



## COLD STORAGE OF FROZEN PACIFIC OYSTERS (CRASSOSTREA GIGAS) - NO. 1<sup>1/2</sup>

### BACKGROUND

Very little information is available on the factors that determine the storage life of frozen oysters. The development of a frozen oyster product with characteristics comparable to those of the fresh product would be of economic value to the oyster industry. Increased acceptance of frozen oysters would result in a larger market and wider distribution.

Certain problems exist in regard to the successful freezing and storage of oysters. These include the formation of excessive "drip" (free liquor in thawed oysters after freezing), and the development of off-flavors, discoloration, and texture changes during storage. The current investigation is to determine the relative importance of these changes and to find practical methods of eliminating or minimizing them.

Members of the oyster industry are also interested in new methods of preparing oysters for the market. Recently there has been considerable activity in the field of specialty products, including canned and frozen oyster stew, and breaded and fried oyster products. Successful development and promotion of these products would give a boost to the industry.

This project was started in October 1954. As with all new projects, some time was spent by the researchers in becoming familiar with the problems involved, making a study of the literature, and developing techniques.

Laboratory work consisted of (1) a preliminary investigation into factors that may contribute to the formation of drip, (2) a study of the possible value of treating oysters with certain antioxidants, and (3) the development of special techniques for improving the quality of frozen breaded and fried oysters.

### STUDIES ON DRIP

Studies by Lanham, Kerr, and Pottinger (1948) with oysters from the Chesapeake Bay area showed that the amount of "bleeding" or free liquor exuded by oysters after they are shucked varies with the season, method of cleaning, location of the oyster beds, and other similar factors. When frozen oysters are thawed, the quantity of drip will vary considerably with the method of thawing and the method and time of draining.

In the present work on Pacific oysters, investigations of factors affecting drip included a study of (a) the effect of damage to the oyster meats during shucking, (b) the effect of holding the shucked oysters before freezing, (c) the effect of blowing time or washing of shucked oysters, and (d) the effect of temperature and time of thawing on the amount of drip developed.

<sup>1/2</sup>This work was carried out under a project financed in part by The Refrigeration Research Foundation.

The method used to determine drip is an adaptation of the Association of Official Agricultural Chemists (1950) procedure for raw shucked oysters and of the method used by Lanham et al. with Chesapeake Bay oysters.

Condition of Oysters	Can Number	Drip	
		Initial <sup>1/</sup> Percent	Final <sup>2/</sup> Percent
Undamaged	1	2.55	3.72
	2	3.35	4.60
	3	1.77	2.81
	4	2.44	3.64
	5	0.65	1.09
	6	1.05	1.82
	7	2.46	3.72
	Average	2.04	3.06
Damaged (Cut or broken)	11	2.92	4.65
	12	2.19	4.54
	13	1.88	3.76
	14	1.01	2.26
	Average	2.00	3.80

<sup>1/</sup> After draining for 2 minutes.  
<sup>2/</sup> Additional drip due to standing an hour at room temperature and being drained for another two minutes.

The shucked Pacific oysters, packed in hermetically-sealed cans, were thawed overnight at 34° F. and were then placed in running tap water (54 ± 2° F.) for 30 minutes. The cans of oysters were then weighed and opened, and the oysters were placed on a No. 4 sieve (4 meshes per inch; 0.185-inch opening), drained for 2 minutes, returned to the can, and reweighed. The percentage drip was calculated from the weight lost during draining.

**EFFECT OF DAMAGE:**

During shucking, the damaged (cut or broken) oysters were placed in a separate group from the undamaged ones. The

two groups were washed, packed in half-pound cans, frozen, stored for 3 days, thawed, and drained on a sieve, as previously described. After being drained and weighed, they were allowed to stand covered for an additional hour at room temperature in order to determine the effect of standing. The oysters were then drained for an additional 2 minutes and reweighed to determine any further loss in weight. The data (table 1) show no significant difference in the amount of thawed drip from the damaged and the undamaged oysters. More data are necessary, however, before a final conclusion can be drawn as to the effect of damage to oyster meats on the amount of drip formed.

**EFFECT OF HOLDING BEFORE FREEZING:** Some oysters are frozen immediately after shucking; others are held at refrigerated temperatures for several days before freezing. Preliminary experiments indicated that, at least in some cases, considerable drip forms in iced shucked oysters even before freezing. This point is being further investigated.

**EFFECT OF BLOWING TIME:** Pacific oysters are washed by bubbling air through them while they are suspended in water. This operation is known as blowing. Some experiments were carried out to determine the effect of blowing upon drip formation in the subsequently frozen oysters.

Blowing time was varied from 0 to 30 minutes, using 7 groups of oysters from the same batch. The blown oysters were packed in 1/2-pound cans hermetically sealed at 18 to 20 inches of vacuum, and frozen at -20° F. They were then transferred to 0° F. for a short period of storage.

Blowing Time in Fresh Water	Drip	Moisture <sup>2/</sup>
Minutes	Percent	Percent
<sup>1/</sup> 0	1.00	77.25
2 1/2	1.72	78.00
5	2.65	78.30
7	2.28	78.60
10	2.22	79.26
15	4.28	79.98
30	3.71	79.53

<sup>1/</sup> Control group.  
<sup>2/</sup> Moisture content of oysters, after removal of drip, using Erabender Moisture Tester.

The average amount of drip was calculated for each group, and the moisture content of the drained oysters was determined by the use of a Brabender Moisture Tester. The drip and moisture content showed a general tendency to vary directly with the blowing time (table 2). More data are needed to verify these findings.

**EFFECT OF THAWING TEMPERATURE AND TIME:** Studies were carried out to determine if differences in thawing time or temperature affect the amount of drip formed. Two experiments were made: series I, experimentally-handled oysters; and series II, commercially-handled oysters.

In series I, shucked Pacific oysters purchased in  $\frac{1}{2}$ -gallon cans in Seattle and transported to the Service's laboratory were sorted, and the undamaged oysters were repacked in  $\frac{1}{2}$ -pound cans; they were then hermetically sealed, frozen at  $-20^{\circ}$  F., and stored for 3 days at  $0^{\circ}$  F. The frozen oysters were divided into 5 groups of 6

Table 3 - Effect of Thawing Time and Thawing Temperature on the Amount of Drip Formed in Frozen Pacific Oysters Upon Thawing

Thawing Temperature Degrees F.	Thawing Method	Thawing Time	Drip	Moisture <sup>1/</sup>
		Hours	Percent	Percent
<b>Series I - Experimentally-Handled Oysters</b>				
34	Still air	42	3.21	78.87
48-52	Still air	25	2.52	78.53
65-70	Air with fan	$2\frac{1}{2}$	2.72	77.70
45-47	Water	4	2.79	78.10
110	Water	$\frac{2}{3}$	3.16	77.90
<b>Series II - Commercially-Handled Oysters</b>				
34	Still air	29	7.78	76.75
48-52	Still air	24	8.16	75.65
65-70	Air with fan	$3\frac{1}{2}$	7.92	76.10
47	Water	$4\frac{1}{2}$	6.81	76.00
110	Water	$\frac{1}{2}$	6.72	76.00

<sup>1/</sup>Moisture content of oysters after removal of drip using Brabender Moisture Tester.

cans each, and each group was thawed under one of the following sets of conditions: (a) in still air at  $34^{\circ}$  F., (b) in still air at  $48^{\circ}$  to  $52^{\circ}$  F., (c) in front of a fan at  $65^{\circ}$  to  $70^{\circ}$  F., (d) in water at  $45^{\circ}$  to  $47^{\circ}$  F., and (e) in water at  $110^{\circ}$  F.

There appeared to be no significant differences in the amount of drip formed under the various thawing conditions (table 3).

In series II, 10-ounce cans of commercially-frozen oysters that had been in storage at  $10^{\circ}$  F. for approximately 9 months were used. These oysters were divided into similar groups and thawed under the same conditions as those in series I.

In this series, there also appeared to be no significant differences in the amount of drip formed under the various thawing conditions (table 3).

The commercially-frozen oysters (series II) gave considerably more drip than did the experimentally-frozen oysters (series I). This difference in amount of drip is probably due to the longer time that the commercial oysters had been in cold storage.

#### USE OF ANTIOXIDANTS

An exploratory series of samples designed to determine the possible value of certain compounds for improving the color and flavor of frozen oysters were placed in storage. The seven variants used are listed on the following page:

Treatment:

- (1) None
- (2) Blanched
- (3) 1-percent ascorbic acid
- (4) 1-percent ascorbic-citric acid (8-percent ascorbic : 92-percent citric)
- (5) 0.05-percent NDGA-BHA mixture<sup>1/</sup>
- (6) 0.05-percent NDGA-BHA mixture in gelatine (1 tablespoon dry gelatine : 1 pint water)
- (7) Gelatine in water (1 tablespoon gelatine : 1 pint water)

<sup>1/</sup> 10-percent nordihydroguaiaretic acid ; 20-percent butylated hydroxyanisole ; 64-percent propylene glycol : citric acid (percentage of citric acid is not known).

The samples were sealed in half-pound cans, half of which were evacuated. These samples have been in storage too short a time to show any trends. If any of the treatments show promise, an extensive series will be prepared for storage.

## SPECIALTY PRODUCTS

Breaded raw oysters freeze together and must be thawed in order to be separated before being fried. If a method could be devised by which this freezing together could be avoided, the product would be much more convenient for use.

There are several possible approaches to the problem, including (a) treatment to firm the oyster meats or (b) coating the breaded product before packaging. Some exploratory work has been done using these two approaches to the problem, but no results are available as yet.

## LITERATURE CITED

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## OIL RESEARCH PROJECT AT THE SEATTLE TECHNOLOGICAL LABORATORY

OBJECTIVES OF THE PROJECT: The oil research project of the Seattle laboratory is a part of the national basic research program on marine oils developed under the Saltonstall-Kennedy Act. Since the beginning of the Seattle project, a main objective has been the preparation of chemical products (i. e., chemical derivatives) by modification of the fatty-acid structures occurring in marine oils. Other objectives of the project include the determination of chemical and physical properties of the products prepared, and the development of procedures for the separation of marine-oil fatty acids and their chemical derivatives.

The need for studies of chemically-modified products lies in the fact that new and better uses for fats and oils depend largely on chemical modification. This fact is evident if one considers the economic importance to the oil industry of processes, such as catalytic hydrogenation, developed early in this century, or the more recent

production of detergents and alkyd resins. Potential developments in fats and oils through chemical modification are virtually limitless.

Although research on new products from most commercial oils is being carried on at an ever-accelerated pace, there have been relatively few publications in the chemical literature describing synthetic chemical work using marine oils as the raw material. Fortunately, there are a variety of reactions known which can be applied to fish oils, and it is the first objective of this project to select some of these reactions, apply them to fish oils, and study the properties of the products obtained.

Modification of marine oils can be brought about in two major ways: (1) by modifying the carboxylic group of the fatty acids to produce such substances as long-chain alcohols, halides, and siloxanes, (2) by oxidizing or adding chemical groups to the double bonds of the unsaturated fatty acids to produce, for example, dicarboxylic acids, poly-halides, and poly-amino acids.

A second objective of the Seattle project is to determine some of the more common chemical and physical constants of the products prepared. These constants include boiling points, melting points, refractive indices, composition, iodine values, and spectrophotometric data.

A difficulty encountered throughout the work has been the lack of samples of individual fatty acids characteristic of marine oils. The preparation of even small fatty-acid samples of a moderate degree of purity is very time consuming. Nevertheless, fairly large samples of fatty acids (in the range of 50 to 100 g.) have been needed in order to work out the difficulties encountered in the chemical reactions involved in the project. For this reason, the inexpensive and easily obtained fatty acids--stearic, palmitic, and oleic acids--have been used in the initial studies of each reaction. The use of these common fatty acids offers an additional advantage in that properties such as boiling points and refractive indices of many of their derivatives, for example, the corresponding alcohols and halides, are known. This fact is of great help to the investigator in the isolation of the reaction product and in computing yields.

After the reaction procedure has been developed to the point where a clean reaction product can be obtained in good yield, the reaction can be applied to marine-oil fatty acids and the products produced can be isolated and studied.

Since marine oils contain a wide variety of fatty acids--varying both in chain length and degree of unsaturation--it is necessary that separations should be carried out to yield pure or nearly-pure fatty acids or their chemical derivatives. In this way, the products produced will have uniform (and measurable) chemical and physical properties. Such uniformity is highly desirable if any commercial application should be attempted. Thus, a third objective of the project is to carry out separations of the marine-oil fatty acids and their derivatives by means of such techniques as vacuum distillation, fractional precipitation, and inclusion-compound formation.

EXPERIMENTAL WORK: The first group of chemical derivatives studied under this project were the long-chain alcohols. These compounds were selected because they are important both from a commercial and research viewpoint as intermediates in the production of a wide variety of other chemicals, such as detergents. There are two general methods available for converting fish oils to alcohols: sodium reduction and catalytic reduction.

Sodium reduction is applicable both to laboratory and industrial use and consequently has been the method used in this work. The procedure, essentially as described by Pryde (1951), involves the suspension of finely-divided sodium in boiling xylene. To this suspension, a mixture of the fatty acid ester (either glyceride or methyl ester), the reducing alcohol, 2-methyl, 4-pentanol, and xylene is added at a

controlled rate of flow. The reaction mixture must be well agitated so that the sodium particles can react with the fatty-acid ester and reducing alcohol. After the addition is completed, the reduction mixture is agitated at reflux temperature for an hour and is then slowly poured into a hydrolysis and steam-distillation apparatus. The long-chain alcohols are liberated from the reduction mixture by hydrolysis, and the reducing alcohol and xylene are removed by steam distillation.

The details of the sodium reduction were worked out by preparing cetyl alcohol from methyl palmitate; octadecyl alcohol from methyl stearate; and oleyl alcohol from methyl oleate. The reaction was then applied to the natural glycerides of menhaden and pilchard oils. The crude mixed alcohols were obtained in 85- to 90-percent yield as brown semisolid oils. They were separated into saturate and unsatu-

Table 1 - Boiling Points and Refractive Indices of Long-Chain Compounds

Compound	Boiling Point		Refractive Index	
	Temperature	Pressure	No.	Temperature
	Degrees C.	Mm. of Hg.		Degrees C.
Cetyl alcohol . . . . .	187 - 191	15	1.4283	79
1-octadecanol . . . . .	207 - 211	15	-	-
Oleyl alcohol . . . . .	207 - 211	15	1.4607	20
Hexadecyl bromide . . . . .	197 - 203	21	1.4593	20
Octadecyl bromide . . . . .	213 - 216	14	1.4441	70
Oleyl bromide . . . . .	142 - 147	1	1.4692	25
Octadecyl iodide . . . . .	180 - 190	7	-	-
Octadecyl chloride . . . . .	190 - 205	12	-	-
Oleyl chloride . . . . .	190 - 202	12	-	-
$\Delta^4$ octadecenyl trichlorosilane	166 - 167	1.5	1.4644	25
Hexadecyl trichlorosilane . . .	199 - 201	10	1.4553	27.5

rate fractions by precipitation from acetone at  $-18^{\circ}$  C. These fractions at present are being separated into more refined fractions by fractional distillation and urea-inclusion compound formation. A publication describing the preparation and properties of the long-chain fatty alcohols from pilchard oil is planned in the near future.

Cetyl, octadecyl, and oleyl alcohols have been used for the preparation of the long-chain halides, another important group of intermediate organic compounds. By the use of the halides, it is possible to prepare quaternary salts, nitrites, amines, and Grignard reagents. Several different methods of converting alcohols to halides have been studied, including the use of hydrogen halide acids, thionyl chloride, and phosphorus trihalides. The latter compounds, especially phosphorus tribromide, gave the best results. It appears to be difficult to convert unsaturated alcohols to the corresponding halides, owing to the reactivity of the double bonds. However, oleyl bromide and oleyl chloride have been made, and the preparation of halides from the polyunsaturated marine-oil alcohols soon will be studied.

The long-chain halides are being used to prepare long-chain alkyl silicone polymers. In the past 20 years, a tremendous amount of work has been done on silicone polymers containing alkyl groups of one to four carbons, and such compounds have become important commercial products. However, practically no information is available concerning silicone polymers containing alkyl groups of 12 to 24 carbons and with unsaturated bonds in the alkyl chain. Since alkyl groups of these chain lengths are readily available from the fatty acids of fats and oils, a study has been started of silicone polymers containing long-chain alkyl groups.

The preparation of the cetyl silicone polymer is typical of the methods used in the work. Cetyl bromide, distilled at  $197^{\circ}$  to  $203^{\circ}$  C./21 mm. of mercury was reacted with magnesium in dry ether to form a Grignard reagent. The Grignard reagent was added with rapid stirring to an ethereal solution of silicon tetrachloride, precooled to  $0^{\circ}$  C. The main product from this reaction was cetyl dichlorosilane, which was distilled off. The cetyl dichlorosilane was hydrolyzed by pouring over cracked ice. After the hydrolysis was complete, the cetyl silanol, which had pre-

cipitated as a white, amorphous solid, was filtered off and dried in vacuo. The dried silanol was then polymerized by heating in a vacuum oven at 90° C. for 18 hours. This crude polymerized cetyl derivative was a tan-colored solid.

Other silicone polymers prepared in addition to the cetyl derivative include the octadecyl and oleyl derivatives.

The boiling points and refractive indices of some of the long-chain alcohols, halides, and chlorosilanes are given in table 1. The data on  $\Delta^9$  octadecenyl trichlorosilane has not been previously published.

The work dealing with separations of fatty acids and their derivatives has involved both conventional fractional-distillation procedures and also the newer technique based on urea-inclusion compound formation. A publication describing the work at the Seattle laboratory on the application of urea to the separation of marine-oil fatty acids recently appeared (Domart, Miyauchi, and Sumerwell 1955). A second paper on this subject will soon be ready for publication.

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## FEDERAL SPECIFICATION FOR CANNED SHRIMP

Federal specification "Shrimp; Canned" (PP-S-311a) was issued by the General Services Administration on September 8, 1955. This specification was developed for the use of all Federal agencies and supersedes Interim Federal Specification PP-S-00311a issued November 18, 1954, and Federal Specification PP-S-311 issued March 31, 1931.

Single copies of the specification for bidding purposes may be obtained, without charge, from the General Services Administration Regional Offices in Boston, New York, Atlanta, Chicago, Kansas City (Mo.), Dallas, Denver, San Francisco, Los Angeles, Seattle, and Washington (D.C.) It is also sold at 10 cents a copy by the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

