grams of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Borax) by means of methylene chloride. After four hours of distillation, 1.28 c.c. of water (equal to 12.8 per cent) was collected.

Hence,
$$
\frac{381.43 \text{ (mol. wt. of borax)} \times 0.128}{18} = 2.78,
$$

assumed to be equivalent to $3 \text{ H}_{2}\text{O}$.

Then, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} - 3\text{H}_2\text{O} = \text{Na}_2\text{B}_4\text{O}_7 \cdot 7\text{H}_2\text{O}$ (final-state).

All pertinent data are condensed in the following table, in which are columns "a" and "b." In the "a" columns are tabulated the per cent of water (w) obtained during each separate distillation, during the time (t) in hours, and in the "b" columns are given the approximate formulas of the corresponding compounds.

Deductions from Experimental Data

Since both time and speed of distillation have eonsiderable bearing upon the amount of water removed from some crystals, it cannot be asserted that a deftnite state of partial dehydration can universally be obtained.

Besides revealing that salts can be prepared that at present appear to have unusual states of hydration, these data have analytical significance. For example, upon applying the distillation method for the determination of moisture in soaps and soap powders containing hydrated salts for fillers and builders, the analyst cannot always assume a completely dehydrated residue remains in the flask but he must take into account the actual salt present and the state of its dehydration in respect to the distillation medium. Also, another matter of analytical interest is that upon knowing the degree of dehydration obtainable with a selected distillation medium, it is possible to determine the original state of hydration of many normally hydrated crystals that have lost a portion of their water of crystallization through drying. The process has been shown to be applicable to salts of both inorganic and organic acids.

BIBLIOGRAPHY

- (1) Dean and Stark, ft. Ind. Eng. Ghem. *10,* 598 (1918). (2) Pritzker and Jungkunz, Chem. Ztg. *50,* 962-3 (1926). (3) R. B. Trusler, Oil and Soap *16,* 239-241 (1939).
-

Detersive Efficiency of Tetrasodium Pyrophosphate – Part II

J. c. HARRIS, J. R. ECK and W. W. COBBS* Central Research Department, Monsanto Chemical Company, Dayton, Ohio

(Continuation of Part I, published January, 1940)

The tentative conclusions for Part I were that tetrasodium pyrophosphate possessed the following advantages :

- 1) Ability to increase suds.
- 2) Ability to increase detergency.
- 3) Ability to increase the amount of builder without diminishing the cleaning efficiency of the soap.
- 4) Low pH for use in household soaps.

It was indicated then, that final conclusions as to its value when combined with other builders would have to await completion of experiments with ternary combinations. It may be said at once that this work in no way alters the conclusions which were then drawn.

The purpose of this paper is four-fold:

- 1) To present concentration vs. efficiency curves for ternary combinations of alkaline builders.
- 2) To discuss more fully the wash test method and the accuracy of the data presented.
- 3) To suggest means for the practical utilization of the data.
- 4) To present a recapitulation of general conclusions.

Concentration vs. Efficiency Curves for Ternary Combinations of Builders

Since results with binary mixtures of builders varied more or less directly with the proportions of the builders present in the combination (and their individual effeetivenesses), it was decided that ternary combinations would be tested in a 1:1:1 ratio, thus reducing the specific effect of any one builder in the combination.

It became evident that the results with the ternary mixtures were indeed dependent upon the ratios of the builders present, hence the total number tested were limited. The individual builders in these combinations were chosen as representative of those finding greatest commercial usage.

Group 17) Soda Ash—1:3.3 Silicate—TSPP

- 18) Soda Ash-1:3.3 Silicate-TSP
- 19) Soda Ash--Metasilicate--TSPP
- 20) Soda Ash—Metasilicate—TSP
- 21) TSPP TSP--1:3.3 Silicate.

A comparison of Groups 17 and 18 indicated no essential differences other than that in hard water the combination containing TSPP was an improvement at 0.37% concentration, while that containing TSP was superior at 0.32%.

The substitution of metasilicate for 3.3 silicate (Groups 19 and 20) results in a general improvement in detergency. This tendency has already been noted for the more alkaline silicate. Wherever high pH values can be tolerated such combinations should prove useful. A strict comparison between TSPP and TSP in these combinations shows an advantage for TSPP when used in these combinations at 0.27% and 0.37% in hard water, while TSP used similarly is superior at 0.32% in hard water. In soft water TSPP produces greater detergency at 0.10% while TSP is superior at 0.15% . No material difference was discernible at 0.20% concentration. It should be noted here that the pH values for the carbonate-metasilicate-TSP combination are extremely high, and since no sodium-ion correction for the glass electrode was made, these values should probably be even greater than shown. The apparently anomalous condition in which the higher concentrations produce less detergency than the intermediate solution concentrations may be attributed to the effect of the highly alkaline salts upon the soap, which results in lower surface activity of the soap-builder combinations.

Comparison of Group 21 with Groups 17 and 18 shows that TSPP and TSP very definitely tend to increase detersive efficiency, and that both are superior in this respect to sodium carbonate which they replace in this comparison.

It should be noted that the TSPP-TSP-3.3 silicate combination was the best of the five tested. However, the detergency produced by this ternary combination is no greater than that produced by the best of the binary mixtures tested.

It is possible that variation of the $1:1:1$ ratio might have achieved slightly different results, but it is doubtful that any marked increase in detergency would have been produced.

The main advantages of the use of ternary combinations would appear to lie in ability to control characteristics such as appearance, alkalinity, pH values and cost.

Wash Test Method

The details of the conditions under which the tests were made follow:

- Standard Soil--Oildag 30g; Wesson oil 7.5g; Carbon Tetrachloride 1800 ml.
- Applicator--Mechanical, comprising a box containing the soil solution, wringer rolls and dryer tube.
- Fabric-Indian Head, 54 x 46 thread count.
- Soap--A nationally merchandised neutral, medium titer soda soap.
- Fabric-Solution Ratio: 1:29.
- Number of replicate swatches--2.
- Artificial hard water-of calcium chloride and magnesium sulfate such that 60% of the hardness is Ca and the balance Mg, as parts per million CaCOa.
- Number of washes-4.
- Duration of wash--10 minutes.
- Volume of wash solution--100 m]. discarded after each wash. Temperature of wash- -140 ± 2 °F.
- Number of rinses--two of water hardness in use.
- Washing apparatus-Standard Launderometer.
- Number of rubber balls used--10.
- Speed of rotation of Launderometer--40 \pm 2 RPM.
- Lather--estimated at second wash. Cannot be greater than 4 inches.
- pH values-determined with wash solutions, using $L & N$ glass electrode.
- Photometer--Lange photoelectric.

The Lange photoelectric photometer was used to measure the degree of soil removal. White, unsoiled but desized Indian Head fabric was used as 100% white (maximum whiteness attainable) and the standard soil used in the particular test was used as 0% white or 100% black, on this basis, soil removed during the washing operation was measurable as direct percentage soil removal.

Concentrations of solutions were so chosen that one point would definitely lie below the optimum washing value, another at approximately the optimum value, and the other at or above this point. In general, the efficiency-concentration curve for a soap combination will level off when the optimum concentration has been reached, and in the presence of relatively large proportions of strongly caustic builders, increasing solution concentration may actually reduce the soil removal.

The method for reducing the test results to a single significant figure was as follows: The wash test results for each of the duplicate 10-minute washes were averaged, and an average calculated from these four. This corresponds to a percentage soil removal value based upon the following equation:

% Soil Removal =
$$
\frac{a+b+c+d}{4}
$$

All the foregoing curves were based upon the average of not less than two complete series of wash tests. For example, duplicate 100% soap tests at 0.10% concentration to be used with the soap-ternary builder combination, soda ash-1:3.3 silicate-TSP were as follows:

The averages for the two series were then averaged to yield 34% soil removal.

The *"standardized"* average percentage soil removal for 100% soap at 0.10% concentration was 39% (see curves). This figure is an arithmetical average of the first eight to ten series tested, and was adopted for subsequent use because a permanent series of curves had already been drawn. Consequently, to correct the curve in question (i.e., the averages for the pure soap Replicates A and B above of 34%) 5% was added to the soap value and to each of the values for the soap-builder mixtures at 0.10% concentration. This same mechanism was used for the other curves since variation in the standard soil will tend to produce differences which vary from the average, but which can thus be reduced to a common figure. In effect, this resulted in raising the whole curve by 5% without changing its shape. It was realized that this procedure was arbitrary and subject to question, since increasing proportions of builder, with reduced amounts of soap (70-30 and 60-40 soap--builder combinations) might not tend to maintain the same high percentage of soil removal. Despite this possibility, and because of the lack of any known factor for its correction, this arbitrary means of expression was adopted, as it appeared to offer the best solution to the problem. The foregoing has no relation to standard error, as indicated above, and has no effect upon the actual experimental variation of a series of results for any given combination.

Since soap was evaluated in each and every series of replicates as a means of control, this accumulation of data was available for statistical analysis (Skinkle, Am. Dyestuff Reporter 26, 528 [1937]). With a Am. Dyestuff Reporter 26, 528 [1937]). series of at least 133 individual tests the following results were obtained:

STANDARD ERROR Solution Concentration

Soft Water			Hard Water		
0.10%	0.15%	0.20%	0.27%	0.32%	0.37%
0.71	በ 67	0.63	0.63	0.57	0.68

The rule states that if the actual difference between two results is greater than twice the standard error, there is an actual difference between the two samples. The maximum standard error above is 0.71, which when doubled is 1.4. This would then mean that a comparison between points on two sets of curves could be obtained, and that if the actual difference between two compositions were greater than].4% soil removal, there would be an actual difference in the relative scouring qualities of the compositions.

As a further check upon the variation of the method a number of replicates were tested simultaneously. This series of experiments Was made in sextuplicate with pure soap at 0.15% and 0.20% concentration in soft water and at 0.32% and 0.37% in hard water. Statistical analysis showed an average (average of the four standard errors) standard error of 1.3% as percentage soil removal for these four tests. The magnitude of this standard error is small considering the fact that it is based upon six replicates. Incidentally, this figure is approximately double 0.71%, the standard error for the large series of tests.

With this statistical information as a basis it is possible to evaluate more exactly the detersive efficiency vs. concentration curves. To double the standard error of the large series of tests would mean that any difference greater than 1.4% would be an actual difference, while doubling the 1.3% of the tests run in sextuplicate would mean that any difference greater than 2.6% would be real. Knowing these limits, and desiring to be highly conservative in our comparisons, we considered differences as real only when they were in excess of six times the standard error of the large series of tests, i.e., 6×0.71 or 4.3%. We preferred to err in this direction, particularly as a difference of approximately this magnitude is required before a marked variation in detergency is visually observable.

Practical Utilization of Curves

Some investigators prefer to plot a rather different type of detergent efficiency curve by determining the point at which no increase in soil removal results when increasing amounts of detergent are used. Such curves have been prepared, and are represented by Figs. 5 and 7 of Group 22. The points on these curves represent the actual percentage of soap concentration,, plotted against average percentage soil removal. For example, the 100-0 curve of Fig. 5 shows the average percentage soil removal at 0.10% ,

 0.15% and 0.20% soap concentrations. In like manner the 90-10 curve (90% soap, 10% builder) shows the soil removal versus the actual soap concentration of the solution, i.e., at 0.10% there is actually 0.09% soap present, etc. It will be noted that these curves tend to flatten out at a soap concentration of 0.20%. It will be further noted, with the exception of the 60-40 combination, that maximum detergency is attained at approximately 65% soil removal. Fig. 7 represents this same type of curve for hard water combinations. In this case the effectiveness of TSPP addition is shown by the relatively rapid rise of the curves to a maximum. It will further be noted that when the 100-0 curve is extended, the maximum soil removal at 0.37% concentration is 57.5%. The results for soap plus sodium carbonate plotted in this manner are shown in Figs. 23 and 24 (Group 22).

The concentration vs. efficiency curves present the relative efficiencies of the mixtures, but to permit the use of the data in a more practical manner the units of soap and builder required to produce a satisfactory minimum of detergency were plotted. In Fig. 9 (Group 23) are shown curves for 57.5% and 65% soil removal. The former percentage was adopted since this could be produced in either soft or hard water. The 80-20 point of Fig. 9 indicates that 57.5% soil removal can be attained with 72 pounds of soap and 18 pounds of builder (TSPP). The material balance for the removal of this quantity of soil is then 90 pounds, in a ratio of 72 pounds soap to 18 pounds TSPP; that is 80-20. Furthermore, this combination will be equilavent to 100 pounds of soap in soil removal value.

The calculations which follow are a further example of the manner in which these curves may be used :

Required: The comparative cost for 57.5% soil removal in hard water, utilizing 70% soap and 30% builder, the builder comprising either TSPP alone, or a 25:75 mixture of TSPP: soda ash.

Calculations: The following costs (anhydrous basis) are assumed :

1:3.3 Silicate $(37.6\%$ solids to	

Refer to Group 23, Fig. 10, and Group 24, Fig. 98, from which the following data are taken:

In other words, to obtain the same degree of soil removal, it would be considerably more economical to use the combination containing TSPP and soda ash as builders.

These data may similarly be used to estimate the value of builders in textile scouring operations and for laundering, or to estimate the comparative value of soap products offered to the household trade.

A few generalizations with regard to this entire group of curves will aid in their usage. In general, the closer the curve approaches the diagonal, the more nearly are equal quantities of soap and builder required. Conversely, the closer the curve approximates the vertical, the more effective the builder, hence a lesser amount is required. Observation of the detergent efficiency-concentration curves will indicate the combinations which produce the maximum amount of soil removal. With these combinations in mind, the unit detergency curves may be consulted to determine the amounts of soap and builder to produce a given unit of detergency, and finally the determination of percentage composition of the combination which will produce such results. These curves reduce the combinations to a common basis for comparison, and may be used for comparing amounts of materials required for scouring operations.

The data which have been presented may be used in a variety of different ways:

- a) The most effective combinations of soap and builder may be ascertained by study of the individual concentration vs. efficiency curves.
- b) Calculation and plotting of the detergency of soap-builder curves as in Figs. 5, 7, 23 and 24 (Group 22) will indicate by the relative slopes, the concentrations of soap required to produce suitable detergency.
- c) Use of the unit detergency curves may be made in calculation of the cost of various soapbuilder mixtures, referring to the concentration vs. efficiency curves as a guide to maximum detergency.
- d) Reference may be made to the unit detergency curves when the relative cost of a detergent or detersive operation is under consideration.

Recapitulation

A recapitulation of the results of these wash tests follows :

SOAP AND SINGLE BUILDERS

There was a wide distribution of effective compounds in the soft water tests and no particular one stood out as most effective in all three solution concentrations. In hard water, TSPP, TSP and metasilicate appeared best in at least two of the three concentrations tested. Of these only TSPP produces mixtures possessing moderate pH values.

The silicates, in order of decreasing efficiency are respectively: metasilicate, $1:2$ silicate, and $1:3.3$ silicate.

SOAP AND BINARY BUILDER MIXTURES

TSPP--Silicates--Optimum soil removal was obtained when the proportion of TSPP was greater than that of the other component. The greater the proportion of 1:3.3 silicate added to TSPP, the greater the reduction in washing efficiency over TSPP alone. *All* such combinations, however, are improvements over the silicate alone. There is also a tendency toward improvement in cleansing action of such combinations over TSPP alone at the higher builder ratios, i.e., 70-30 and 60-40 soap-builder combinations. Metasilicate or 1:2 silicate combined with TSPP produce washing results superior to either component alone. In considering combinations for household soaps, only the 1:2 and 1:3.3 silicates would be useful (unless the $90-10$ soap-builder combination could be considered), due to the high pH values produced when metasilicate is used.

TSP-- Silicates-- In soft water the 2:1 ratio of $TSP \rightarrow 1:3.3$ silicate produced maximum effectiveness and the combinations were all more effective than the single components. In hard water there were no pronounced differences. The efficiency of TSP is lowered by the addition of 1:3.3 silicate in proportion to the amount of this silicate added. Those combinations containing metasilicate in general were improvements over TSP alone, but were practically identical with metasilicate alone: In general, the pH values for the TSP-metasilicate combinations were high, as were those for the 2:1 ratio of TSP-I:3.3 silicate at 70-30 and 60-40 soap-builder mixtures.

Pho.sphates--Soda Ash--In soft water there were no major differences between Soda Ash-TSPP and Soda Ash-TSP except at 0.1%. At the 2:1 ratio TSP was superior while at 1:2 TSPP was superior. In hard water TSPP produces results markedly superior to TSP either at the $2:1$ or $1:2$ ratios. The pH values for the TSPP combinations even at the higher soda ash contents are not greater than 10.6 with 70-30 soap-builder mixture.

SOAP AND TERNARY BUILDER MIXTURES

The ternary builder combinations tested did not result in increased detergency over the best binary mixtures investigated. Different effects might have been produced by varying the ratio from the 1:1:1 proportion investigated.

GROUP₁₇

FIG. 172. Concentration vs. efficiency of combinations of soap with $1:1:1$ ratio of sodium carbonate, $1:3.3$ silicate and T.S.P.P. 50 P.P.M. soft water.

FIG. 173. Concentration vs. efficiency of combinations of soap with 1:1:1 ratio of sodium carbonate, 1:3.3 silicate and T.S.P.P., 300 P.P.M. hard water.

GROUP 18

FIG. 176. Concentration vs. efficiency of combinations of soap with 1:1:1 ratio of sodium carbonate, 1:3.3 silicate and T.S.P. 300 P.P.M. hard water.

GROUP 19

FIG. 184. Concentration vs. efficiency of combinations of soap with 1:1:1 ratio of sodium carbonate, meta silicate and T.S.P.P. 50 P.P.M. soft water.

FIG. 185. Concentration vs. efficiency of combinations of soap with 1:1:1 ratio of sodium carbonate, meta silicate and T.S.P.P. 300 P.P.M. hard water.

GROUP 20

FIG. 187. Concentration vs. efficiency of combinations
of soap with 1:1:1 ratio of sodium carbonate, meta sili-
cate and T.S.P. 50 P.P.M. soft water.

FIG. 188. Concentration vs. efficiency of combinations
of soap with 1:1:1 ratio of sodium carbonate, meta sili-
cate and T.S.P. 300 P.P.M. hard water.

FIG. 5. Detergency of soap-T.S.P.P. combinations básed on soap con-
centration. 50 P.P.M. soft water.
Fra. 23. Detergency of soap-sodium carbonate combinations based on
soap concentration. 50 P.P.M. soft water.

FIG. 7. Detergency of soap-T.S.P.P. combinations based on soap concentration. 300 P.P.M. hard water.
FIG. 24. Detergency of soap-sodium carbonate combinations based on soap concentration. 300 P.P.M. hard water.

FIG. 97. Unit detergency produced by combinations of soap with FIG. 98. Unit detergency produced by combinations of soap with T.S.P.P. and sodium carbonate. 50 P.P.M. soft water. 57.5% soil T.S.P.P. and sodium carbonate.

	O-75% T.S.P.P.-25% Sodium Carbonate	
	□-50% T.S.P.P.-50% Sodium Carbonate	
	A-25% T.S.P.P.-75% Sodium Carbonate	

FIG. 109. Unit detergency produced by combinations of soap with T.S.P.P. and "N" silicate. 300 P.P.M. hard water. 57.5% soil removal. with T.S.P.P. and "N" silicate. 50 P.P.M. soft water. 57.5% with T.S.P.P. and "N" silicate. 300 P.P.M. hard water. 57.5%
soil removal.

 \Box --1 Part T.S.P.P.--2 Parts 1:2 Silicate

FIG. 123. Unit detergency produced by combinations of soap with T.S.- P,P. and 1:2 silicate. 300 P.P.M. hard water. 57.5% soil removal. C) --2 Parts T.S.P,P.--1 Part 1:2 Silicate

[] --1 Part T.S.P.P.--2 Parts 1:2 Silicate

GROUP 26

 57.5% soil removal. 57.5% soil removal.

FIG. 199. Unit detergency produced by combinations of soap FIG. 195. Unit detergency produced by combinations of soap
with 1:1:1 ratio of sodium carbonate, meta silicate and T.S.P. with 1:1:1 ratio of T.S.P.P., T.S.P., an 57.5% soil removal, soil removal,

FIG. 174. Unit detergency produced by combinations of soap FIG. 186. Unit detergency produced by combinations of soap
with 1:1:1 ratio of sodium carbonate, 1:3.3 silicate and T.S.P.P. with 1:1:1 ratio of sodium carbonate,

 Q --50 P.P.M. Soft Water

IT] --300 P.P.M. Hard W~ier