TABLE II

Effect of Various Concentrations of Phospholipid and Hydroquinone, Used in Combination, on Carotene Stability in Refined Cottonseed Oil. Samples Stored at 75° C.

Concentration of antioxidants		Time for 20% destruction of carotene
Hydroquinone	Phospholipid	
per cent	*per cent*	*hours*
1.0	5.0	148
1.0	2.5	140
1.0	0.5	136
1.0	0.05	120
0.5	5.0	120
0.5	2.5	122
0.5	0.5	112
0.5	0.05	105
0.05	5.0	96
0.05	2.5	90
0.05	0.5	85
0.05	0.05	78
0.01	5.0	75
0.01	2.5	72
0.01	0.5	57
0.01	0.05	56

in the refined cottonseed oil were also determined, and similar studies were made on cottonseed oil after the addition of 1.2 mg. of carotene per gram of oil.

In the refined cottonseed oil the formation of peroxides occurred concurrently with the destruction of carotene and was greatly accelerated as the carotene disappeared. In mineral oil solutions, no peroxides were found until after the carotene had become completely decolorized.

Although alpha-tocopherol was very effective in stabilizing carotene when added to mineral oil solutions neither the naturally present nor added tocopherol was effective in a more unstable solvent such as refined cottonseed oil. To make the tocopherol effective in such a solvent it is necessary first to stabilize the solvent. When the combination of phospholipid and hydroquinone was added to the refined cottonseed oil, the oil was stabilized and a very marked increase in carotene stability was obtained.

While the combinations AH, APH, TAH and TAPH did not stabilize the carotene during the early part of the storage tests, they did become effective after about 20 per cent of the carotene had been destroyed and were as effective as PH and TPH when measured at the 50 per cent point. The reason for this ineffectiveness during the preliminary period of storage is not apparent.

Acknowledgments

The authors are indebted to Dr. H. S. Olcott of this laboratory for the cottonseed phospholipids, to the Oil and Fat Division of the Eastern Regional Research Laboratory for the l-ascorbyl palmitate, and to Ross and Roe, Inc., of New York for the soybean phospholipids.

LITERATURE CITED

(1) A.O.A.C.—Jour. A.O.A.C., *24*, 80 (1941).
(2) Baumann, C. A., and Steenbock, H., J. Biol. Chem., *101*, 561 (1933).
(3) Bickoff, E., and Williams. K. T., Ind. Eng. Chem., Anal. Ed., *15*, 266 (1943).
(4) Golumbic, C., and Mattill, H. A., J. Am. Chem. Soc., *63*, 1279 (1941).
(5) Golumbic, C., Oil and Soap, *20*, 105 (1943).
(6) Holmes, H., Corbet, R., and Hartzler, E., Ind. Eng. Chem., *28*, 133 (1936).
(7) Morgal, P. W., Byers, L. W., and Miller, E. J., Ind. Eng. Chem., *35*, 794 (1943).
(8) Olcott, H. S., Science, in press.
(9) Olcott, H. S., and Mattill, H. A., J. Am. Chem. Soc. *58*, 2204 (1936).
(10) Olcott, H. S., and Mattill, H. A., J. Am. Chem. Soc., *58*, 1627 (1936).
(11) Quackenbush, F. W., Cox, R. P., and Steenbock, H., J. Biol. Chem., *145*, 169 (1942).
(12) Riemenschneider, R. W., Turer, J., Wells, P. A., and Ault, W. C., Oil and Soap *21*, 47 (1944).
(13) Swift, C. E., Rose, W. G., and Jamieson, G. S., Oil and Soap, *19*, 176 (1942).
(14) Wheeler. D. H., Oil and Soap *9*, 89 (1932).

Rosin—Use in Salt Water Soap

B. S. VAN ZILE and J. N. BORGLIN
Hercules Experiment Station, Hercules Powder Company
Wilmington, Delaware

The problem of washing on shipboard at sea has probably existed since man built and sailed his first seagoing boat. In the days of sailing ships, it appears that cooking and eating utensils were washed by scrubbing with a mixture of sand and wood ashes. Soap for toilet, bath or laundry use seems to have had little demand. In latter years any available soap seems to have been used until someone hit upon the idea of a salt water soap made from coconut oil.

In this country considerable work has been done on coconut oil soap for this purpose until the product covered by Federal Specification PS611 containing about 3% of salt, 3% of soda ash, 39% coconut oil soap, and 55% water was developed. Few people, it seems, have tried to improve upon it. Pech (1, 2) patented a salt water soap composed of coconut oil 100 parts, caustic soda 4.75 parts, sodium silicate 5 parts, caustic potash 6 parts, and 100 parts of a 4% solution of potassium chlorate. The silicate probably helped the soap but whether or not the chlorate had any value is problematical. Brunet (3) suggested that for washing in sea water a soap containing much glycerol and alkali would remove "epithilial debris" and grease. Miyoke, Kimoshita and Tomeoka (4) prepared a salt water soap by boiling 2 parts of red algae in 50 parts of water and filtering. To the filtrate, mixed with 18-19 parts of caustic soda and 6-8 parts of soda ash, add 100 parts of palm oil while hot. Then add 1.5-2.5 parts of ammonium chloride and 5 parts of ammonium sulfate. So far as we could discover, nothing was said about how the extract of red algae and the ammonium salts improved the cold process palm oil soap.

The problem of washing in sea water is, of course, that of getting sufficient soap into solution to do the job. In the presence of 25,000 p.p.m. of salt and 12,000 to 13,000 p.p.m. of calcium and magnesium salts, a film of insoluble soap is formed on the surface of an ordinary soap which retards solution to such an extent that the soap is considered insoluble. If the insoluble film is removed as fast as it forms by some kind of abrasion sufficient soap will be dissolved to react with the hardness and saturate the salt solution with soap. One of the physical chemists working in the field of detergents is of the opinion that the film of insoluble soap acts as a dialyzing membrane, holding back the salt and passing pure water. The pure water is thought to dissolve the soap and finally build up sufficient pressure to break the membrane, allowing the soap solution to disperse and react with the hardness. A new membrane forms around the soap and the dialysis process starts on another cycle. This process is repeated until sufficient soap is dissolved to react with the hardness, disperse the curd and have sufficient active soap in solution to do some washing. Moisture in the soap greatly accelerates the process, hence a salt water soap should carry all the moisture possible. In our experience the quickest way to make a solution of soap in sea water is to melt the soap in a small amount of sea water and dilute the paste so formed.

Besides containing as much moisture as possible, a soap to be used in sea water must contain protective agents which help to get the soap into solution.

After the Japanese cut off our supply of coconut-type oils, the Navy issued an ad interim specification for Salt Water Detergent, Bar Form, 51D7 (INT) containing 50% soap, 20% synthetic detergent, and 30% neutral salts. The physical chemistry of the functioning of this mixture in sea water is a controversial subject in which the present authors have no desire to become entangled. We will content ourselves with a statement of some of the views that have been expressed and allow the reader to take his choice. Some workers in this field believe that in the presence of hardness, soap and a synthetic detergent form a complex perhaps of the nature $\mathrm{Ca}<^{\text{soap}}_{\text{synthetic}}$. This complex not only acts as a precipitant for hardness, but having greater solubility than the calcium soaps, it aids in dispersing the insoluble curd. When the hardness has all been precipitated and dispersed, sufficient synthetic will be left to aid the soap in doing a wash job. Others feel that the soap alone precipitates the hardness and the synthetic does the washing. If such is the case the soap is wasted because the synthetic could be used alone and should do just as good a job without softening the water. Another school of thought is that the soap precipitates the hardness, the synthetic then disperses the insoluble soap and allows the excess soap to do the actual washing. Whatever the physical chemical mechanism, the fact remains that the combination of soap and synthetic works better than either one alone. Also the combination works at a relatively low concentration which seems to rule out any thought of the complete precipitation of the hardness.

While soap and certain synthetic detergents work well in sea water it is unfortunate that many synthetics are not suitable for this use. Some are unsuitable because they are made from strategic materials, others because they are available in very limited quantities, hence are high in cost. Some others because the bar does not have the right physical properties, and lastly many do not meet the performance tests. As a consequence, when practically all of the suitable synthetics are taken for salt water soap the production is still far beneath the needs of the Armed Services. It was imperative, therefore, that soaps prepared without synthetics that would perform in sea water be produced. We, therefore, started a study of other soap builders or adjuncts which might produce a soap that functions in sea water at a concentration sufficiently low as to be usable both from a cost and performance angle.

There are several alkaline salts which, when used in sufficient quantities, will protect soap in sea water and allow it do a fairly good washing job. All of the polyphosphates (tripolyphosphate, tetraphosphate and hexametaphosphate) are very effective in such a composition. However, each appears to be ruled out either by cost, scarcity or acid reaction. Tetrasodium pyrophosphate does a very effective job, is low in cost and relatively easy to obtain. It also works well as a protective agent when used in conjunction with other alkaline salts such as the silicates. Unfortunately, the quantity of alkalies required is large compared to the amount of soap and makes the production of such a composition in bar form next to impossible. It seemed desirable, therefore, to add a noncrystalline protective agent which would allow the reduction of the quantity of alkaline salts necessary for the protection of the soap.

W. D. Pohle (5) has compared the solubility of the resinates of calcium and magnesium with that of the calcium and magnesium soaps and found that the resinates were much more soluble. In our work we had also found that an excess of a resinate of an alkali metal would solubilize calcium and magnesium resinates. This is especially true if there is sufficient free alkali to raise the pH to about 11.0. He also found (6) that the resinates had good detergent properties. Borglin, Mosher, Noble and Punshon (7) also found this to be the case. Since the resinates offered desirable protective and detersive properties and aid in producing a nice smooth bar of soap their use in conjunction with soap and alkalies was thoroughly investigated.

The performance test used was that outlined in the Navy's ad interim Specification 51D7 which is briefly as follows: Wool fabric is soiled by passing through a soiling solution a sufficient number of times to reduce the reflectance to 30% (±2.5%). The soiling solution is composed of

Edible tallow	2.0 g.
White mineral oil	6.0 g.
Lamp black (Grinder No. 2)	0.125 g.
Carbon tetrachloride	4.0 liters

After soiling, the wool fabric is washed by the following procedure: Dissolve the sample in 1000 ml. of artificial sea water, warming if necessary. Cool to room temperature. Take 250 ml. of this solution in an 8 in. evaporating dish and wash a 4 in. square piece of the soiled wool fabric by squeezing it vigorously 50 times in the detergent solution within two minutes. Rinse in warm soft water and dry. The reflectance is then compared with that of an unsoiled piece of the wool fabric which has been squeezed 50 times in artificial sea water, rinsed and dried.

The composition of the artificial sea water is

Magnesium chloride ($MgCl_2 \cdot 6H_2O$)	11.0 g.
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	1.6 g.
Sodium sulfate (Na_2SO_4)	4.0 g.
Sodium chloride (NaCl)	25.0 g.
Water to make	1.0 liter

The concentration of detergent used in this test was varied until a solution was obtained which would remove all of the visible black from the wool fabric. The lowest concentration which would accomplish this was considered the optimum for that detergent. Coconut oil salt water soap (PS611) required 7% of dry solids or over 15% on the 55% moisture basis. The addition of alkaline builders reduces the necessary concentration. Mixtures of 50 parts of soap with 50 parts of trisodium phosphate, metasilicate, N silicate or soda ash required about 6%, while a 50-50 mixture of soap and tetrasodium pyrophosphate required only 4.75%.

For use in salt water sodium resinate alone aids soap very little, but in combination with alkalies it is very effective. For instance, it requires only 3% of a mixture of 50% tallow soap, 25% resinate and 25% pyrophosphate to meet the above test. The soap containing synthetic detergent as specified in 51D7 requires between 2.0 and 2.5% to do the same thing. By using a slightly higher concentration, we have succeeded in getting as good detergent action in sea water without the use of synthetics.

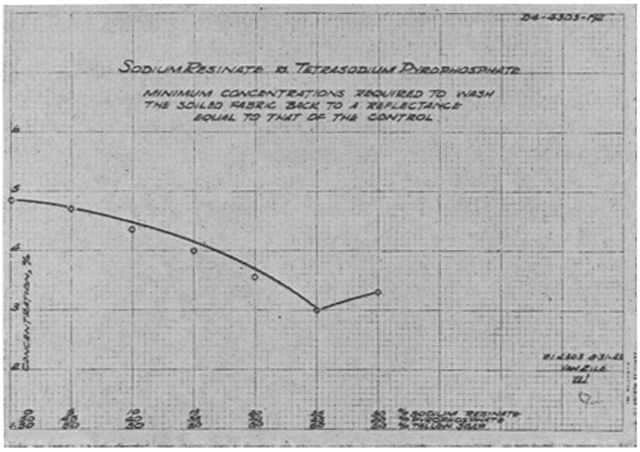

FIG. 1

Since a mixture of one part of tallow soap and one part of pyrophosphate required a concentration of 4.75% to remove all of the visible carbon black, we endeavored to reduce the necessary concentration through the addition of sodium resinate. Starting with the 50-50 mixture we added sodium resinate in increments of 5% from 5% to 30% and reduced the pyrophosphate by a like amount. The results are plotted in Figure I. You will note that we obtained the most protection with the 50% tallow soap, 25% resinate and 25% pyrophosphate mixture.

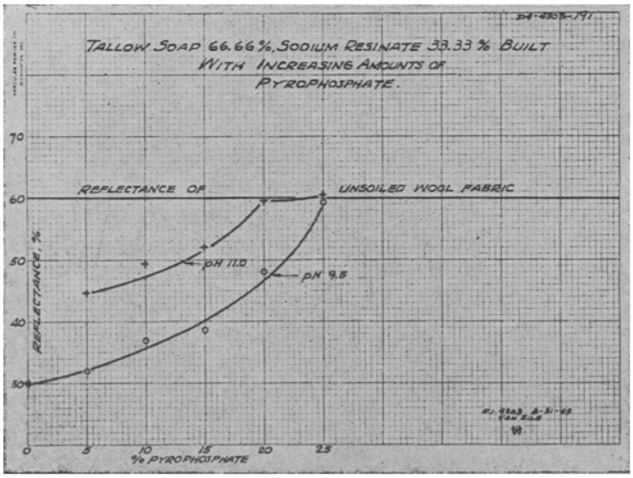

FIG. 2

Working from the other angle we used a mixture of two parts of tallow soap to one part of resinate and added pyrophosphate in increments of 5% from 5% to 25% decreasing the amount of soap resinate mixture a like amount. The results are plotted on the lower curve of Figure II. These solutions were at a pH of 9.5 which is about the normal pH of a 3% concentration of the salt water soap in artificial sea water. If we raise the pH to 11.0, we obtain the results shown by the upper curve. This result can be obtained by finishing the soap at a slightly higher alkalinity.

As shown above, we found that the most effective composition was two parts of tallow soap to one part of resinate and one part of alkali salts (part of which must be pyrophosphate). Of the alkaline salts we found that 50 to 60% could be metasilicate, N silicate or trisodium phosphate with the balance tetrasodium pyrophosphate. The effectiveness of these combinations is illustrated in Figure III.

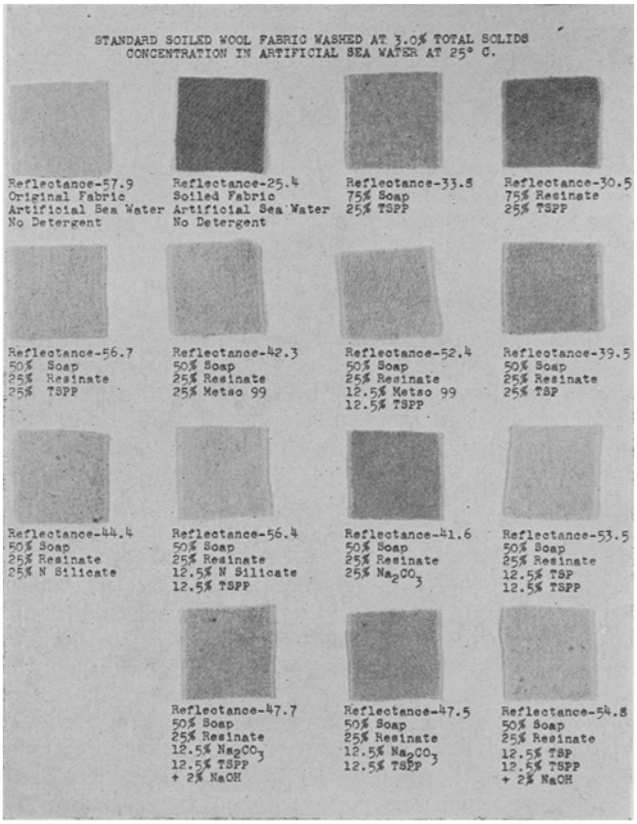

FIG. 3

The soap used in this work was a 42° titer tallow soap produced by Colgate-Palmolive-Peet under the trade name Arctic Crystal. The sodium resinate was a spray-dried material made by the saponification of refined wood rosin and sold under the trade name Dresinate. The alkaline salts were the usual grade used in soap production.

LITERATURE CITED

1. Pech, P. L. E., British Patent 156,591.
2. Pech, P. L. E., U. S. Patent 1,462,243.
3. Brunet, F., Chem. Abs. 17-2160.
4. Miyoke, Kimoshita and Tomeoka, Japanese Patent 42,569.
5. Pohle, W. D., Oil and Soap, p. 244, December, 1941.
6. Pohle, W. D., and Speh, C. F., Oil and Soap *17*, 214-16 (1940).
7. Borglin, J. N., Mosher, P. R., Noble, Barbara and Punshon, T., Oil and Soap, *20*, 77-84 (1943).