spectively. It is to be expected that the operator must learn to boil soap by this method in exactly the same sense that a man learns to boil soap in a kettle on the large scale, with this important exception in favor of the laboratory operation: it is possible to see what is taking place through the glass apparatus, while on the large scale the operator depends upon observation of the soap on a trowel.

On the other hand it must be remembered that the large-scale operation is capable of finer manipulation through the use of closed steam coils for which our boiling water bath is in no way a substitute.

Nevertheless, the laboratory method is a useful device capable of providing a reliable answer to many chemical problems connected with the making of soap. Where larger quantities of soap are required for further processing, we use a battery of three steel kettles of 50 gallon capacity each, which we hope to describe in a later paper.

Acknowledgment

We wish to acknowledge our indebtedness to members of the technical staff of the Procter and Gamble Company for helpful suggestions which led us to the particular adaptation and procedure described herein.

Detersive Efficiency of Tetrasodium Pyrophosphate - Part I

W. W. COBBS, J. C. HARRIS, & J. R. ECK
THOMAS AND HOCHWALT LABORATORIES DIVISION, MONSANTO CHEMICAL COMPANY
DAYTON, OHIO

THE data in this paper are the result of an intensive laboratory program to determine the value of tetrasodium pyrophosphate as a soap builder, with particular reference to its use in household built soaps. It was felt that the first step in the program was to determine the effect of single builders with soap in order to obtain data on the specific action of each alkali. For this reason a series of tests were run in which soap was combined with only one builder. The list of alkalies include tetrasodium pyrophosphate, 1:3.3 silicate, 1:2 silicate, metasilicate, trisodium phosphate, disodium phosphate, soda ash and borax.

Since most built soaps contain a mixture of two or more builders, the program was extended to include both binary and ternary combinations of alkalies. To date, however, only the single and binary combinations have been completed. It is expected that the ternary combinations will be completed within the next few months and results of these tests could be the subject of a second paper.

During the first series of runs the ratios of soap to builder were 95:5, 90:10, 80:20, 70:30, and 60:40. The 95:5 ratio was dropped soon after the program was under way since the early results showed that this combination seldom showed an appreciable effect on the shapes of the curves. The reason for not increasing the amount of builder above 40% will be apparent from the data since they show that in most cases maximum detergency was almost always reached at higher ratios than 60:40 of soap to builder.

Three concentrations were used for each series of tests, namely, 0.10%, 0.15% and 0.20% in "soft" water (50 ppm hardness) and 0.27%, 0.32% and 0.37% in "hard" water (300 ppm hardness). These points were chosen to represent, first, a decided deficiency in detergent strength, second, a slight deficiency and third, maximum soil removal. Previous tests had shown that the concentrations of detergent in the hard water tests would have to be increased appreciably over the concentrations used in the soft water tests. Hence, concentrations were increased in these tests so as to obtain approximately the same degree of soil removal as in the soft water series.

All builders and soaps are used on the anhydrous basis.

pH values and height of suds were determined for each wash test. These data are recorded on the charts.

Description of Wash Tests

The washing tests will be described but briefly in this paper since Committee D-12 of the A.S.T.M. is now conducting a cooperative program in an effort to set up a standard method for this procedure. Mr. Harris is a member of this committee. A launderometer is used for all tests. The cloth used is Indianhead, a cotton fabric, which has been desized and then soiled with a mixture of Oil-dag and vegetable oil. The test swatches are 6" by 5". The initial swatch is first given a ten minute wash in the detergent solution. After the first wash, a strip representing a quarter of the total is cut off, rinsed, dried, and the soil removal measured. The remainder of the swatch is then washed 10 minutes longer in a fresh detergent bath and another 1½" strip removed. This procedure is repeated until the last strip, representing one-fourth of the original swatch, has been washed for 4 ten minute periods each time in a fresh detergent solution. Each determination was made in duplicate and the results for each series were then repeated. Each point in the curves therefore represents the average value of four determinations.

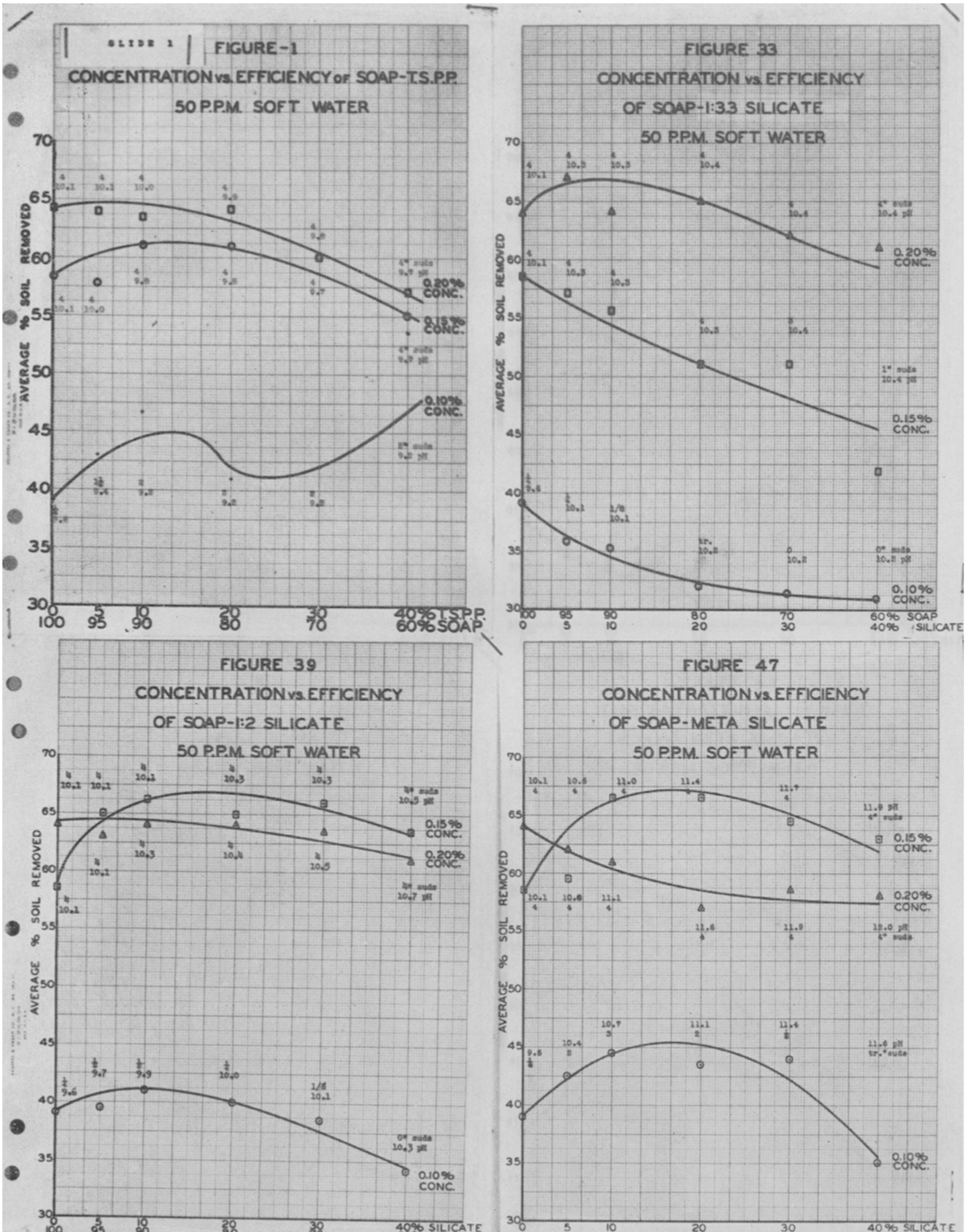
The soil removal is measured by a photoelectric photometer. The results shown in this paper are the average percent soil removal for the four washes.

The temperature used in all cases was 140° F. (±2°)

The soap used throughout the program was a well known medium titre soap. The alkalies used were all industrial grade products.

Curves for tetra sodium pyrophosphate, 1:3.3 silicate, 1:2 silicate and metasilicate in soft water are presented in the first group of graphs. They show that there is little advantage to be obtained from the use of builders in soft water, particularly at the higher concentrations. 1:3.3 silicate is actually detrimental rather than advantageous at the two lowest concentrations. 1:2 silicate and metasilicate give slightly better results at 0.15% than at 0.20%. This is believed to be due to the fact that the high concentration of hydroxyl ions reduces the surface activity through a salting-out effect on the soap.

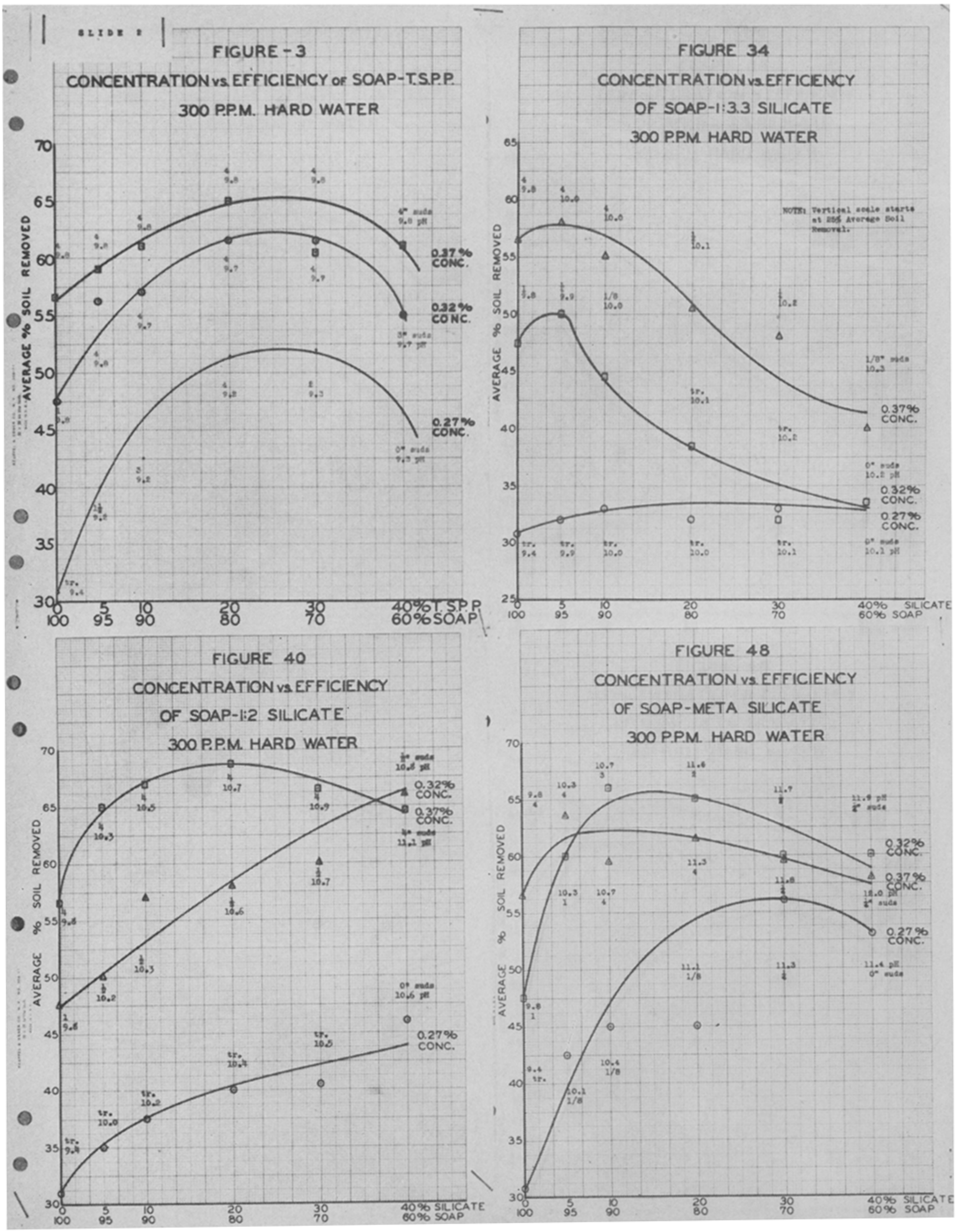
Group No. 2 shows the results of these same materials in hard water. The curves for tetra sodium pyrophosphate indicate that maximum soil removal is obtained when the builder concentration is between 20 to 30%. 1:3.3 silicate shows an adverse effect at all concentrations and the results are believed to be due to a specific lack of water softening activity in the presence of soap. 1:2 silicate, because of increased pH over 1:3.3 silicate gives excellent results. It is noteworthy that at 0.32% concentration the soil re-



Group 1.

moval reaches a maximum with the 60-40 combination and that even at the highest concentration the 60-40 combination is practically equal to that produced by the other combinations. As in the soft water tests, metasilicate exhibits better washing effects at the intermediate concentration than at the highest concentration.

The pH values for tetra sodium pyrophosphate and 1:3.3 silicate are ideal for household types of soaps where the hands must come in contact with the washing solution. The pH's of the 1:2 and metasilicate solutions while satisfactory for commercial laundries are too high for household soaps. The figures for suds show that over the whole range of concentrations,

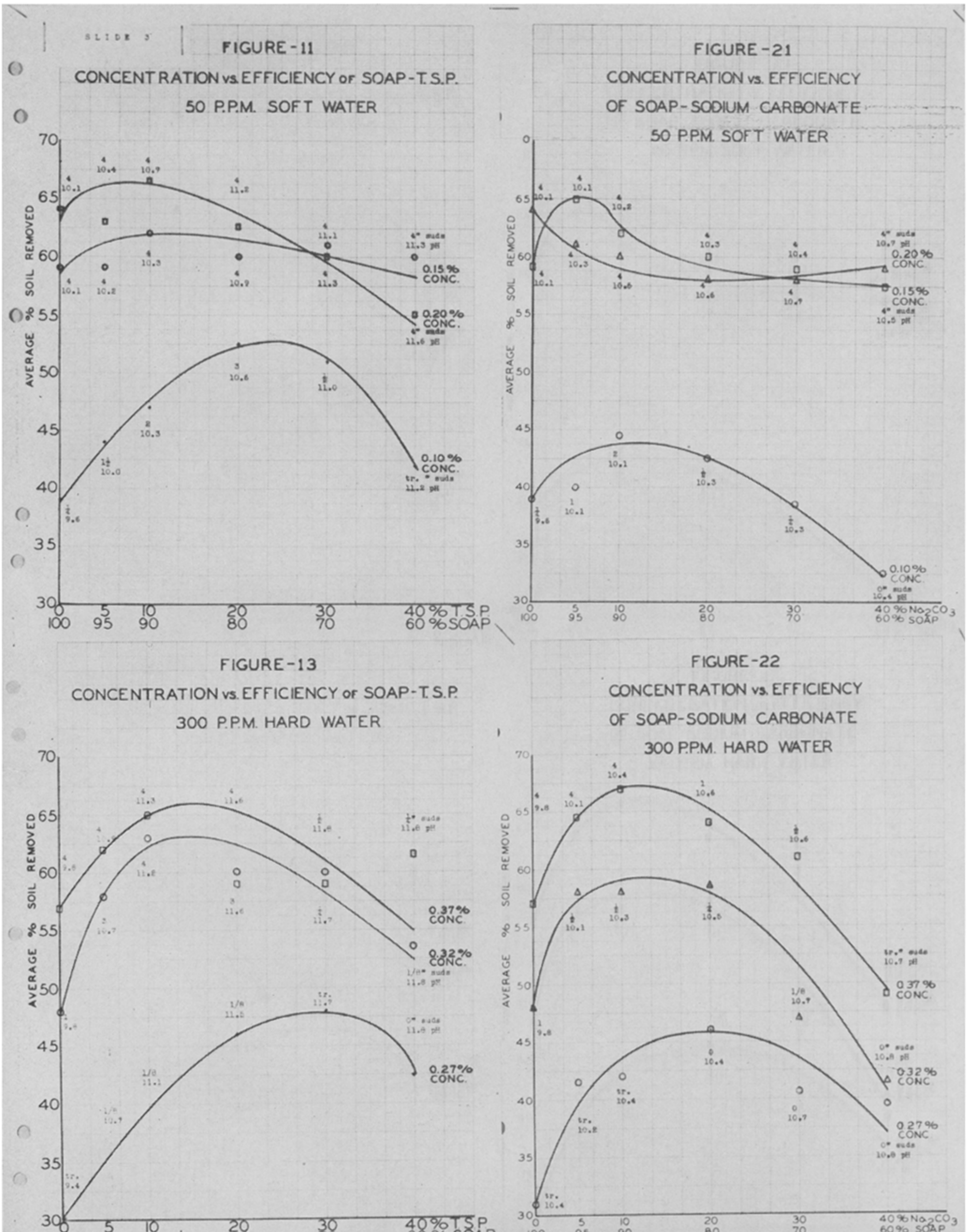


Group 2.

pyrophosphate gives greater lathering effect than any of the silicates.

The results with trisodium phosphate and soda ash in both soft and hard water are set forth in group No. 3. The results of the soft water tests are quite similar to those shown in the first slide, i.e., no particular advantages are obtained. Both of the products show an advantageous effect in hard water. However, tri sodium phosphate reaches maximum detergency when the soap builder strength is between 10 to 20% while with soda ash optimum results are obtained with only 10-15% builder.

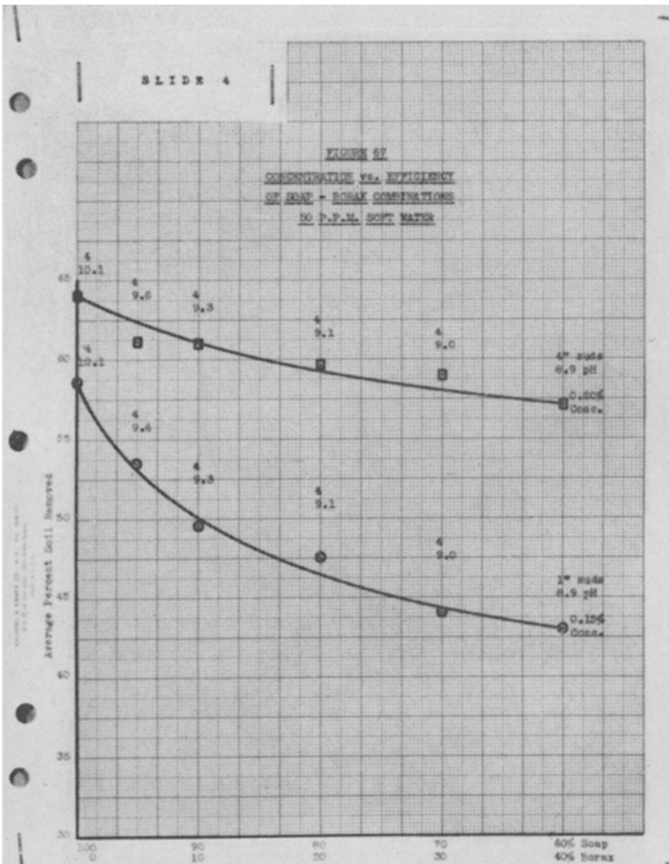
The pH of the trisodium phosphate solutions are all high ranging from 10.4 to 11.8 at the high concentra-

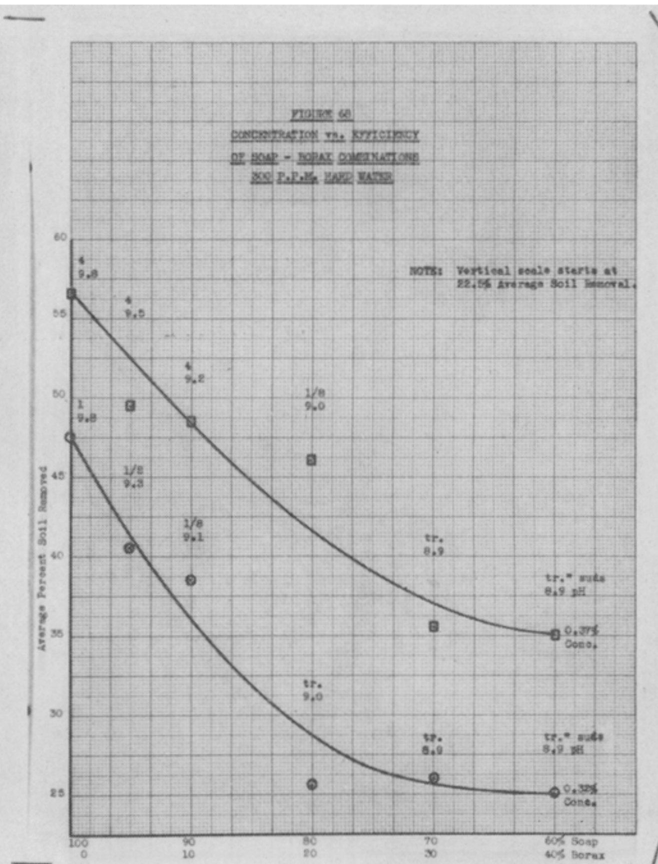


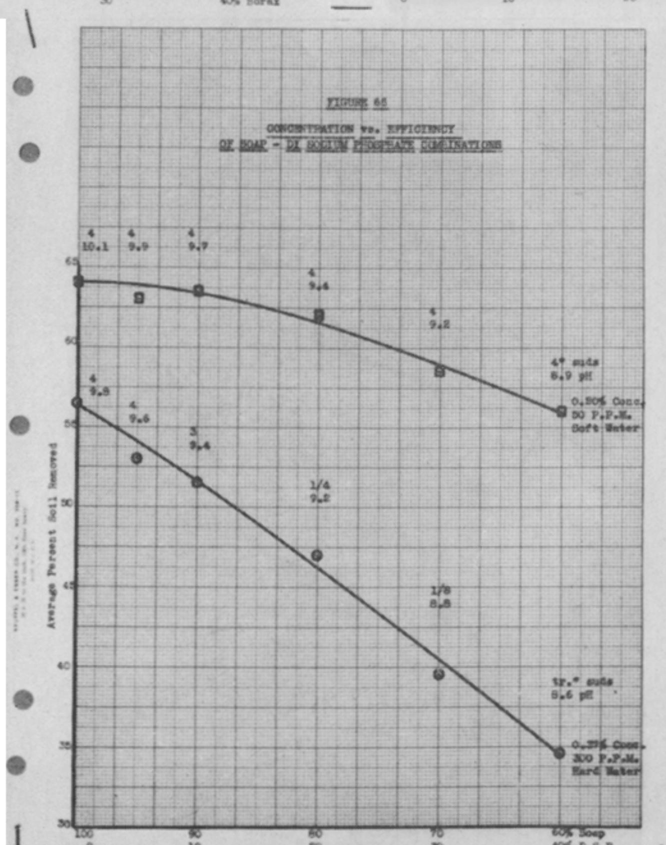
Group 3.

tions. The soda ash curves show that only about 10% of this material can be incorporated in soap if the pH is not to exceed 10.5. Sudsing effect of both of these products in hard water is noticeably less than that of tetra sodium pyrophosphate.

Group No. 4 exhibits the effect of both borax and disodium phosphate. Borax was run at only the intermediate and highest concentrations since previous experience had indicated that this product is not effective as a soap builder because of low pH. For the same reason di sodium phosphate was run at only the highest concentrations. The results show that both of these materials have an adverse effect and that unless they are used in conjunction with stronger alkalies





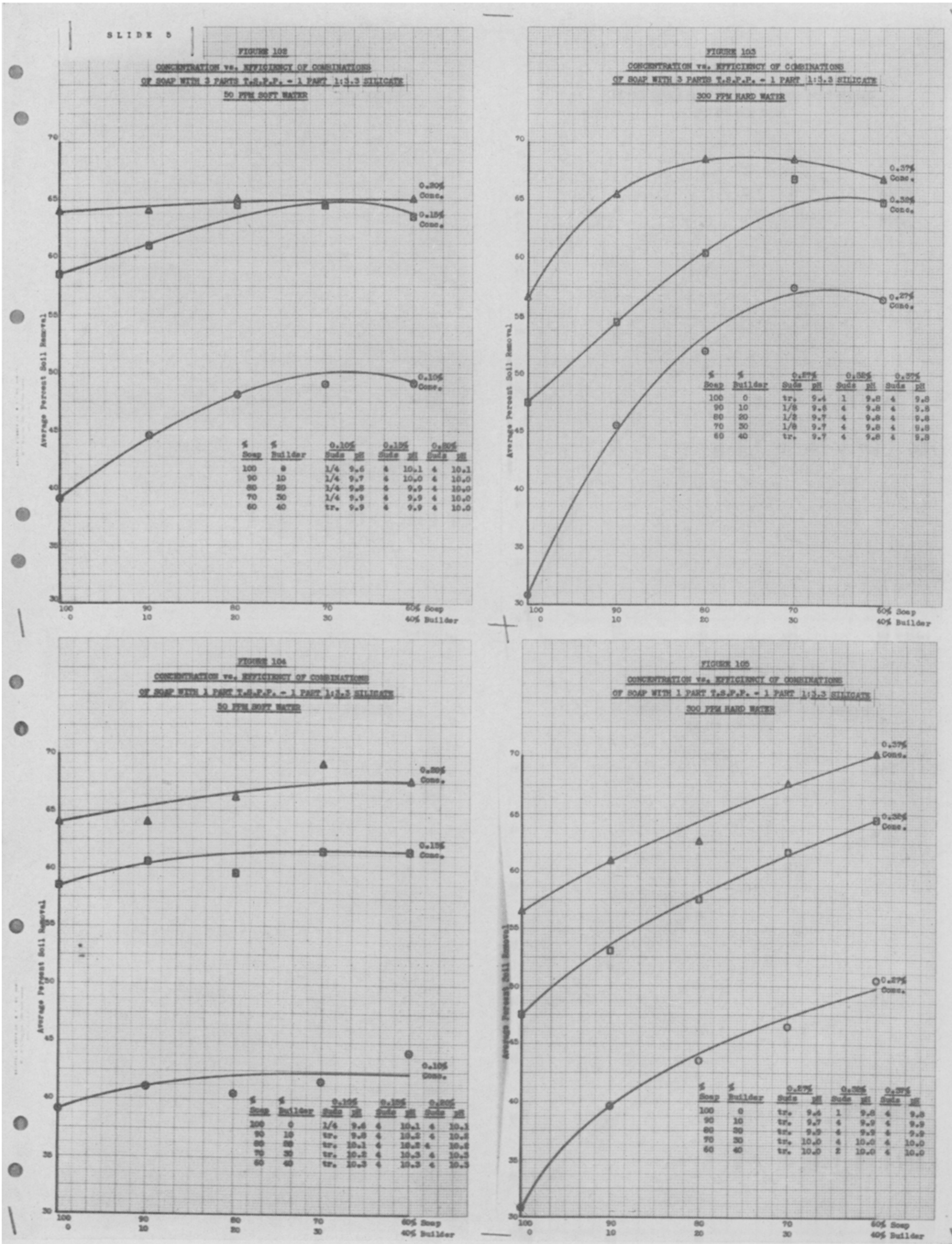


Group 4.

they are detrimental rather than beneficial.

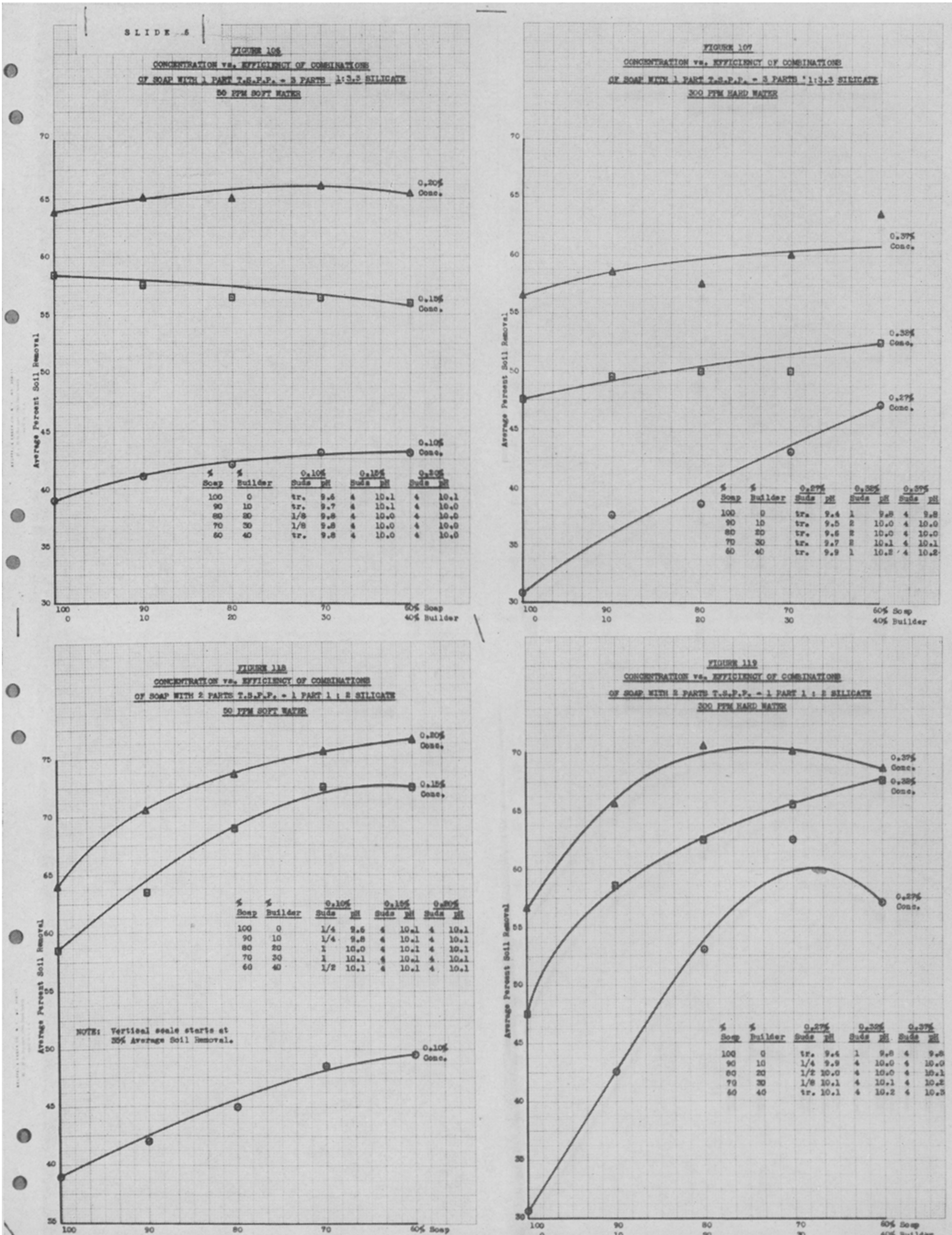
Group No. 5 expresses the results with the first of the binary combinations. At first, this series was run at 3:1, 1:1 and 1:3 ratios of builder A to B, but was later reduced to 1:2 and 2:1 combinations since it was felt that these two combinations gave sufficient information.

The results with tetra sodium pyrophosphate and 1:3.3 silicate are shown in groups No. 5 and No. 6. The curves for both hard and soft water show that the



Group 5.

addition of tetrasodium pyrophosphate to the silicate prevents the adverse effects obtained when silicate is used alone. Also, the results were better than when tetrasodium pyrophosphate was used alone. A notable effect of these combinations is that the maximum washing efficiency is attained when the soap-builder combination approaches the 60:40 ratio whereas straight pyrophosphate showed this effect at about the 75:25 ratio. It should also be noted that when the ratio of silicate to pyrophosphate is increased to 3:1

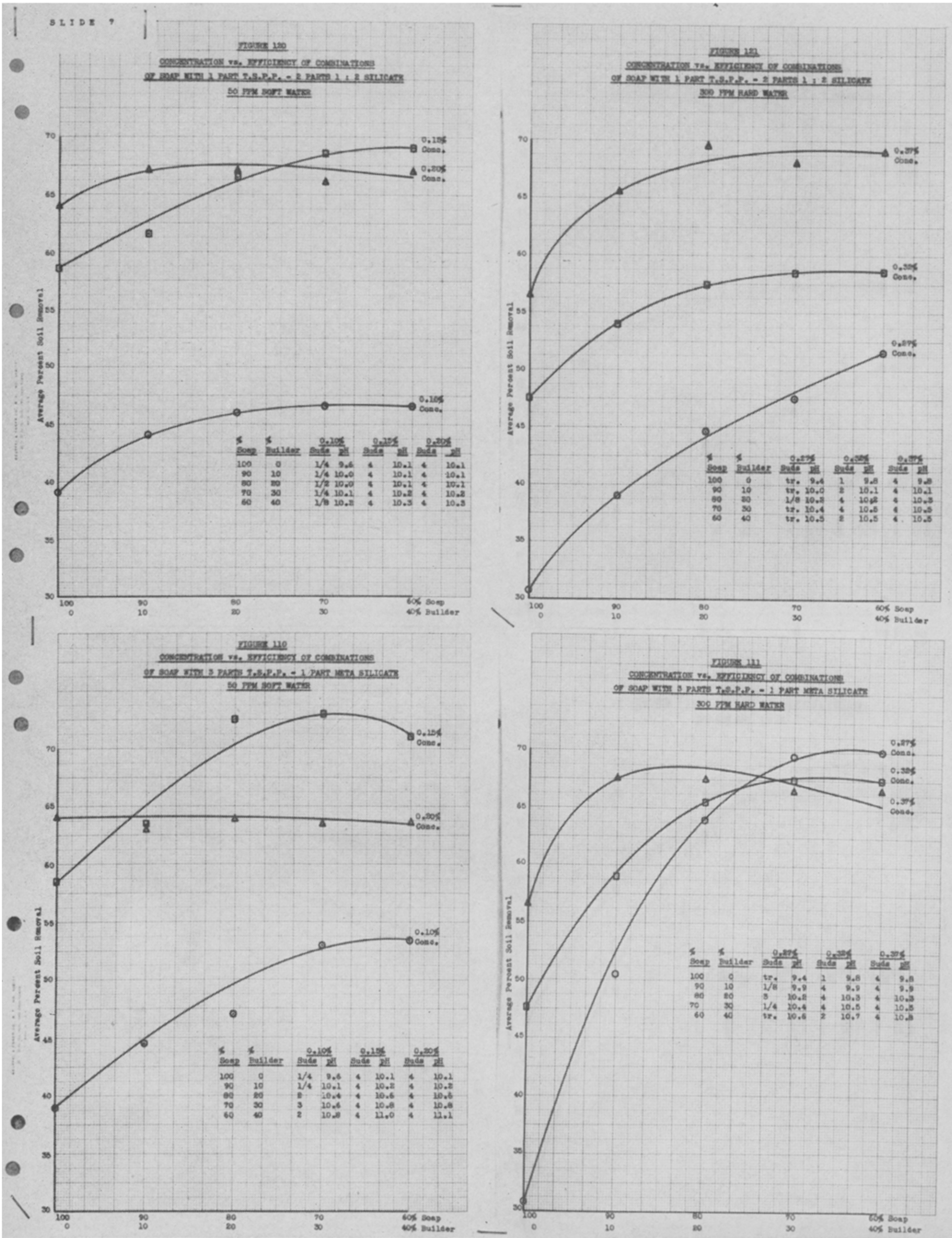


Group 6.

the washing effectiveness decreases.

The pH's of these combinations are ideal for household soaps and the sudsing effect is excellent except for the mixtures containing the largest amounts of silicate in hard water.

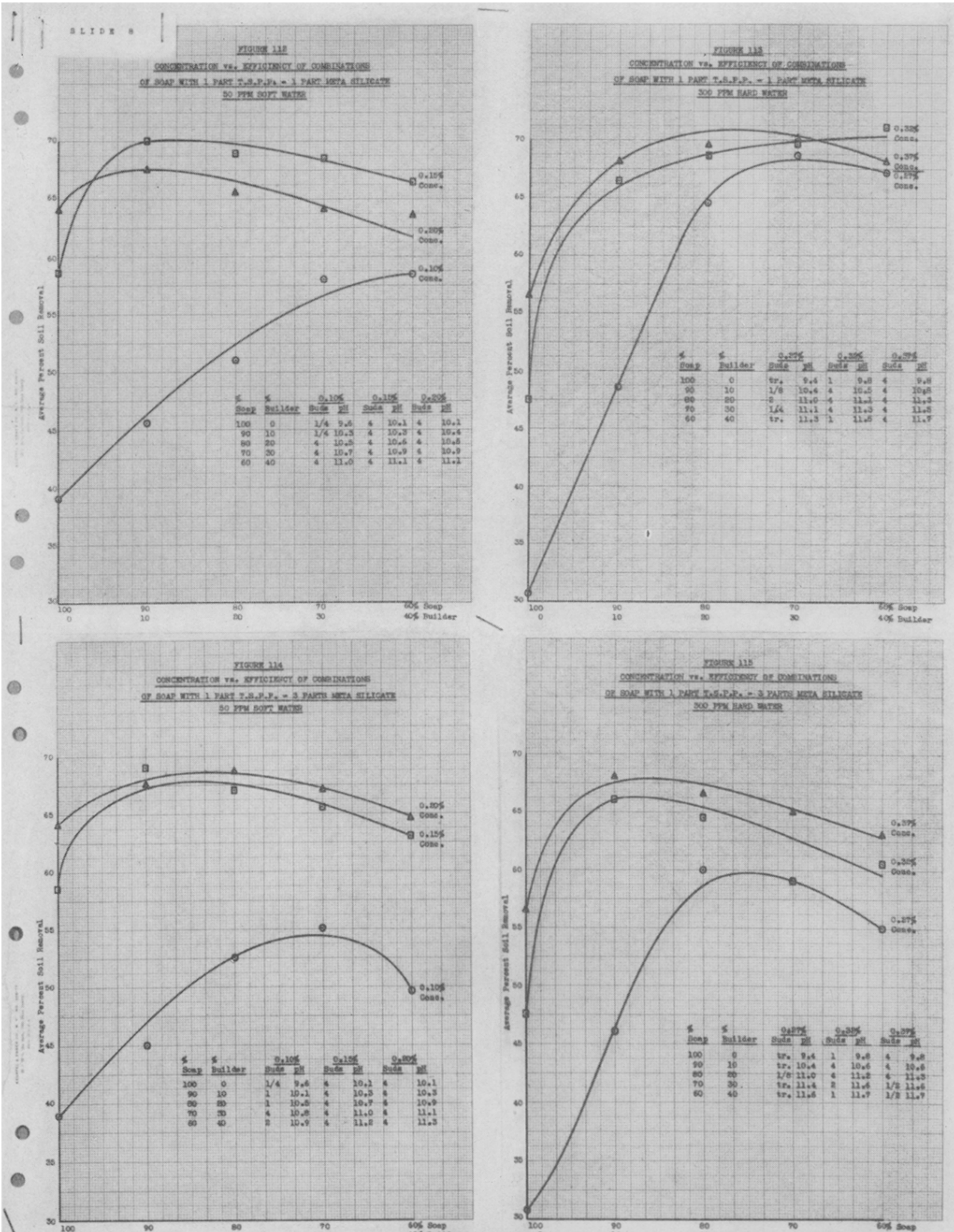
The curves for tetrasodium pyrophosphate and 1:2 silicate are presented in groups No. 6 and No. 7. The results of the soft water tests were unusually high when the pyrophosphate to silicate ratio was 2:1 (it should be noted here that the base line has been



Group 7.

changed from 30 to 35 average percent soil removal). The results in hard water were excellent for both ratios and it is important to note that maximum detergency is reached at proportions of 60:40 ratio of soap to builder. Pyrophosphate acts to modify the alkalinity of the 1:2 silicate, so that even when the ratio of pyrophosphate to silicate is 1:2 the maximum pH attained is only 10:5.

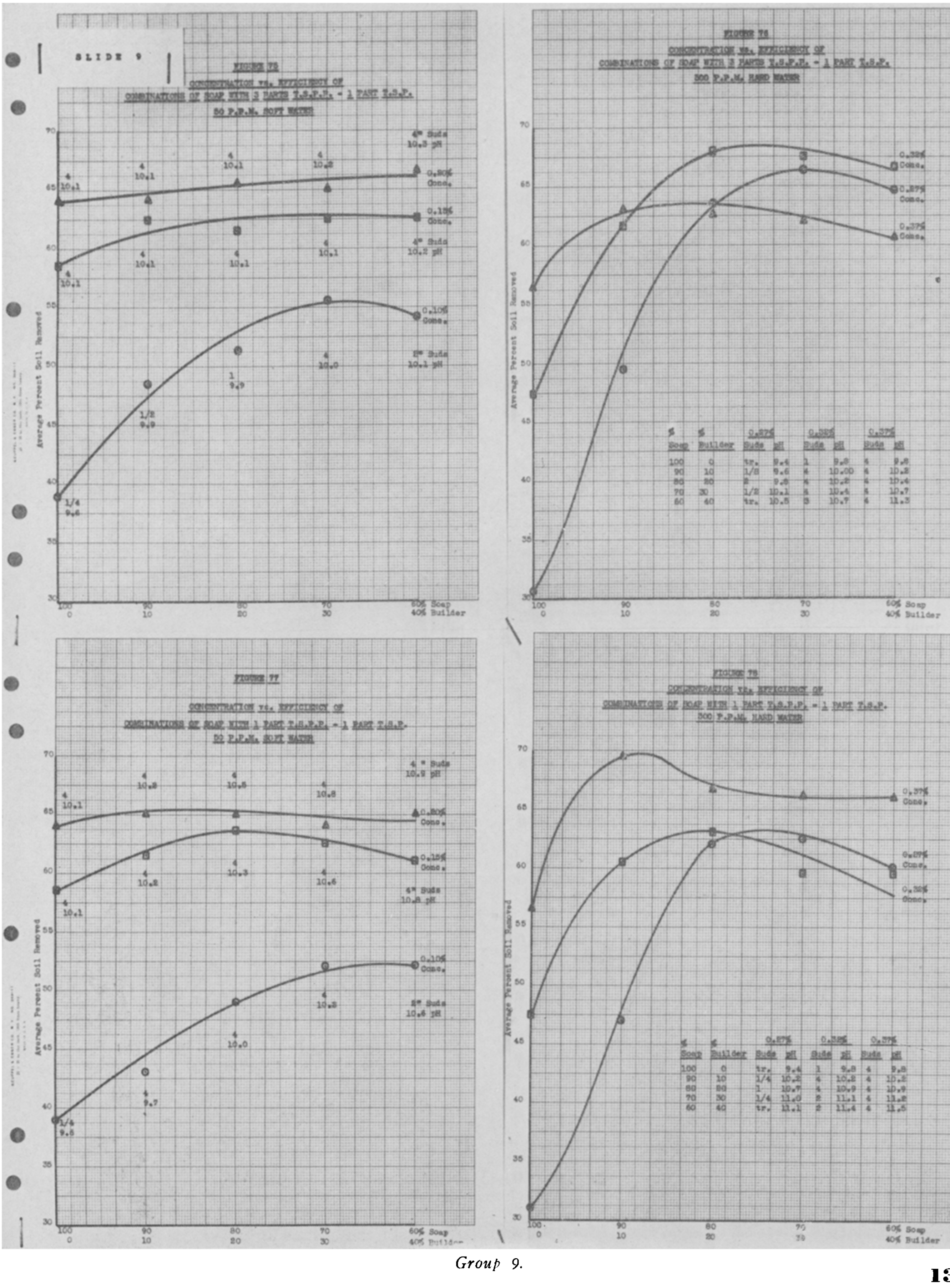
Groups No. 7 and No. 8 express the data for pyrophosphate and meta silicate. These combinations



Group 8.

show an improvement over the pyrophosphate — 1:2 silicate combinations, particularly at the lower concentrations. However, as the ratio of metasilicate to pyrophosphate is increased, the effectiveness of the builder combination decreases toward that of metasilicate alone. The high pH's of these combinations exclude their use for household soaps but not for commercial laundry operations.

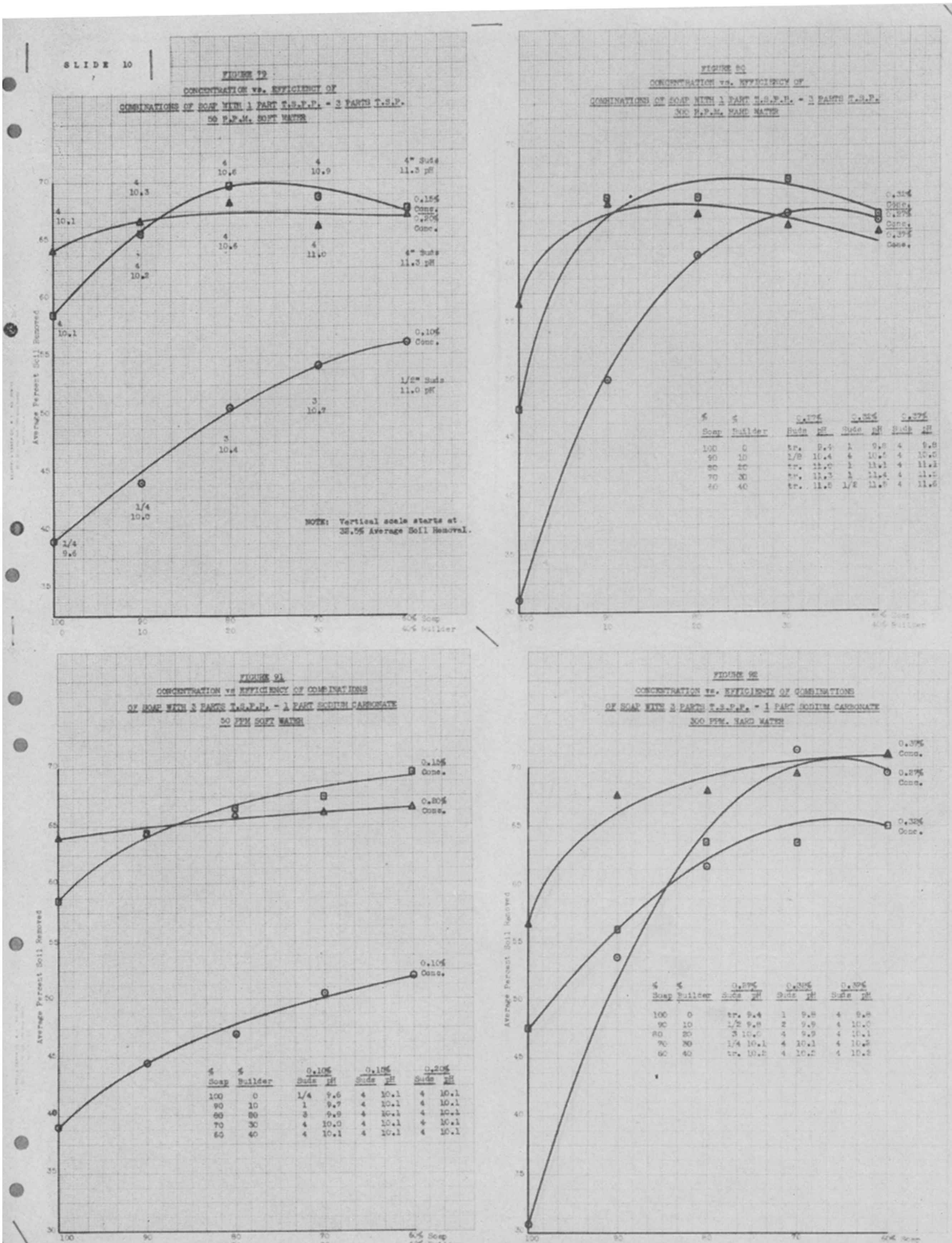
The results with tetrasodium pyrophosphate and trisodium phosphate are shown in groups No. 9 and No. 10. No outstanding results are apparent except



Group 9.

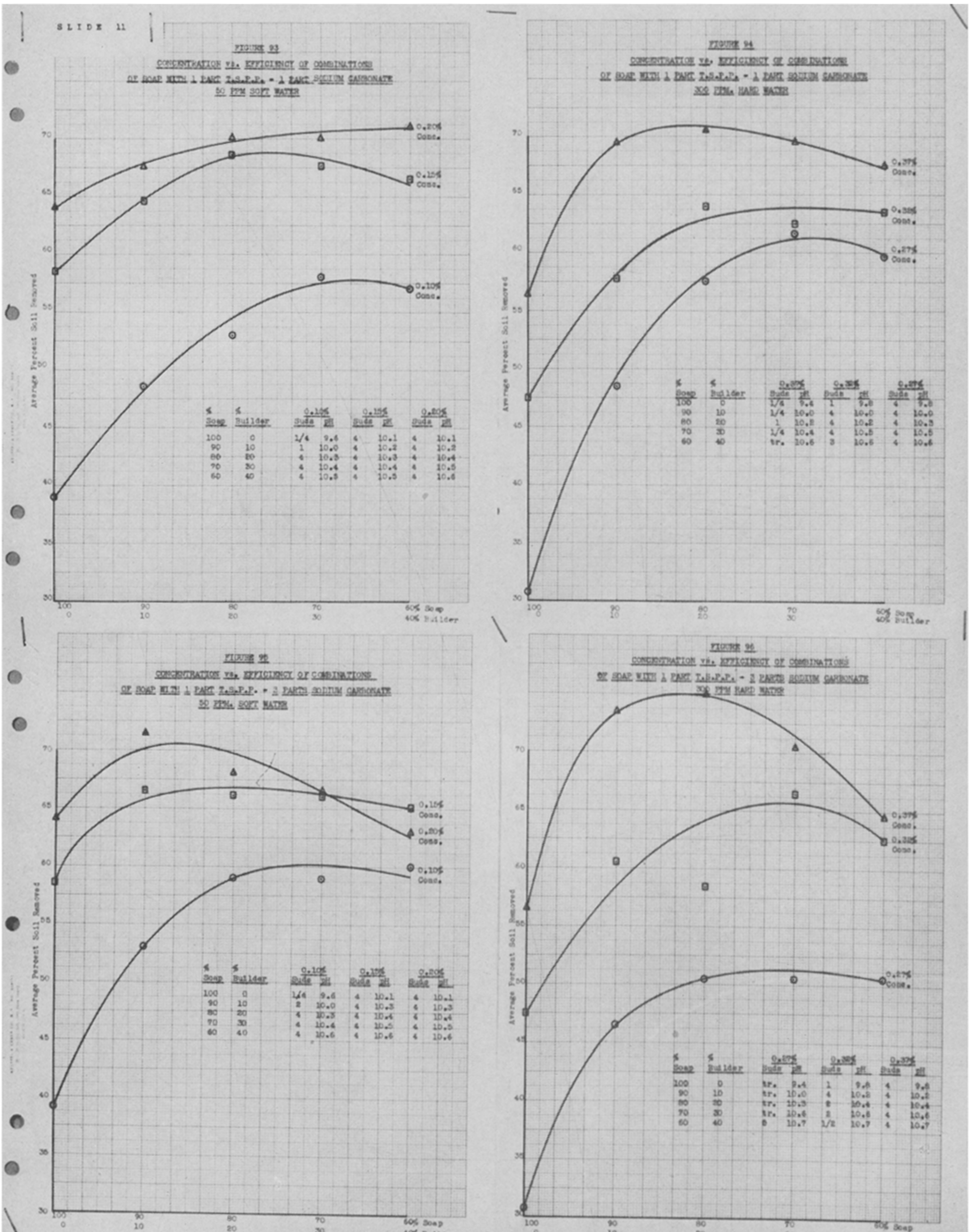
that the lower concentrations in general give excellent soil removal. Pyrophosphate serves to modify the adverse effect of high pH produced by trisodium phosphate, particularly when the ratio of pyrophosphate to trisodium phosphate is 3:1. In general, though, at the high concentrations amounts of builders above 10% give pH's above 10.5. In the hard water tests, the average sudsing effect decreases as the proportion of trisodium phosphate is increased.

Groups No. 10 and No. 11 exhibit the figures for



Group 10.

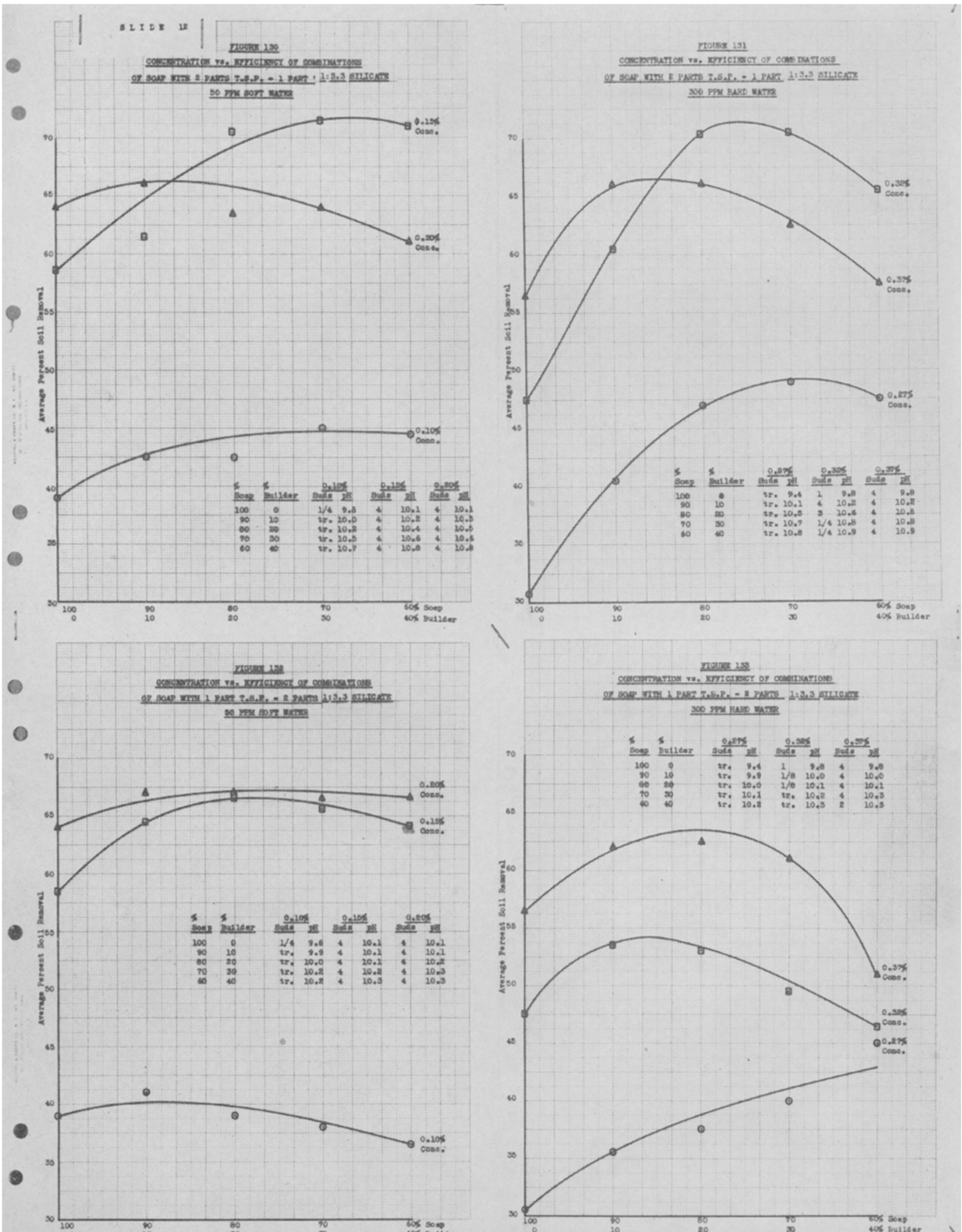
the tetrasodium pyrophosphate — soda ash combinations. A comparison of the results of this series with pyrophosphate — trisodium phosphate mixtures demonstrate that there are no essential differences in detergency produced by such combinations, although exceptionally good results were obtained in hard water at 0.37% concentration with the combination of 1:3 pyrophosphate to soda ash at 20% of the total. The pH values of most of the combinations were satisfactory for household soaps but with large proportions of soda ash at high concentrations the pH tends to become too high.



Group 11.

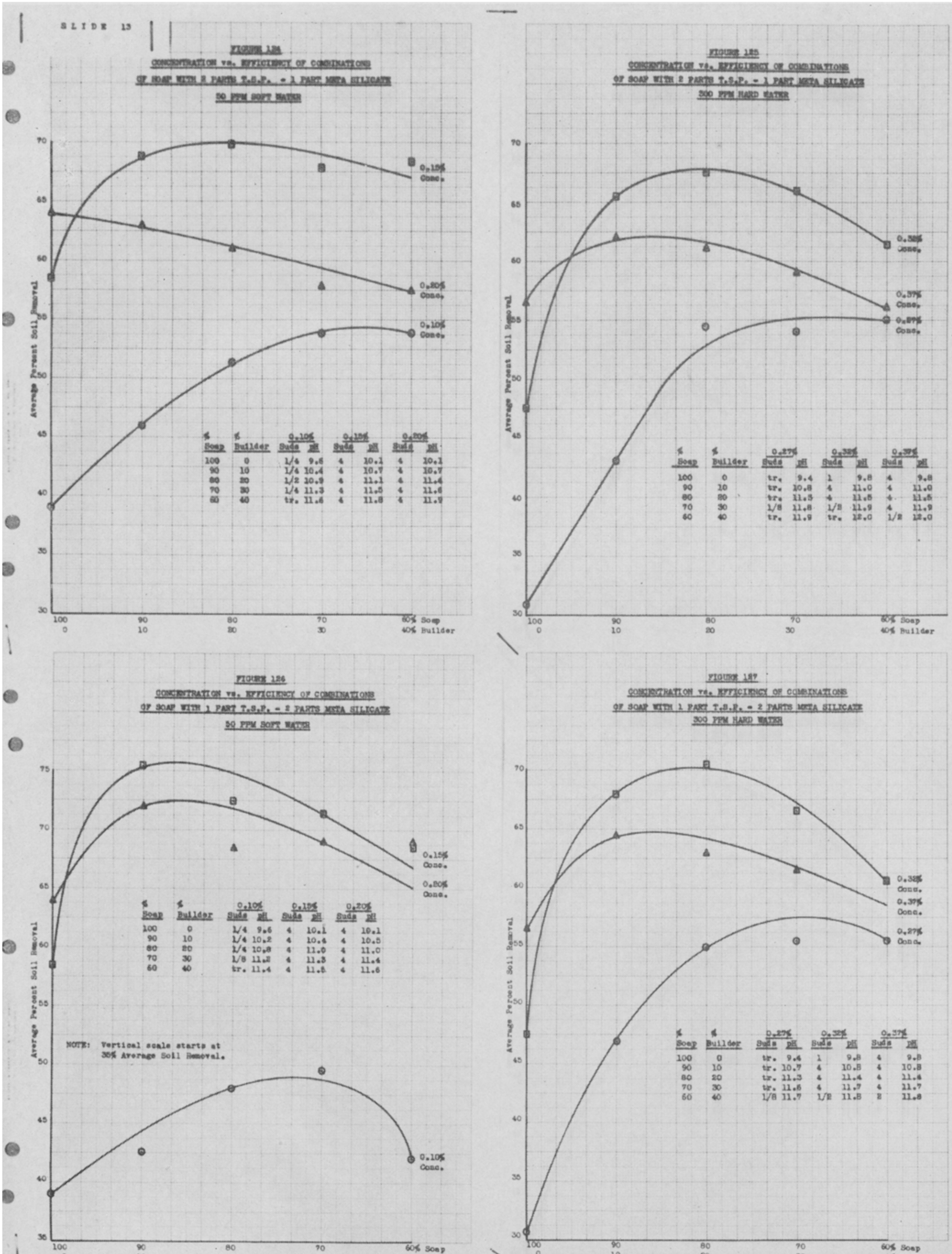
The results with the trisodium phosphate — 1:3.3 silicate are given in group No. 12. A comparison of these results wth those for pyrophosphate — 1:3.3 silicate shows that the pyrophosphate combination maintains greater detergency in the soap containing large proportions of builders. The pH's of the 1:2 trisodium phosphate — 1:3.3 silicate mixtures are satisfactory for household soap but except for the low builder combinations the 2:1 ratios give pH's above 10.5.

Group No. 13 presents the data on trisodium phosphate — metasilicate combinations. In comparison



Group 12.

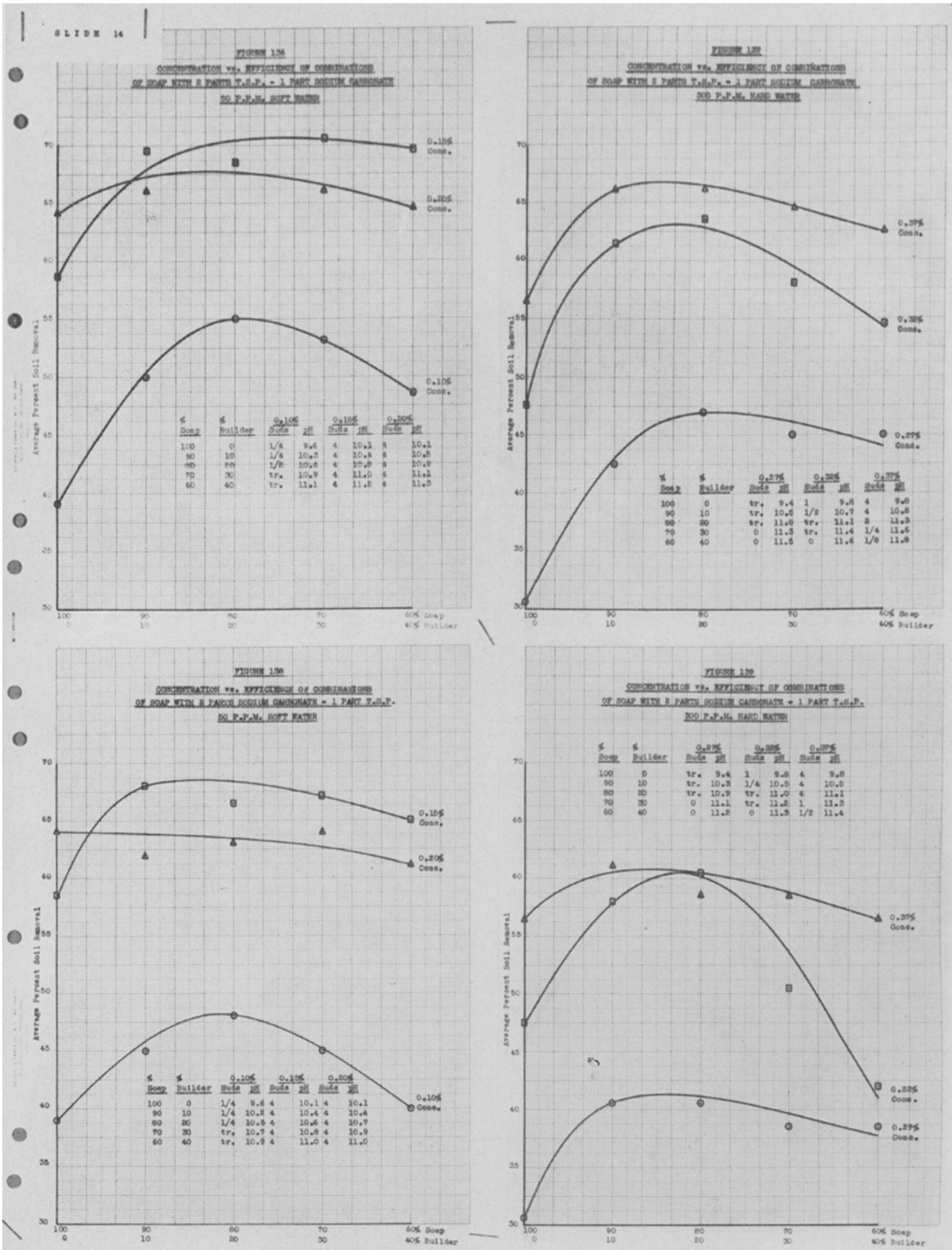
with the tri sodium phosphate — 1:3.3 silicate results there is little to choose between these two combinations. The metasilicate combinations show slightly better washing effect at low concentrations. A comparison of the three curves with pyrophosphate — metasilicate curves again shows that the pyrophosphate combinations maintain greater washing effectiveness when the proportion of builder to soap is



Group 13.

high. pH values are practically all too high for household soaps.

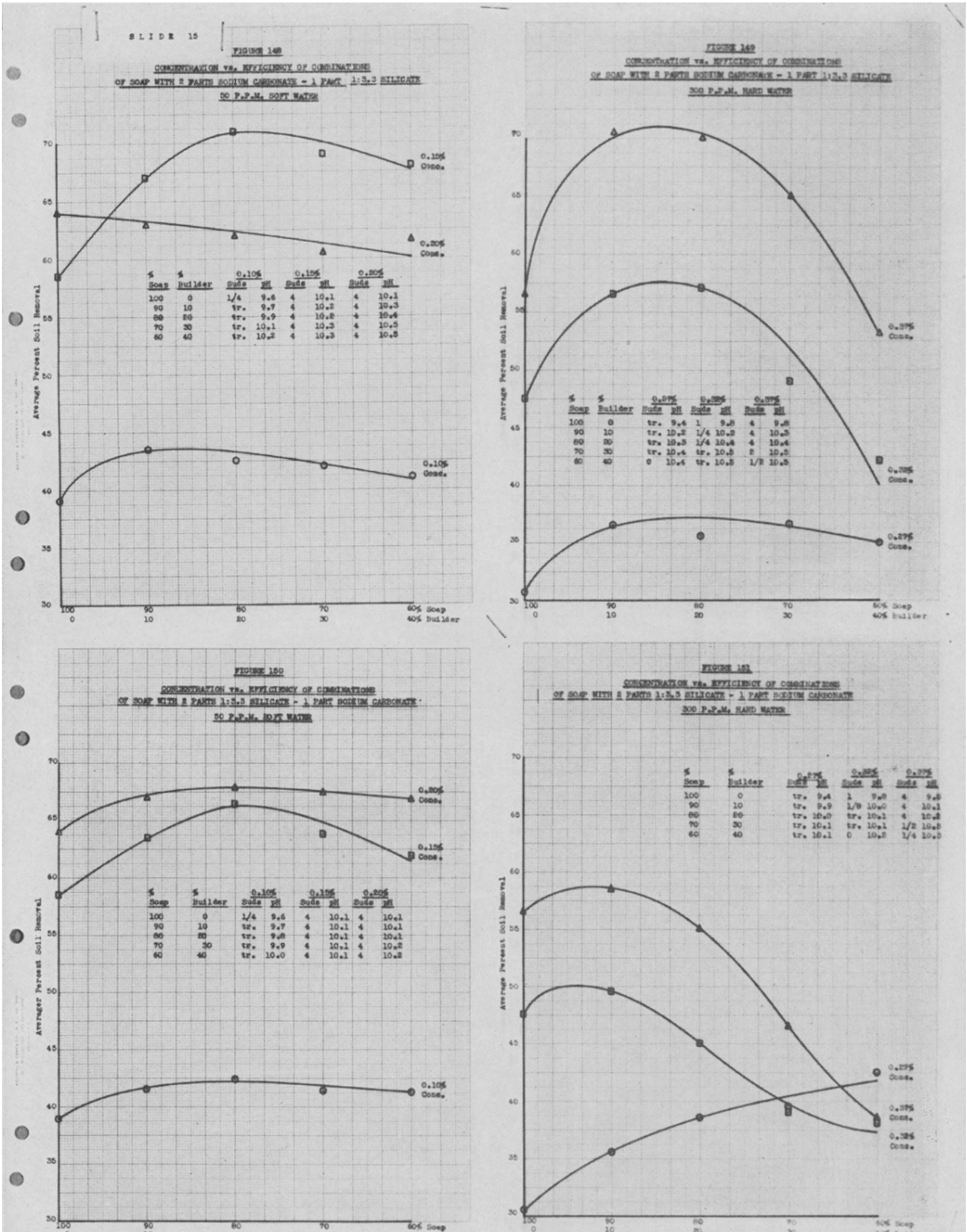
Results of the trisodium phosphate — soda ash curves are set forth in group No. 14. When compared with the pyrophosphate — soda ash curves, the results are generally inferior and the effect of adding large amounts of builder is more detrimental. Most of the combinations gave high pH values and showed



Group 14.

sudsing values distinctly inferior to the pyrophosphate — carbonate combinations.

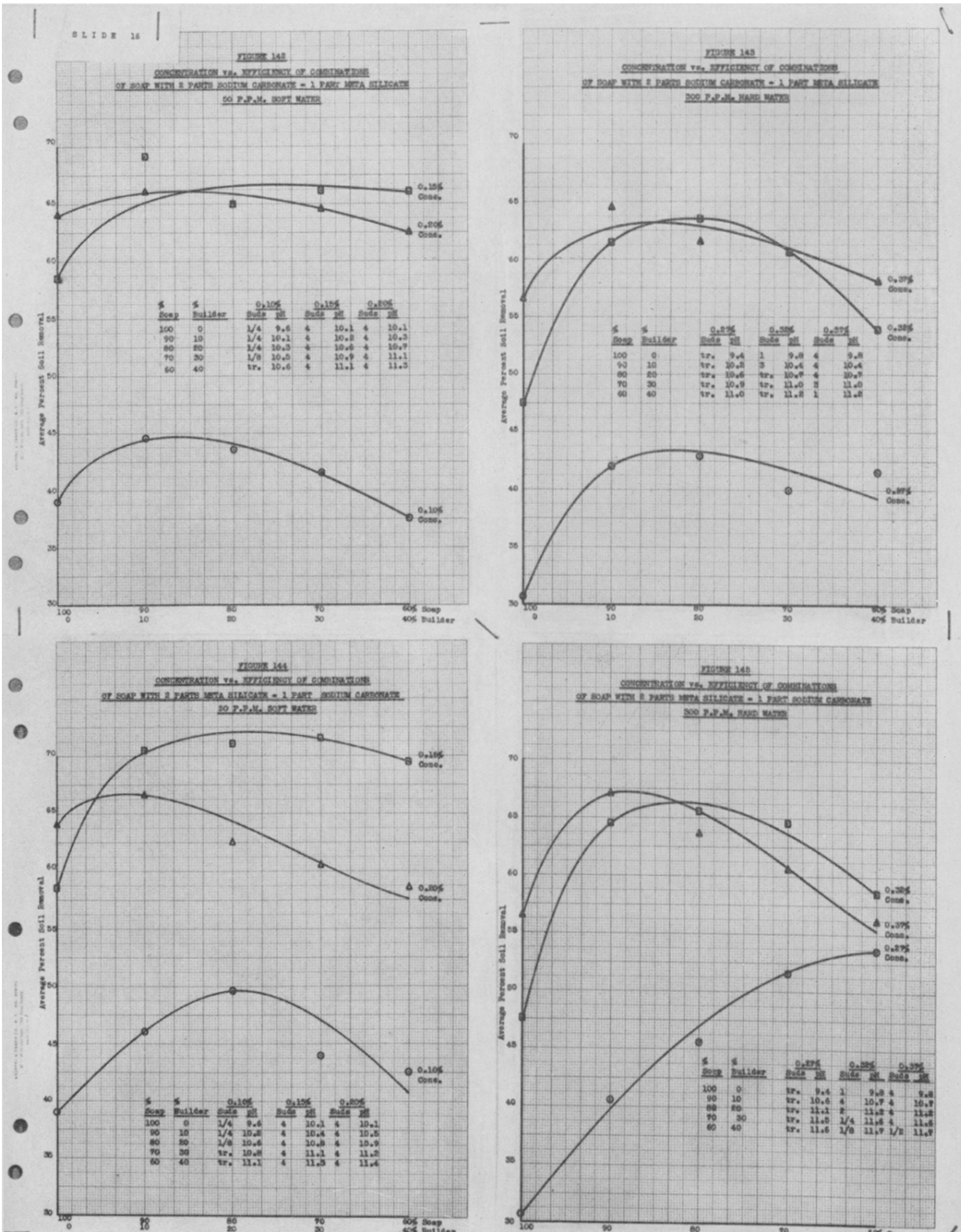
Group No. 15 gives the results of the Na_2CO_3 — 1:3.3 silicate combination. This combination gave fairly good results at a ratio of 2:1 of carbonate to silicate. However, in the hard water tests the maximum effectiveness is reached when the percentage of builder is between 10 and 20%. When 40% builder is used the efficiency falls off rapidly. The results of the 1:2 ratio are notable for the very poor results obtained in the hard water tests. This can only be explained by the incompatibility of this combination



Group 15.

when used with soap. All of the combinations give satisfactory pH values for household soaps but there is a striking deficiency in the sudsing effect in the hard water series.

Group No. 16 shows the soda ash — sodium metasilicate combinations. There are no outstanding effects. The results in hard water for the 2:1 ratio of Na_2CO_3 to metasilicate were rather poor in that the maximum results for 0.37% concentration were no better than the maximum obtained with 0.32% concentration. With the reverse ratios excellent results were obtained with the 0.15% conc. in soft water but



Group 16.

the 0.20% concentration produces low results which may be attributed to lowered surface activity. The results from both combinations in hard water show that maximum effect is reached when the builder concentration was only about 15 percent. Practically all of the combinations gave high pH values.

Summary

Tetrasodium pyrophosphate has been shown to possess the following outstanding advantages as a component in built soaps:

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

Final conclusions as to its value in combination with other builders must await completion of the work on ternary and quaternary combinations which are now under way.

The authors wish to acknowledge the work done by Mr. E. L. Brown who has conducted most of the actual launderometer tests in this investigation.

ABSTRACTS

Oils and Fats

Edited by
M. M. PISKUR

PROCESSING OF RAPE OIL. M. Gordienko. *Fette u. Seifen 46,* 684-5 (1939).

PROCESSING A WHALE. W. Picker. *Fette u. Seifen 46,* 682-3 (1939).

FAT TRAPS FOR WASTE WATER. W. Passavant. *Fette u. Seifen 46,* 583-5 (1939). Several equipments are illustrated and described.

COTTONSEED HULLS AS AN INDUSTRIAL RAW MATERIAL. D. M. Musser and R. F. Nickerson. *Ind. & Eng. Chem. Ind. 31,* 1229-33 (1939). A review.

SEPARATION OF SATURATED FROM UNSATURATED FAT ACID. H. Fiedler. *Fette u. Seifen 46,* 579 (1939). Method of prepg. oleic acid according to Hartusch (*J. Am. Chem. Soc. 61,* 1142-4) yielded the purest product.

ANTIOXIDANTS AND THE AUTOXIDATION OF FATS. F. E. Deatherage and H. A. Mattill. *Ind. and Eng. Chem. 31,* 1325-31 (1939). An apparatus for the study of the autoxidation of fats and related materials has been designed to permit the collection and analysis of the various volatile products formed in the reaction, the measurement of the oxygen consumption, and analysis of the oxidation residue. Oleic acid, oleyl alcohol, methyl oleate, butyl oleate, and cis-9-octadecene appear to be autoxidized in a similar manner to yield the same types of products — among others, peroxides, peracids, aldehydes, substituted ethylene oxides, acids, alcohols, combinations of these, and water.

After the addition of oxygen to form peroxides at the ethylene linkage, these peroxides may cleave to give aldehydes; they may react with another double bond to give two moles of ethylene oxide; or they may aid in the further oxidation of the carbon chain. The aldehydes formed also autoxidize to give peracids and acids.

The oxygen consumption per mole of double bond destroyed is least for oleic acid, most for oleyl alcohol. The amount of oxygen consumed is about the same for methyl oleate and cis-9-octadecene. In each case about one-fourth of the oxygen taken up appears as water.

Oxido derivatives are among the main products of the autoxidation process. When oleic acid is oxidized, oxidooleic acid does not appear as such but is apparently converted to half esters of dihydroxy stearic acid. The oxido derivatives are all of the same geometrical configuration and correspond to the high-melting dihydroxy isomeric derivative of the original substrate in each case.

CHARACTERISTICS AND REACTION PRODUCTS IN GOING TALLOWY. E. Glimm and H. Nowack. *Fette u. Seifen 46,* 632-5 (1939). A review.

IS TRIMETHYLAMINE THE CAUSE OF FISHINESS IN BUTTER? W. Mohr and A. Arbes. *Fette u. Seifen 46,* 678-82 (1939). Efforts to identify trimethylamine in fishy butter were futile. Trimethylamine could be detected when it was added to fresh butter.

DETERMINATION OF PHOSPHATIDES. A. Schramme. *Fette u. Seifen 46,* 635-8 (1939). Briefly the method for detn. of phosphatides in soybeans comprises: extn. with benzol-alc. (80:20) soln., evapg., redissolving in ether, drying with glauber salt, filtering, evapg. and detg. P. The P figure is multiplied by 25.4 to convert to per cent lecithin.

THE COURSE OF THE REACTION IN AUTOCLAVE SPLITTING. L. Lascaray. *Fette u. Seifen 46,* 628-32 (1939). Temp., splitting agent amt. or type can affect the speed of splitting but do not influence the equil. of the reaction. The amount of splitting water increases the limit of the reaction without influencing the speed of the reaction. The splitting reaction in a heterogeneous system is a homogeneous reaction which takes place at the boundaries of the phases. The new theory indicates that splitting agents act through increasing the solubility of water in the fat phase.

THE EFFECT OF COD LIVER OIL AND FISHMEAL ON THE FLAVOR OF POULTRY PRODUCTS. E. M. Cruickshank. *U. S. Egg & Poul. Mag. 45,* 752-4,762 (1939). Two percent of cod-liver oil in the fattening ration or two percent of best quality cod-liver oil plus a 15 per cent level of high grade fishmeal fed for a six-month period up to the time of killing was without detrimental effect on the flavor of the carcasses, either fresh or stored, of Light Sussex chickens. A 15 percent level of low grade fishmeal (fat content 20 percent) plus two percent of cod-liver oil fed for a four-week or six-month period up to killing produced a slight fishy flavor in a few of the fresh carcasses though not in the stored carcasses. Individual differences in the development of fishy flavor on the same ration appear to exist. Eggs from birds fed the high-