The Function of Tetrasodium Pyrophosphate in Soap Mixtures*

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RECENTLY there has been a marked change in the composition of soap mixtures for household use which has made them better washing compounds without added cost to the consumer. The compound which has brought about this improvement is tetrasodium pyrophosphate, $Na_4P_2O_7$.

It is the purpose of this paper to discuss why tetrasodium pyrophosphate improves soap mixtures. To do this, let us consider in simple terms what constitutes a good washing operation. We can say it is the transfer of dirt from the object to be cleaned to the washing solution and the ultimate removal of the dirt and washing solution to the drain. In general, plain or built soaps would do a good job of washing, if used in sufficient amount, in soft water.

Effect of Soap Concentration

The effectiveness of soap as a cleansing agent is shown by Figure 1. Artificially soiled cloth is washed in distilled water solutions of anhydrous soap at concentrations of 0.05, 0.075, 0.10, 0.125, and 0.15%. To each 100 cc of washing solution 2.5 cc of N/10 NaOH were added as a builder. It is evident that cleansing improves with an increase in soap concentration and slight changes in soap concentration appreciably effect the cleansing action.

These washes were made in a Launder-Ometer which we have found to be a useful tool in evaluating soap mixtures, if all of the factors involved in a washing operation are closely controlled.

FIGURE-1
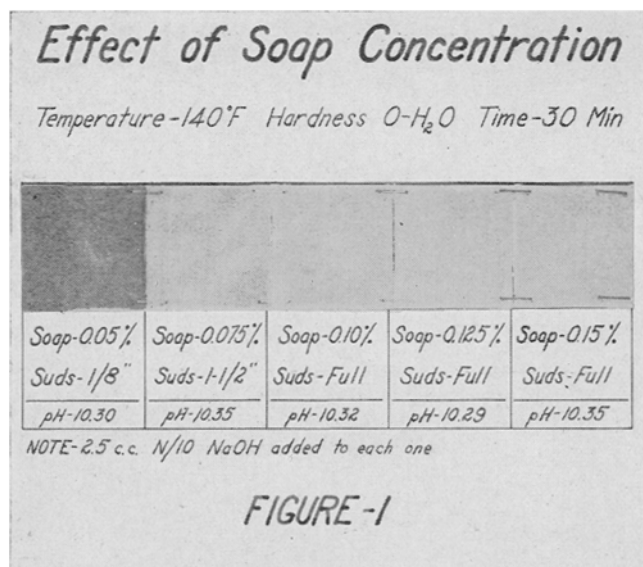
Effect of pH

It is a well established fact that soap functions best at an optimum pH. The pH at which best washing is effected depends on other constituents of the soap solution. To illustrate the pH at which soap functions best we are showing the results of washing tests at a constant soap concentration over a range of pH values. Figure 2 shows the effect of pH on the cleansing ability of soap and the effect of sodium ion concentration on the effective pH.

FIGURE-2
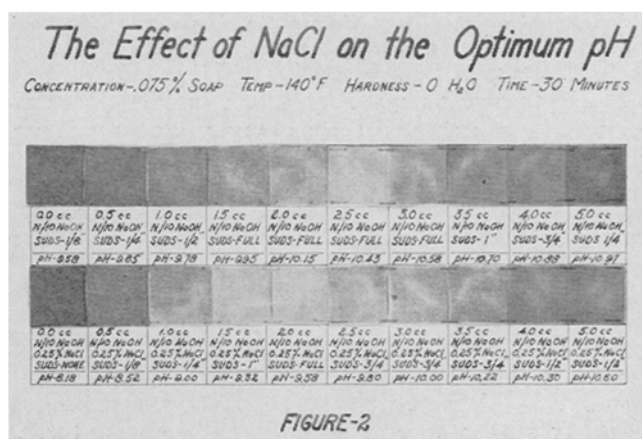
Artificially soiled cloth was washed in distilled water containing 0.075% soap at 140°F over a pH range of 9.58 — 10.97 using N/10 NaOH to vary the pH. The optimum pH is 10.4. Repeating the above wash except for the addition of 0.25% NaCl in each solution, it is noted that the optimum pH is lowered to 9.58.

We have introduced these figures to show the effect of pH and the necessity of the maintenance of an optimum pH. This can not be accomplished with tetrasodium pyrophosphate alone and requires the aid of another builder.

We have chosen soda ash in our illustrations for this purpose because it has a sufficiently high pH, a high total alkalinity, a good buffering action, and it is cheap.

Action of Soap in Hard Water

We have shown how effective soap is in distilled water. Unfortunately soft water is not common while hard water exists quite generally, usually of such degree as to be a significant factor in soap use.

Every one knows that insoluble calcium and magnesium soaps are formed in hard water, causing loss of active soap and actually creating a potential source of contamination when the amount of soap used is insufficient to disperse this precipitate. These curds are enmeshed in the cloth, thus creating the well-known "tattle-tale grey." Clothes of this nature are likely to develop off odors from rancidity of the insoluble soaps retained in the cloth.

Soap is an excellent dispersing agent, a property which makes it an important cleansing agent, and if used in sufficient quantity in hard water, it will prevent the formation of curds by dispersing the calcium and magnesium soaps.

Figure 3 illustrates the dispersing effect of dissolved soap on insoluble soaps. The hardness of the water is 400 ppm. The temperature of the water is 140° F and the soap concentrations are 0.1, 0.2, 0.3, 0.4, and 0.5%. The dispersion of the curd by an increase in soap concentration is clearly shown.

Action of Builders

Although soap is an excellent dispersing agent capable of producing the type of solution essential to good washing, its use alone is a costly method of attaining such a solution and attempts to soften water with

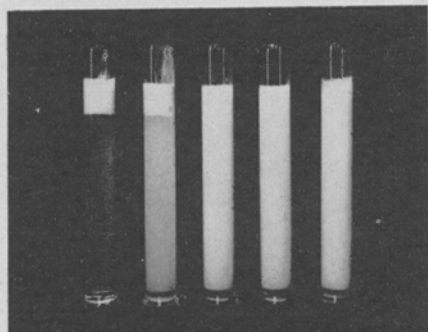Effect of Soap Concentration on Dispersion of Insoluble Soaps.

FIGURE-3

Softening Effect of Builders in the Presence of Soap

Grams of Builder per gram of Soap

FIGURE-4

cheaper ingredients have been made. Compounds used for this purpose are soda ash, T.S.P., sodium silicate, borax, etc. Unfortunately these compounds when introduced with soap afford very little water softening action since the insoluble soaps formed are less soluble than the inorganic calcium and magnesium compounds and soap ultimately becomes the major water softening agent.

This fact is demonstrated very easily by determining the hardness of samples of water treated with equal amounts of any common builder, but using a filtered sample for one determination and an unfiltered sample for the other. The filtered sample will be found to be of lower hardness than the unfiltered sample. This indicates quite conclusively that the soluble soap and the insoluble inorganic precipitates react and come to equilibrium when a certain amount of soluble soap has been removed in the form of insoluble calcium or magnesium soap. For example, water having a hardness of 800 ppm was treated with 0.30% $Na_3PO_4.12H_2O$ and the residual hardness on a filtered and unfiltered sample of water was determined. The filtered sample contained 72 ppm hardness and the unfiltered 265 ppm hardness.

It is true that initially there may be more soap made available when some of these alkaline compounds are added with soap. Usually the soap is slowly soluble in comparison to the akaline compounds so that temporary softening is produced by the alkaline compound. Eventually, however, equilibrium is reached when the soap has become the major water softening agent and the soap available originally is lost.

The behavior of common builders as water softening agents in the presence of soap is shown in Figure 4. This is a series of curves which gives the water softening action of various soap builders when used with soap in hard water. 2 grams of soap plus builder were dissolved in distilled water made up to 500 cc volume, and this solution was titrated against 50 cc of hard water until permanent suds were formed. The hard water contains 100 ppm calcium hardness and 50 ppm magnesium hardness. The ordinate shows the cc's of soap solution required to produce permanent suds. 16.0 cc represents the requirement of 100% soap. The abscissa shows the weight of builder per gram of soap and the curves show the decrease in soap usage as the amount of builder is increased.

The silicate used was 40° Be′ sodium silicate having a ratio of $Na_2O:SiO_2$ of 1:3.25. The soda ash was regular soda ash having an Na_2O content of 58%. The
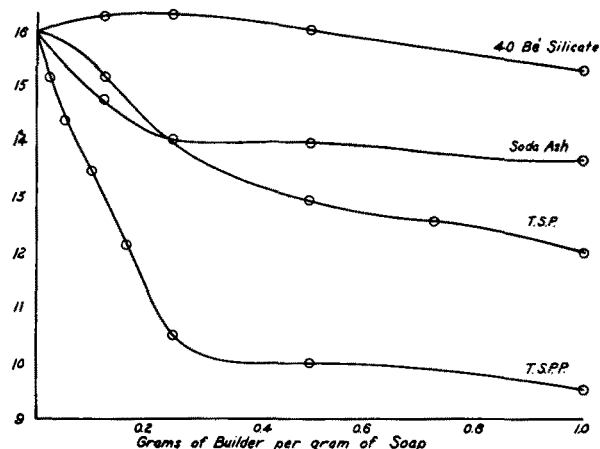
T.S.P. was crystalline T.S.P. designated as Na_3PO_4.$12H_2O$. The tetrasodium pyrophosphate used was the anhydrous compound, $Na_4P_2O_7$.

Tetrasodium pyrophosphate is shown to be the most effective water softening agent under these conditions.

The criterion of the housewife for judging the amount of soap to add is the formation of suds. If, with an ordinarily built soap or a plain soap, she adds enough product to get a good suds, the chances are that she will not have suds at the end of the washing operation, unless she added a large excess. The losses of soluble soap during the washing operation may be due to delayed water softening action, neutralization by acidic constituents of the soil and adsorption by the cloth. The occurrence of a "flat" wash water at the end of the washing operation is not uncommon. Such a wash water allows redeposition of the soil, may increase the total solids in the cloth, and makes rinsing very difficult.

Elimination of Magnesium Hardness

Anything that can be done to minimize curd formation in the wash water will aid in the production of cleaner clothes. Tetrasodium pyrophosphate plays an important role in this respect. It completely eliminates magnesium as a precipitant for soap when used in proper amount with soap mixtures. It does this by eliminating the magnesium ion either as soluble complex compound having the probable formula Na_2-MgP_2O_7 or as $Mg_2P_2O_7$, a compound more insoluble than magnesium soap.

Figure 4 demonstrates this point very nicely. At 10.5 cc the concentration of tetrasodium pyrophosphate is at an optimum considering the degree of improvement in water softening action per unit of tetrasodium pyrophosphate added. Further additions of tetrasodium pyrophosphate fail to reduce the soap usage appreciably. At this point the titration has been reduced from 16.0 cc for the pure soap to 10.5 cc for the soap and tetrasodium pyrophosphate mixture or a reduction of hardness equal to 34.4%. The water used contained 33.3% magnesium hardness. At this point the magnesium has been completely repressed and further additions of the tetrasodium pyrophosphate have little effect on the repression of calcium. This is substantiated also by the results shown in Figure 6.

The inability of the common builders to produce a similar effect is shown by the other curves in Figure 4.

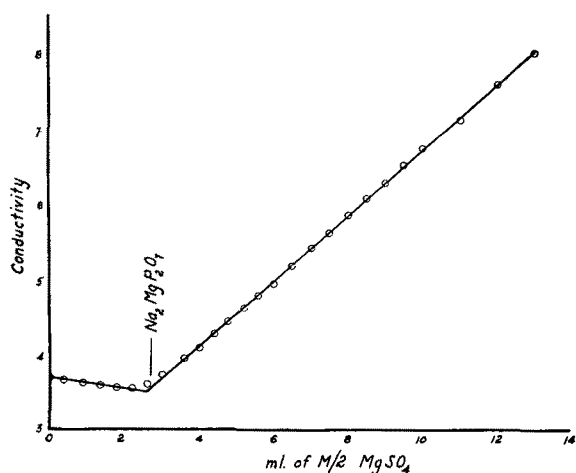## Conductimetric Titration of 0.545g $Na_4P_2O_7 \cdot 10H_2O$

FIGURE-5

Figure 5 shows a curve resulting from the con-
ductometric titration of a tetrasodium pyrophosphate
solution containing 1.22 millimols of tetrasodium
pyrophosphate with a 1/2 molar $MgSO_4$ solution. By
plotting reciprocal ohms against the cc's of $MgSO_4$
solution added, the point of intersection on the curve
indicates a molecular ratio of $1Na_4P_2O_7 : MgSO_4$,
or the probability of the compound $Na_2MgP_2O_7$. At
elevated temperature the magnesium may be removed
as $Mg_2P_2O_7$. Whatever the mechanism, the removal
is so complete that no magnesium soap is precipitated
when tetrasodium pyrophosphate is used in the proper
amount in soap mixtures. Calcium is also removed to
some extent but with the amounts of tetrasodium
pyrophosphate usually employed, this amount is in-
significant. Its action on magnesium is so efficient that
1 lb. of tetrasodium pyrophosphate will release ap-
proximately 2.2 lb. of soap. At best it will release only
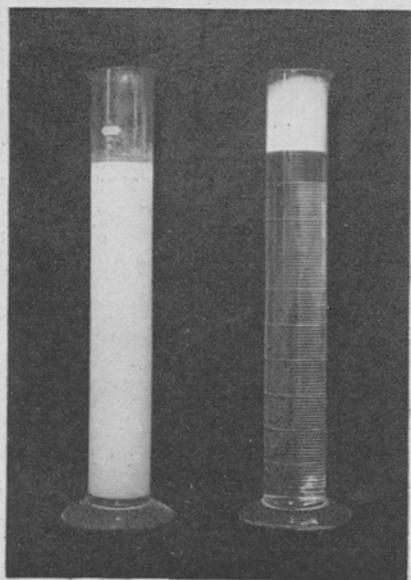0.3 lb. of soap with respect to calcium.

FIGURE-6

Figure 6 shows the difference in action on cal-
cium and magnesium. A solution of $MgSO_4$ and a
solution of $Ca(NO_3)_2$ equivalent to 200 ppm $CaCO_3$
were treated with 0.1% soap and 0.08% $Na_4P_2O_7$ at
140° F. The magnesium solution is clear and produces
suds. The calcium solution is turbid and displays no
suds indicating precipitation of the soap. The repress-
ing value of tetrasodium pyrophosphate is very likely
dependent on the type of fatty acid used in making the
soap, as the solubility of magnesium soaps varies ap-
preciably. By a choice of fatty acids more highly
efficient soap mixtures should be possible.

An example of this is the repression value of tetra-
sodium pyrophosphate toward magnesium in the
presence of sodium oleate and sodium stearate. At
room temperature the repression value of tetrasodium
pyrophosphate toward magiesium in the presence of
sodium oleate was 2.75 times the repression value in
the presence of sodium stearate.

FIGURE-7

The reason for this difference in repression value
is evidently due to the variation in the solubility of
the various magnesium soaps. The data given in the
International Critical Tables are as follows:

	Grams of Soap in 100 grams of Water		
	15° C	25° C	50° C
Magnesium Stearate	0.003	0.004	0.008
Magesium Oleate	0.022	0.024	0.030

The fact that natural hard waters contain appre-
ciable amounts of magnesium hardness means that
through the use of tetrasodium pyrophosphate a sav-
ing in soap as high as 20 - 30% is possible, depending
on the composition of the water and the soap mixture.
This means that equivalent washing can be accom-
plished at less cost or that better washing can be ac-
complished at equivalent cost when compared with
soap products which do not contain tetrasodium pyro-
phosphate. It also gives the housewife a 20 - 30%
safety factor toward having active soap present at the
end of the washing operation. It also diminishes the
total amount of insoluble soaps in the washing solution
by 20 - 30% which reduces the chances of retaining
insoluble soaps in the cloth by this amount.

Comparative Washing Tests

Figure 7 shows the improved washing effect that
results from the use of tetrasodium pyrophosphate
compared with ordinarily used builders. The wash-
ing was done in water having a natural hardness of
400 ppm. The concentration was 0.35% of the soap
mixture used and the the temperature, 140° F. The
same type of soap was used in making up the various

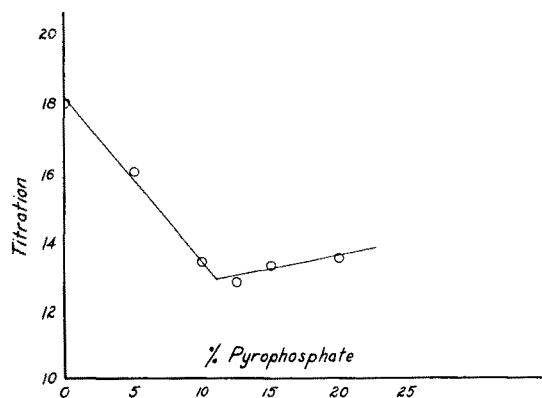Determination of Optimum % of TSPP in a Soap Mixture

FIGURE-8

mixtures. The T.S.P. is $Na_3PO_4.12H_2O$, the soda ash is Na_2CO_3, the silicate is 40° Be' sodium silicate with a 1:3.25 ratio and the pyrophosphate is $Na_4P_2O_7$.

The cloth washed in the presence of the tetrasodium pyrophosphate is the cleanest and yet no more soap was added than was used with the ordinary builders.

Figure 8 shows a curve used for determining the amount of tetrasodium pyrophosphate which will give any particular soap mixture its greatest water softening power. 2.5 grams of the soap mixture are dissolved in 10% alcohol (a mixture of distilled water and alcohol) and made up to 500 cc. with the dilute alcohol to eliminate gel formation. This solution is then titrated against 50 cc. of hard water containing 100 ppm. calcium hardness and 50 ppm. magnesium hardness. The curve shows that the greatest water softening effect occurs at an optimum concentration.

This curve differs in character from the curve shown in Figure 4 where a mixture of soap and tetrasodium pyrophosphate also was used. In Figure 4 the soap concentration of the solution is a constant and the tetrasodium pyrophosphate is a variable. The conditions under which the curve in Figure 8 results are such that the concentration of soap decreases with each increase in tetrasodium pyrophosphate content and an optimum concentration results while in Figure 4 the curve continues downward and shows an improvement in water softening action with each addition of tetrasodium pyrophosphate. The volume of soap solution shown in Figure 4 required to produce a permanent suds before the addition of tetrasodium pyrophosphate is 16.0 cc. and that in Figure 8 to be 18.0 cc. with zero per cent. $Na_4P_2O_7$.

In Figure 4, 2.0 grams of anhydrous soap were contained in 500 cc. of dilute alcohol solution while 2.5 grams of a commercial soap mixture approximating 60% anhydrous soap or only approximately 1.5 grams of anhydrous soap were contained in 500 cc. of the diluted alcohol solution. This was a built soap containing a mixture of soap, 1:3.25 sodium silicate, soda ash, T.S.P. and moisture. This explains the consumption of a greater volume of soap solution with an apparent higher soap concentration, than of a solution of soap of lower concentration for the same volume of water having the same hardness.

Our illustrations have been confined to home laundry operations, because this phase of cleaning could be demonstrated more easily than that of general cleaning, dishwashing, etc., but the advantages shown in these laundry operations also apply to other types of cleaning.
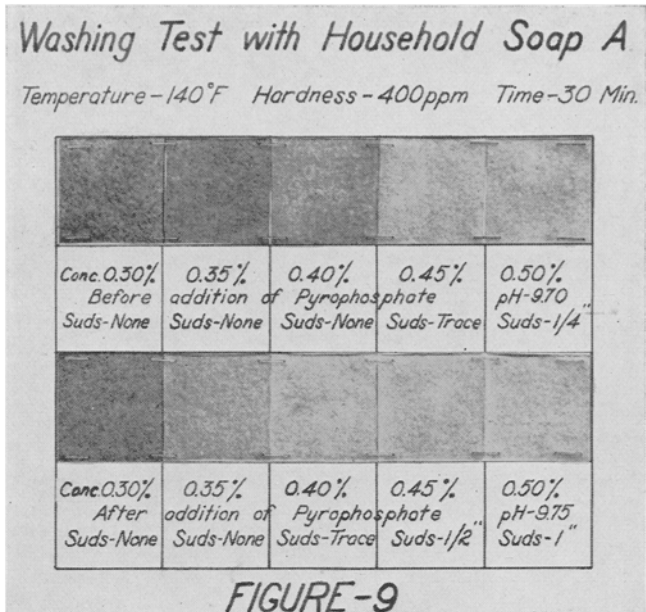
FIGURE-9

The practical application of tetrasodium pyrophosphate, as exemplified by two commercial soap mixtures, is illustrated by Figures 9 and 10 which show the difference in washing efficiency before and after the incorporation of the tetrasodium pyrophosphate. The washing was done in water of 400 ppm. hardness over a range of concentrations. The concentrations shown are those of the soap mixture as is. The approximate compositions of the products are shown in the following table:

	SOAP A		SOAP B	
	Before	After	Before	After
Anhydrous Soap	72	63	72	62
Soda Ash	6	9	6	5
Crystalline T.S.P.	—	—	4	—
Anhyd. 1:3.25 Silicate	16	9	12	15
Anhydrous T.S.P.P.	—	10	—	10
Moisture	6	9	6	8
	100%	100%	100%	100%

The results indicate that after the inclusion of the

FIGURE-10
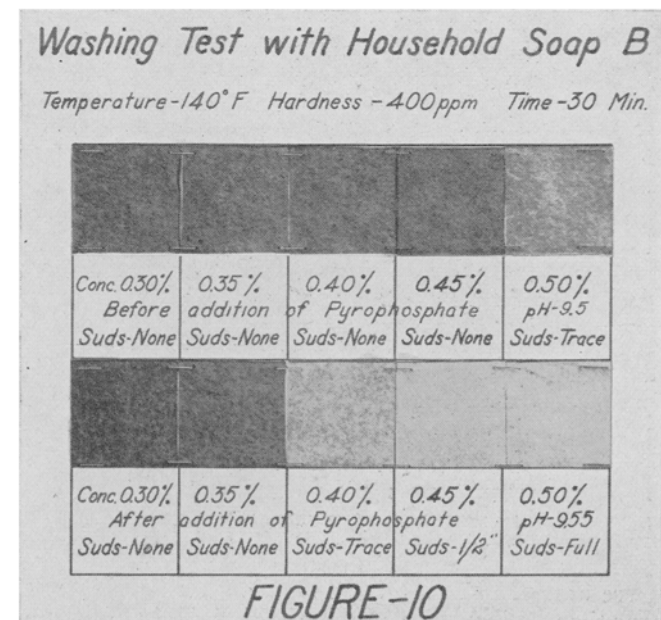
tetrasodium pyrophosphate, the products were improved to the extent of approximately 25%.

Conclusions

In the foregoing discussion we have shown how tetrasodium pyrophosphate functions in soap mixtures. A summation of the advantages resulting from its use is given:

1. Tetrasodium pyrophosphate, when it constitutes 10 - 15% of the soap mixture, saves soap to the extent of 20 - 30% by completely preventing the magnesium ion from precipitating soap. At higher levels a partial elimination of the calcium ion will also result.

2. It reduces the insoluble soap content of the wash water by 20 - 30% because it reduces the magnesium and calcium ion content of the solution by this amount.

3. Because of these facts, more soap is made available for washing and dispersing the solids, less insolubles are present to complicate dirt removal, resulting in better washing solutions at no additional cost.

A Study of Factors Influencing the Color Contributed to Soap by Gum Rosin

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THE color of commercial soaps containing rosin varies from yellow to dark brown, depending upon the grade of fat and rosin used. Difficulty is sometimes encountered in reproducing a given color in the paler rosin soaps. To what extent and in what manner rosin contributes to this difficulty is not known. To the best of our knowledge, beyond the recognition of the existence of the problem, no particular stress is placed upon it in the literature of soap and soap making, although the problem has been encountered by the naval stores trade and manufacturers of soap. The fact that rosins of the same color grade do not always give the same results is not surprising as the color of the rosin is due principally to the length of face, kind and condition of cups, scrape and distilling practice, factors which are not related to the density, acid number, saponification number, or the other usual constants. These latter properties vary within a limited range for all grades of rosin and do not necessarily bear any relation to the color contributed to a soap by the rosin itself. In general, the lighter colored rosins will impart less color to soap than the darker ones.

Due to the absence of published methods for evaluating the color contributed to a soap by rosin, it was necessary to develop one for this purpose. The method adopted was applied to resin and rosin acids, modified resin and rosin acids, as well as to rosins and modified rosins.

A Method for Evaluating the Color Contributed to Soap by Rosin

The method developed involves two steps: (1) The preparation of a rosin soap by a method that resembles the full-boiled or settled soap process, rather than the semi-boiled or cold process, since the former is used most extensively in the manufacture of rosin soaps; and (2) Smoothing and measuring the reflectance of the rosin soap each week until the difference in weekly reflectance measurements is less than half the maximum variation between duplicate samples. The value is then recorded as the final reflectance of the sample.

Preparation of the Rosin Soap Cake

In a 400 ml. beaker, 70 ml. of water and rosin-free white stock soap (white floating soap, referred to later as stock soap) equivalent to 40 gm. of fatty acids were heated and stirred until homogeneous. The soap was then grained with 25 ml. of 34° NaOH and 10 gm. of freshly powdered rosin were added. To avoid oxidation the rosin should be powdered and weighed not more than 20 minutes before using. When the rosin was saponified and evenly distributed in the curd by boiling and stirring, the beaker was removed from source of heat and another 25 ml. of 34° NaOH added to complete the graining. Without being stirred the alkali was heated just to a boil, allowed to stand for a minute or two, and the settled lye removed with a pipette. Then with slight stirring the curd was washed by adding 35 ml. of water, warming the beaker at the same time. If this washing was carried out properly most of the wash water could be removed with a pipette. Then sufficient water was added (usually 30 to 35 ml.) to give the soap the proper smooth consistency when it is heated to boiling with stirring. The beaker was then placed in a water bath maintained at 82° to 84° C. for eight hours. At the end of this period the liquid soap was poured into a mold and allowed to solidify. The mold was a metal ring 2-1/2 inches in diameter and 5/8 inch high, set on a glass plate. The rosin soap prepared as described above filled the mold and the resulting soap cake when dry fits the photo-electric photometer. After the soap had solidified, that extending above the ring was sliced away with a sharp knife. If reflectance measurements on the wet soap cake are desired, this gives a smooth surface.

The method for preparing the rosin soap cakes might be varied in several ways without changing the method fundamentally. Any good grade of fat that will produce a white soap might be saponified, grained and used in place of the white stock soap. The rosin could be added to the soap stock before it is first grained with alkali, but this procedure did not yield as homogeneous soap curds and uniform rosin soap cakes as the method described. The following variation was also tried: The stock soap in 70 ml. of water was grained with 10 ml. of 34° NaOH, 10 gm. of freshly powdered rosin added, mixed thoroughly by boiling and stirring, and placed in a water bath (82° to 84° C.) for one hour. When removed, it was grained with 100 ml. of 25 per cent NaCl solution, and again placed in the water bath for one hour to permit complete graining. The salt solution was then removed, 50 ml. of water added, boiled, stirred and placed in the water bath for eight hours. Rosin soaps