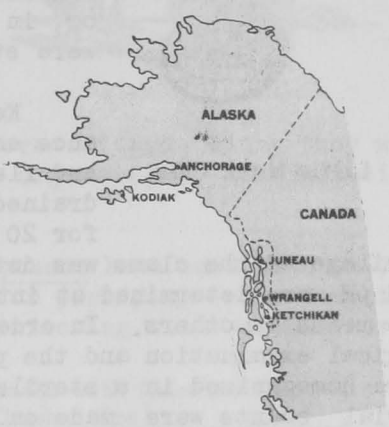
PRESERVATION OF SHUCKED ALASKA CLAMS

By Frank Piskur and Maurice E. Stansby *

Because of the depletion of the clam beds in Washington and Oregon, there is an unsatisfied demand for fresh clams in the markets of the Pacific Northwest. Abundant supplies of various clams are located in Alaska. Butter clams are taken in Southeastern Alaska and razor clams in the vicinity of Cordova. The greater part of the annual yield of these species is canned commercially, and only a small portion is sold fresh. Because freshly-shucked clams spoil readily, even at temperatures as low as 32° to 34° F., it is impossible to ship them to distant markets in a fresh condition.



It was the purpose of this investigation to develop methods for handling and storing fresh Alaska clams which would permit their distribution to markets on the Pacific Coast and possibly farther inland.

Very little work has been done on the preservation of fresh clams, although in recent years, there have been several reports on the preservation of fish and fish fillets. Chen and Fellers (1926) reported that ice containing 0.02 percent available chlorine was effective as a perservative for fish. Stansby and Griffiths (1936) showed that whole haddock stored in CO_2 from the time they were caught kept approximately twice as long as those stored in air. Tarr and Sunderland (1938) demonstrated that dips in 20 percent brine, containing 0.1 percent benzoic acid, exerted a favorable effect on the keeping quality of fillets and that this action was not improved by the addition of other acidic substances. The addition of citric acid, lactic acid, or potassium acid phosphate to the brining solution did not appear to improve the keeping quality of smoked fish. Tarr and Bailey (1939) found only a slight improvement in the keeping quality of dressed halibut and black cod which were stored in crushed ice containing 0.1 percent benzoic acid. Fellers and Harvey (1940) showed that benzoate treatment of fish fillets improved their keeping quality. In a later report, Tarr and Sunderland (1940) reported that ice containing small amounts (0.1 or 0.5 percent) of sodium nitrate was a markedly better preservative than ordinary ice.

Clams were obtained at five beaches near Ketchikan, Alaska:

Refuge Cove Mud Bay Peninsula Point Rosa Reef Mountain Point

These beds are situated five to seven miles from the city, so the clams were considered free of contamination from sewage and waste. The species found, in the order of their predominance, were butter clams (Saxidomus giganteus), Little Neck clams (Paphia staminea), cockle clams (Cardium corbis), horse clams (Schizothaerus nuttalliii), and mud clams (Mya arenaria). With the exception of one test with mud clams, only butter and Little Neck clams were used in the experiments.

As soon as they were dug, the clams were washed in fresh water and placed in a tank containing sea water, or 2 percent brine. A small amount of corn meal was

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added to the brine, and the clams were allowed to cleanse themselves for 8 to 10 hours by replacing sand with corn meal. This is a practice commonly used by some of the local clam canneries. The clams are then washed again and opened by hand. After being washed in fresh water, the meats were placed in a jar surrounded by crushed ice.

The meats were weighed into 8-ounce, wide-mouthed, screw-capped jars and covered with a definite volume of test solution. That is, 100 grams of clams was added to 100 ml. of storage solution, except that in Series C of Table 3 (see p. 8) the proportion of clams to storage solution was varied. Each sample was prepared in triplicate, or, in some cases, in quintuplicate, and the covered jars were stored at 32° to 34° F.

Little Neck Clam

Keeping quality of the raw clams was judged by appearance and odor. Some final lots also were rated for odor and flavor after cooking. For cooking tests, the meats were drained slightly, washed under fresh water, and then steamed for 20 minutes. The average time required for complete spoilage of the clams was determined from appearance and odor. Bacterial counts and pH were determined at intervals, on the storage solution in some cases and on the meats in others. In order to obtain representative samples for the bacteriological examination and the pH determinations, the meats were homogenized in a sterile Waring blendor. All bacterial counts were made on nutrient agar after 3 to 5 days incubation at 30° C. In several cases, particularly the experiments with sodium benzoate, the presence of a considerable number of pin-point colonies prevented accurate counting. Attempts were made to correlate bacterial counts and pH with keeping quality; however, considerable data on the change of pH of the storage solutions and bacterial counts have been omitted since no relationship was found.

Butter Clam

EFFECT OF pH OF STORAGE SOLUTIONS: Series A of Table 1 shows the effect of using 2 percent phosphate buffers as storage solutions at pH values of 4.5, 5.0,

Table 1 - Storage Life of Fresh Shucked Clams in Two Percent Buffer Solution
(In Glass Containers Packed in Crushed Ice)

Test Series	Storage solution[1]	pH	Average storage life	Average time elapsed before complete spoilage
			Days	Days
A	Phosphate buffer	4.5	8-9	over 12
	" "	5.0	8-9	over 12
	" "	5.5	8-9	over 12
	" "	6.0	5	8
	" "	6.5	5	8
	" "	7.0	4-5	6
	Tap water	-	2-3	6
	2% salt solution	-	2-3	5-6
	Clam nectar	-	2-3	5-6
B	Phosphate buffer	5.25	5-6	10
	Citrate buffer[2]	5.25	5-6	over 17
	Raw sea water, 3% salinity	-	2	4
C	Citrate buffer[2]	5.25	10	15
	Raw sea water, 3% salinity	-	3	7
D	Citrate buffer[2]	5.25	9	20
	Raw sea water, 3% salinity	-	2	5

1/ 100 grams clams per 100 cc. storage solution.
2/ The meats were found to be slightly bleached.
NOTE: Storage life is defined as limit of edibility (judged from appearance, odor, & taste).

5.5, 6.0, 6.5, and 7.0. Samples stored in fresh water, clam nectar, and 2 percent brine were used as controls. Storage in the phosphate buffer solution at pH 5.5 was effective in increasing the keeping quality of fresh clams 6 to 7 days over that of the controls. A solution of pH less than 5.0 tended to discolor the meats and to precipitate the protein; while at pH values above 6.0 the buffers had little perservative value. The pH of unbuffered samples decreased with storage time. In the cases of the buffered samples, the pH changes were quite irregular, and since no correlation was found, these data were omitted. In similar tests, 2 percent citrate buffer[1] at pH 5.25 (Series B, C, and D of Table 1) seemed to bleach the meats slightly and was as effective as phosphate buffer. Bacterial counts were omitted, since they were quite irregular and showed little correlation with organoleptic determinations of spoilage.

EFFECT OF CHEMICAL PRESERVATIVES: Chlorine compounds have been used in fish plants for disinfecting utensils and apparatus and for purifying water supplies. In Table 2 is shown the effect on clam meats of disinfecting the sea water prior

Table 2 - Storage Life of Fresh Shucked Clams in Water Treated with Chlorine Compounds (In Glass Containers Packed in Crushed Ice)

Test Series	Storage solution[1]	Preliminary treatment of clams	Average storage life	Average time elapsed before complete spoilage
			Days	Days
A,B,C	Raw sea water, 3% salinity	None	2	5
	Chlorinated sea water[2]	"	2	5
	Raw sea water, 3% salinity	Dipped in 10 times their weight of sodium hypochlorite solution containing 500 ppm. free chlorine for 15 seconds, and then drained.	2	4
	Raw sea water, 3% salinity	Dipped in 10 times their weight of "Nipicide" solution containing 500 ppm. available chlorine for 15 seconds, then drained.	2	5

1/ 100 grams clams per 100 cc. storage solution.
2/ Raw sea water, 3% salinity, treated with sodium hypochlorite to concentration of 5 ppm. available chlorine and allowed to stand approximately 10 hours, after which time 1 ppm. available chlorine remained in the solution.
NOTE: Storage life is defined as limit of edibility (judged from appearance, odor, & taste).

to use as storage solution. Fresh sea water was collected and treated with sodium hypochlorite to 5 p.p.m. available chlorine. The solution was allowed to stand approximately 10 hours, after which time there remained approximately 1 p.p.m. of available chlorine. It was found that clams stored in sea water treated in this manner did not have a longer storage life than those stored in untreated water.

Table 2 also lists the results obtained by using chlorine solutions as dips, and shows the comparison of the action of sodium hypochlorite and an organic chlorine compound in the dip. Such organic chlorine compounds may be more stable than inorganic hypochlorites and, consequently, be effective over a greater length of time. There are a number of these compounds which have been suggested for use

1/ Clark, W. M. (1928). p. 214.

with food. For these particular experiments, the commercial product known as "Nipicide" was employed. In each case, clams were dipped for 15 seconds in 10 times their weight of test solution, containing an equivalent of 500 p.p.m. available chlorine,[1] drained slightly, and placed in covered jars containing brine. Neither treatment proved to be of any value in enhancing the keeping quality of fresh clams.

Preliminary experiments indicated that sodium benzoate, although not consistently retarding bacterial growth, did have a marked action in augmenting keeping quality. Benzoate was applied in two ways: Directly to the solution in which the clams were stored, and dissolved in a dip used prior to storage of the meats in other solutions.

Series A and B of Table 3 shows the effect of adding 0.1 percent sodium benzoate directly to the storage solutions. Benzoate extended the storage life 5 to

Table 3 - Storage Life of Fresh Shucked Clams in Sodium Benzoate Solution
(In Glass Containers Packed in Crushed Ice)

Test Series	Storage solution[1]	Ratio of clams to storage solution[2]	Total sodium benzoate[3]	Average storage life	Average time elapsed before complete spoilage
			Percent	Days	Days
A	Raw sea water, 3% salinity	1:1	0	2	5
	0.1% sodium benzoate in raw sea water, 3% salinity	1:1	0.05	7	10
	0.1% sodium benzoate in citrate buffer	1:1	0.05	10	over 20
B	Raw sea water, 3% salinity	1:1	0.00	2	4
	0.1% sodium benzoate in raw sea water, 3% salinity	1:1	0.05	7-8	10-11
	Phosphate buffer	1:1	0.00	5-6	10
	0.1% sodium benzoate in phosphate buffer	1:1	0.05	10-11	over 17
	Citrate buffer	1:1	0.00	5-6	over 17
	0.1% sodium benzoate in citrate buffer	1:1	0.05	9-10	over 17
C[4]	0.50% sodium benzoate in citrate buffer	3:1	0.12	22-23	over 26
	0.40% sodium benzoate in citrate buffer	3:1	0.10	22-23	over 26
	0.30% sodium benzoate in citrate buffer	3:1	0.074	20-21	over 26
	0.20% sodium benzoate in citrate buffer	3:1	0.05	17-18	21-22
	0.10% sodium benzoate in citrate buffer	3:1	0.025	17-18	25
	0.05% sodium benzoate in citrate buffer	3:1	0.012	15-16	23
	0.10% sodium benzoate in citrate buffer	1:1	0.05	17	over 26
	Citrate buffer	1:1	0	13	over 26
	0.10% sodium benzoate in raw sea water, 3% salinity	3:1	0.025	17	over 26
	0.50% sodium benzoate in raw sea water, 3% salinity	1:1	0.12	22-23	over 26
	0.10% sodium benzoate in raw sea water, 3% salinity	1:1	0.05	17-18	over 26

1/All buffer solutions were of 2% concentration and at pH 5.25.
2/Ratio of 1:1 refers to 100 grams of clams per 100 cc. storage solution, etc.
3/Total percent sodium benzoate as calculated from total weight of clams and storage solution.
4/Mud clams only used in this series.
NOTE: Storage life is defined as limit of edibility (judged from appearance, odor, & taste).

1/Determined by arsenious oxide titration method. A.O.A.C. Ed. 5, p. 73, 1940.

9 days. Buffers containing added benzoate tended to increase the keeping time about 3 days longer than brine containing benzoate. This increased effectiveness of sodium benzoate in media of lower pH is similar to its action in the preservation of other foodstuffs.

Series C of Table 3 shows the effect of using smaller proportions of the citrate buffer solution and the effect of varying the concentration of sodium benzoate. The meats were placed in jars, and only enough storage solution was added to cover the meats. The highest concentration of benzoate used was a 0.5 percent solution, or a total of 0.12 percent, as calculated from the total weight of clams and storage solution.

Buffer solutions containing 0.1 to 0.13 percent sodium benzoate (total concentration of 0.05 percent), as well as sea water containing 0.1 percent sodium benzoate (total 0.025 percent), showed considerable protective action during 17 to 20 days' storage time, but higher concentrations of benzoate in the citrate buffer solution produced a slightly pungent odor (not a spoilage odor) which, however, was not evident after cooking. Only soft clams were used in this series, therefore, it is possible that the general increase in keeping quality was really a species characteristic.

A dip of sodium benzoate was quite effective also in prolonging the storage life of fresh clams (Table 4, p. 10). Individual samples of clams in this series were dipped for 30 minutes in one of the following solutions:

5 percent sodium benzoate in fresh water.

2.5 percent sodium benzoate in 2.5 percent brine.

1 percent sodium benzoate in 4 percent brine.

0.1 percent sodium benzoate in 4.9 percent brine.

The meats were drained and stored in sea water, benzoated brine, or a buffer solution.

In the second group of tests in Series A of Table 4, quintuplicate clam samples were dipped in the 1 percent sodium benzoate in 4 percent brine solution and then stored in sterilized sea water. Other samples of clams were dipped in the various benzoate solutions and stored in citrate buffer as a comparison. In addition, undipped samples, to serve as controls, were stored in sea water, citrate buffer, and 0.1 percent sodium benzoate in 3.5 percent brine. The sea water used in the experiments of Series A, Table 4, was first sterilized in an autoclave to eliminate any errors due to unnecessary contamination by extraneous bacteria.

Bacterial counts of both the dipped and undipped control samples stored in sterile sea water remained consistently low, while undipped samples stored in citrate buffer gave high counts after 2 and 7 days, although in organoleptic tests, the meats were judged as still being in good condition. The counts in the latter samples increased further with additional storage time. In the case of the clams dipped in benzoate brine and stored in the buffer solution, there was an actual decrease in bacterial count for a certain time, after which the counts again increased. Fellers and Harvey (1940), in their experiments with fillets, found that the protective action of benzoates appeared greater when odor and taste were used as criteria of spoilage rather than the number of bacteria. Tarr and Sunderland (1938) observed that benzoic acid suppressed trimethylamine formation without affecting the bacterial population of fish and concluded that either certain species of bacteria are inhibited or that the preservative alters the metabolism of the organisms.

The counts of the dipped samples stored in citrate solution remained consistently lower than those of the untreated samples, even at the point of inedibility. This seems to indicate that aerobic counts may be used for following the relative course of spoilage in a buffered sample, but that they are not an absolute criterion of the degree of spoilage at any given time. The pH of the meats decreased slightly as storage continued, although the changes were not great enough or consistent enough to be considered an accurate means of indicating the degree of spoilage.

Table 4 - Storage Life of Fresh Shucked Clams Dipped in Sodium Benzoate (In Glass Containers Packed in Crushed Ice)

Test Series	Storage solution 1/	Preliminary treatment of clams 2/	Storage time	Bacteria per gram clams	pH of clams	Average storage life	Average time elapsed before complete spoilage
			Days	Number		Days	Days
A	Autoclaved, raw sea water, 3% salinity	None (Control)	2	580	6.10		
			4	450	6.09		
			7	380	5.84	3	7
			9	440	5.81		
			11	300	5.88		
	Autoclaved, raw sea water, 3% salinity	1% sodium benzoate in 4% brine	2	190	6.09		
			7	360	5.93		
			11	300	5.89	9	16-17
			14	330	5.88		
			21	450	5.90		
	Citrate buffer	None (Control)	2	1.23×10^6	5.66		
			7	1.5×10^6	5.68		
			11	1.95×10^6	5.65	10	15
			14	22.8×10^6	5.67		
			21	13.6×10^6	5.64		
	Citrate buffer	1% sodium benzoate in 4% brine	2	720,000	5.70		
			7	440,000	5.68		
			11	420,000	5.70	10	21
			14	780,000	5.71		
			21	2.5×10^6	5.74		
B	Citrate buffer	5% sodium benzoate	7	1,130	-	14-15	over 20
			16	85,000	-		
	Citrate buffer	2.5% sodium benzoate in 2.5% brine	7	920	-	14-15	over 20
			16	1.34×10^6	-	14-15	over 20
	Citrate buffer	1% sodium benzoate in 4% brine	7	2,370	-		
			16	3.45×10^6	-	14-15	over 20
	Citrate buffer	0.1% sodium benzoate in 4.9% brine	7	3,150	-		
			16	150,000	-	9	18-19
	Citrate buffer	None (Control)	7	41,000	-		
			16	1.0×10^6	-	9	20
	Autoclaved, raw sea water, 3% salinity	" (")	7	2.13×10^6	-		
			16	-	-	2	5
	0.1% sodium benzoate in 3.5% brine	None	7	1.05×10^6	-	12-13	20
			16	45×10^6	-		

1/ 100 grams of clams to 100 cc. storage solution. All buffer solutions were of 2% concentration and pH 5.25.

2/ Clams were dipped in four times their weight of solution for 30 minutes.

NOTE: Storage life is defined as limit of edibility (judged from appearance, odor, & taste).

The protective action of sodium benzoate was, in general, fairly effective. The dipped samples remained in good condition in brine for about 9 or 10 days, which was approximately 6 or 7 days longer than the untreated samples. As was previously shown, storage of fresh clams in citrate buffer solutions seemed to augment the keeping quality. In this series, preliminary treatment with sodium benzoate and storage in buffer solutions was even more effective. The untreated

samples stored in citrate solution showed a storage life of 9 days. On the other hand, the benzoate-dipped samples stored in the same solution had a storage life of approximately 14 to 15 days.

The clams stored in 0.1 percent sodium benzoate in 3.5 percent brine had a keeping time of 12 to 13 days, while those stored in citrate buffer kept for only 9 days. Dipping the clams in a benzoate-salt mixture followed by storage in citrate buffer seemed to be the most effective treatment, inasmuch as samples so treated had a keeping time of approximately 14 to 15 days. The untreated samples stored in brine were not edible after 2 days. The spoilage rates of the clams were the same whether they were stored in raw or autoclaved sea water.

Chemical analysis (Association of Official Agricultural Chemists, 1940) of clams dipped 30 minutes in 1 percent sodium benzoate in 4 percent brine and stored over-night in 2 percent brine (100 grams clams--with 100 ml. brine) showed an average of 0.051 percent sodium benzoate absorbed by the meats and an average of 0.05 percent sodium benzoate remaining in the storage solution. Clams stored overnight in 0.1 percent sodium benzoate in 2 percent brine (100 grams clams and 100 cc. benzoate brine) were found to have absorbed an average of 0.050 percent sodium benzoate.

Samples of the clams stored for several days in buffer solutions, or in 0.1 percent sodium benzoate brine, and of those dipped in 1 percent sodium benzoate dissolved in 4 percent salt solution with storage in buffer and brine, were cooked for organoleptic tests. Comparisons were made with fresh untreated clams. For cooking tests, clams were first drained of their storage solution, washed slightly with fresh water, and finally steamed for 20 minutes. The treated samples compared favorably with the controls, and the taste panel observed no off-flavor or odor due to treatment with sodium benzoate or buffer solutions.

Conclusions

1. Storage in 2 percent phosphate or citrate buffer solutions tended to enhance slightly the keeping quality of fresh-shucked clams.

2. Dipping in hypochlorite or "Nipicide" prior to storage appeared to be of no value.

3. The use of sodium benzoate enhanced the keeping quality of fresh-shucked clams, and both dipping and storing in benzoate-brine solutions were found to be effective.

4. Samples treated with benzoate-brine and subsequently stored in citrate or phosphate buffer solutions at pH of 5.2-5.3 were found to have a storage life slightly longer than samples treated in the same manner but stored in 2 percent brine.

5. Clams that were dipped or stored in dilute sodium benzoate-brine were found to contain considerably less sodium benzoate than the 0.1 percent permitted in several other food products.

6. Sodium benzoate, in either the dipping or storage solutions, did not alter the flavor or palatability of fresh-shucked clams.

7. The use of sodium benzoate, together with buffer solutions, increases keeping quality sufficiently to permit shipment of fresh-shucked clams from Southeastern Alaska to consuming markets in the Pacific Northwest.

BIBLIOGRAPHY

1940. Association of Official Agricultural Chemists. Official and tentative methods of analyses. Ed. 5. 456 pages.

TUNG PAI CHEN and FELLERS, C. R.

1926. Fish Preservation by Hypochlorites. University of Washington Publication in Fisheries 1: pp. 205-227.

CLARK, W. M.

1928. The Determination of Hydrogen Ions. The Williams and Wilkins Company. Ed. 3, p. 210 and p. 214. Baltimore.

FELLERS, C. R., and HARVEY, E. W.

1940. Effect of Benzoated Brine Dips on Keeping Quality of Fish Fillets. Food Research 5: pp. 1-12.

STANSBY, M. E., and GRIFFITHS, F. P.

1935. Carbon Dioxide in Handling Fresh Fish. Ind. and Eng. Chem. 27: 1452 pp.

TARR, H. L. A., and BAILEY, B. E.

1939. Effectiveness of Benzoic Acid Ice for Fish Preservation. J. Fish. Res. Bd. Can. 4, 5: pp. 326-327.

------ and SUNDERLAND, P. A.

1938. Preliminary Note on the Keeping Quality of Lightly Smoked Fish. Progress Reports, Pacific Fisheries Experimental Station. Vol. 7, No. 37. Prince Rupert, Canada.

1940. Preservation in Ice. Use of Sodium Nitrate. Modern Refrig. 43, No. 503.