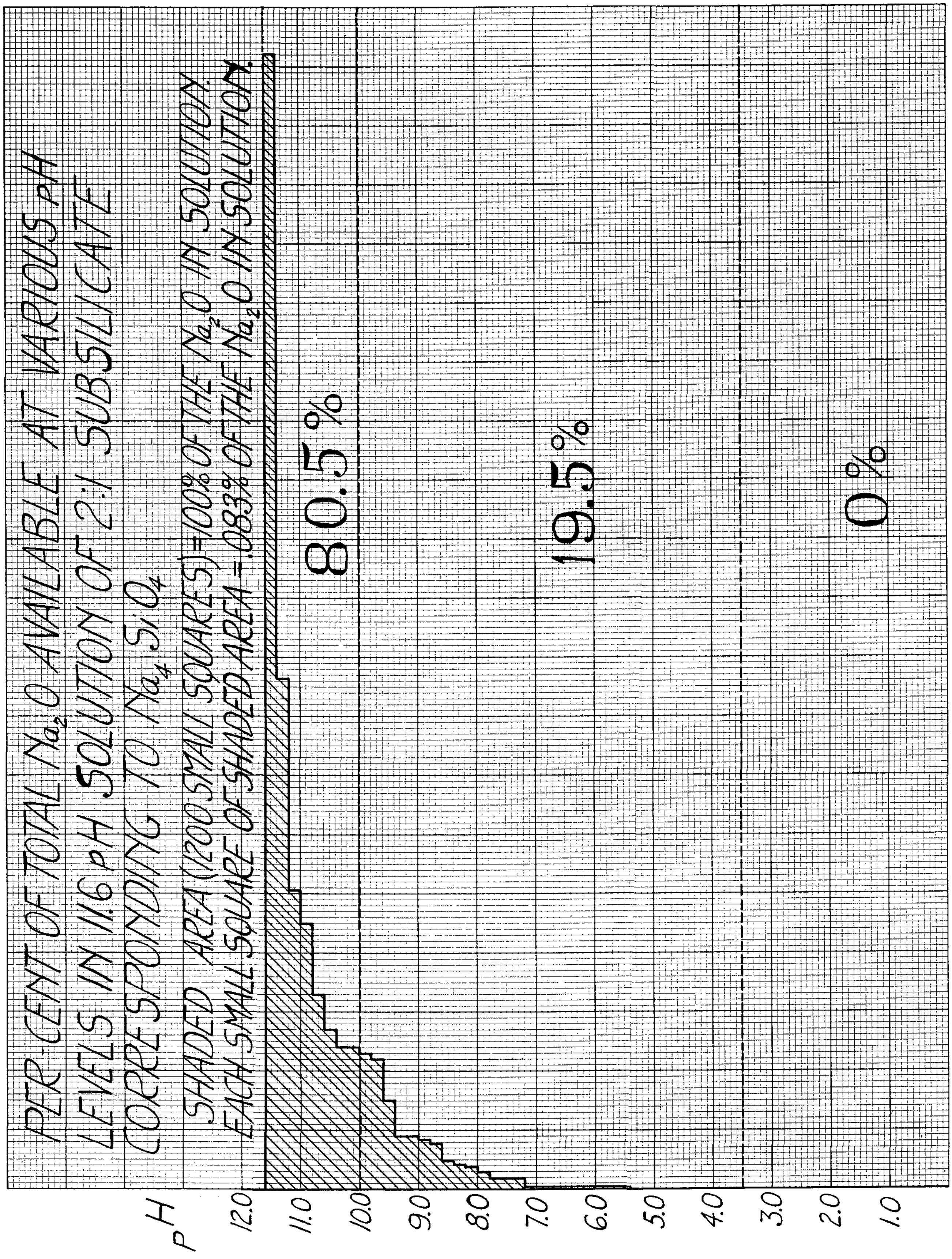

PER-CENT OF TOTAL Na_2O AVAILABLE AT VARIOUS pH
LEVELS IN 11.6 pH SOLUTION OF 2:1 SUBSILICATE
CORRESPONDING TO Na_4SiO_4
SHADED AREA (1200 SMALL SQUARES) = 100% OF THE Na_2O IN SOLUTION.
EACH SMALL SQUARE OF SHADED AREA = .083% OF THE Na_2O IN SOLUTION.
80.5%
19.5%
0%
pH
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

CHART No 4

TABLE C

REPORT OF TEST AT ROYAL STANDARD LAUNDRY, CHISWICK, LONDON, ENGLAND

Load washed in each test: 170 lbs. medium soiled sheets.

Operation	Test	B.L.R.A. washing formula using Metasilicate and Soda Ash as Alkalis a/b (see Note 1)	Same washing formula but with subsilicate substituted for the other alkalis	Same formula but with 2:1 subsilicate substituted for the other alkalis and used entirely in the first washing operation
No. 1 (washing)	Titration	28/55u.	30/40u.	30/40u.
	pH	10.5	11.8	11.4
No. 2 (washing)	Titration	30/60u.	20/30u.	15/20u.
	pH	10.6	11.0	11.0
No. 3 (rinsing)	Titration	10/20u.	8/11.5u.	5/9u.
	pH	10.2	10.0	9.8
No. 4 (rinsing)	Titration	3/11u.	3/7u.	2/7u.
	pH	9.7	9.7	9.5
No. 5 (rinsing)	Titration	2/7u.	2/6u.	1/6u.
	pH	9.5	9.2	9.0
No. 6 (rinsing)	Titration	1/6u.	1/5u.	1/5u.
	pH	9.0	8.8	8.8

Notes:

(1) The titration figures are expressed in units equivalent to (a) the number of drops of N/10 acid required to lower the pH of a ten c.c. sample of the washing solution to 8.6 (Phenolphthalein Point) and (b) the total number of drops of N/10 Acid, including (a) required to lower the pH of the sample to 3.4 (Methyl Orange Point). In absolute terms each drop indicates 0.0023% Na_2O or 2.6 grains of Na_2O per imperial gallon expressed as $CaCO_3$ equivalent.

(2) It will be observed that in both washing operations (Nos. 1 and 2) the ratio of available Na_2O/Total Na_2O is superior in cases of the tests in which 2:1 subsilicate was used.

(3) It is to be noted that in the washing operations using the technically anhydrous 2:1 subsilicate, higher pH values are attained with the use of less alkali as shown by total titration figures "b." This indicates faster washing with less alkali to rinse out.

(4) The ease with which orthosilicate (2:1) solutions are rinsed out is readily apparent by comparing the total alkali figures "b" given in the rinsing operations 3, 4, 5, 6 with the corresponding figures when Meta Silicate and Soda Ash are used. It is to be seen from this that rinsing is as complete in three operations with orthosil as in four operations when the other products are used.

(5) Mr. Wallis, Assistant Manager of the laundry, stated that the quality of the work using the technically anhydrous 2:1 subsilicate was equal to that in which Metasilicate and Soda Ash were used as soap builders.

These same findings regarding the excellent rinsing behavior of the 2:1 sodium subsilicate are continually being confirmed in field reports from commercial laundries using the builder in this country.[4]

V. CONVENIENT FORM FOR USE

The builders most commonly used in the past, such as sodium carbonate and trisodium phosphate, are suitable for addition to laundry wash wheels along with soap, and for addition to soap in the plants of the soap manufacturers. Certain other chemicals, such as water glass and caustic soda, are at a decided disadvantage from the standpoint of convenience in use, since the first is a viscous sitcky liquid, carrying a large burden of water, and the second is a highly corrosive chemical, which is safest in the hands of the technically skilled worker.

The sodium subsilicates are available in technically anhydrous form, either as free flowing granules for use by the laundryman, or as a powder for direct incorporation into the soap or soap mixtures by the soap manufacturer.

Although the 2:1 ratio sodium subsilicate is the one which is widely used by the laundries themselves, other ratios, from 1.5 Na_2O: 1 SiO_2 to 7 Na_2O: 1 SiO_2, are being made in the same convenient, technically anhydrous form. The direct process by which these subsilicates are manufactured has allowed them to be made available to laundries and to soap manufacturers at very low cost, per unit of soap building performance.

GENERAL

In the above discussion, sodium subsilicates have been considered with regard to the five proposed requirements of an ideal soap builder. In each case it appears that the subsilicates, (particularly the technically anhydrous 2:1 product) are eminently suitable as soap builders in commercial laundering.

This conclusion is confirmed in the report[3] of the Research Fellowship No. 13 at the American Institute of Laundering which tested the technically anhydrous 2:1 ratio sodium subsilicate in fifteen different commercial laundry formulas, on various types of loads. In all cases tensile strength losses after twenty washings were less than the 10% allowable in "first quality laundering." Likewise, the whiteness retention of test pieces after twenty washings, was always greater than the 94% required in "first quality laundering."

The report concludes that:

"the technically anhydrous 2:1 sodium subsilicate is safe to use in cotton and linen washing formulas representing general commercial laundry practice" and

"this subsilicate is suitable as an alkali detergent and soap builder in commercial laundering."

Further confirmation of the effective behavior of the product is given by Bayley[2] of the Division of Chemistry, of the National Research Council of Canada. His conclusions are as follows:

"The results obtained in our studies have indicated that the technically anhydrous 2:1 ratio sodium subsilicate possesses very definite value as a laundry soap builder. The relatively high alkalinity which it possesses, together with its excellent detergent characteristics, make it possible to use this compound with very considerable success in any laundering formula in which a medium to high degree of alkalinity is required.

"The tensile strength losses shown by test pieces processed in the formulaeusing the technically anhydrous 2:1 ratio sodium subsilicate indicate that the compound is without deleterious effect in this regard.

"The degrees of detergency (soil removal) and whiteness retention obtained in the tests were satisfactory and indicate that a high quality of washing efficiency can be obtained by the use of the compound with soap."

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