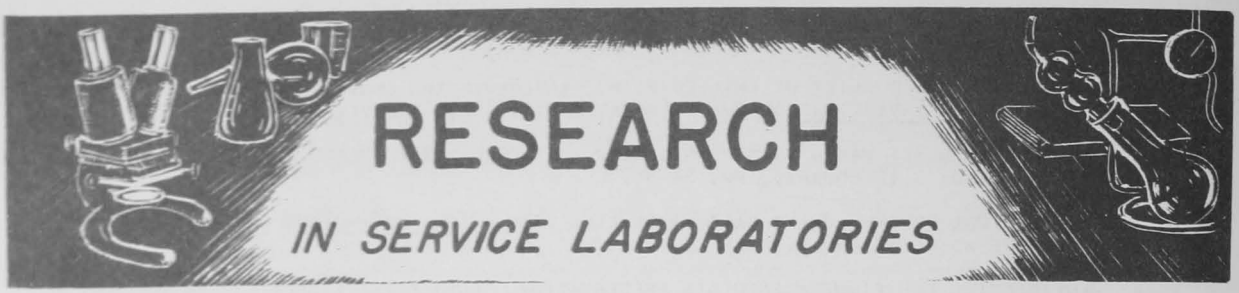

PROGRESS ON STUDIES IN UTILIZATION OF FISH-OIL DERIVATIVES IN ORE FLOTATION[1/]

By S. R. B. Cooke*

PREFATORY ABSTRACT

THIS PAPER DESCRIBES THE FLOTATION PROCESS, THE MECHANISM OF COLLECTION, AND THE FLOTATION OF IRON ORE WITH FISH-OIL DERIVATIVES AS COLLECTORS. IT SUMMARIZES EXPERIMENTAL FINDINGS TO DATE AND OUTLINES FUTURE WORK.

BACKGROUND

FLOTATION PROCESS: Flotation is a process of ore concentration used to separate a specific mineral or group of minerals, called the concentrate, from another mineral or group of minerals, known as the gangue or tailing. To effect the separation, operators use chemical reagents. These reagents are commonly divided into four groups known, respectively, as collectors, frothers, activators, and depressants. Most reagents function uniquely as a member of only one of the designated groups. Occasionally, a reagent may function as both a collector and a frother.

Collectors develop hydrophobic surfaces upon certain minerals, permitting them to become attached to the gas-liquid interface. Such "surfaced" mineral particles, upon collision with gas bubbles created in the pulp by various means become attached to the bubbles and will be buoyed to the surface of the pulp. Minerals that have hydrophilic surfaces, intentionally created or otherwise, remain in the body of the pulp and will not be spacially separated in the pulp.

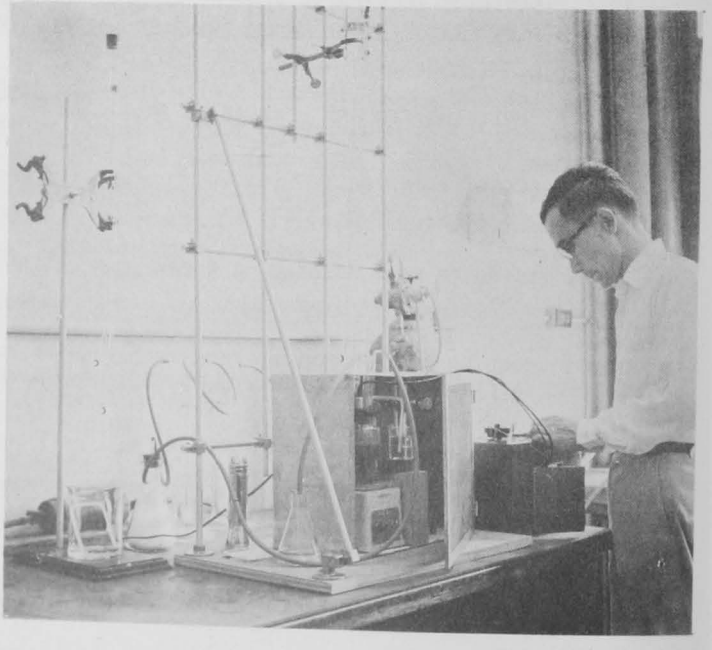

FIG. 1 - PORTION OF FLOTATION RESEARCH LABORATORY, SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MINNESOTA. DR. I. IWASAKI IS INVESTIGATING THE INTERFACIAL PROPERTIES OF FERRIC OXIDE.

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1/THIS PAPER WAS PRESENTED IN PART AT THE PACIFIC FISHERIES TECHNOLOGISTS' MEETING AT YAKIMA, WASH., MARCH 26, 1957.

NOTE: THIS STUDY IS BEING CONDUCTED UNDER A BUREAU OF COMMERCIAL FISHERIES CONTRACT BY THE UNIVERSITY OF MINNESOTA, AND FINANCED WITH FUNDS PROVIDED BY P. L. 466, 83RD CONGRESS, SIGNED JULY 1, 1954 (SALTONSTALL-KENNEDY ACT).

Frothers are reagents that, when added to the pulp in the presence of a gas phase, develop a reasonably stable foam or froth at the surface of the pulp. This froth normally carries the hydrophobic mineral, and can be removed from the flotation system by overflow or by raking. Frothers not only permit the generation of very fine bubbles within the pulp, thereby increasing the probability of collision with hydrophobic minerals, but they also increase the total gas-liquid interfacial area at the surface of the pulp and so enhance enormously the capacity of the system for separating mineral.

Activators are reagents that, upon being added to the system, induce flotation of a mineral which is not otherwise responsive to a given collector.

Depressants are the inverse of activators, in that they specifically inhibit the flotation of minerals that otherwise would float in the presence of a given collector.

High specificity of a reagent in its given function should result in a highly selective flotation separation; that is, concentrate should be quantitatively separated from tailing. This is an ideal that rarely, if ever, is realized. Specificity, on a practical basis, may be approached by adjustment of many variables, some of which are listed below:

(a) Level of reagent addition.

(b) pH of the pulp.

(c) Ratio of solids to liquid in the pulp.

(d) Temperature and time of conditioning and of flotation.

(e) Type of frothers, collectors, activators, and depressants employed.

(f) Anions and cations naturally present in the liquid.

(g) Type of aeration.

Probably the most selective separations made today are those between the sulphide minerals and gangue minerals such as oxides, carbonates, quartz, and silicates. These separations are effected by using certain sulphydryl collectors such as the alkyl xanthates and the organic dithio-phosphates. Control of certain of the variables listed may even permit successive flotation of individual sulphide minerals, such as galena, sphalerite, and pyrite, in that order. Because of the low unit cost of the sulphydryl collectors and their extraordinary effectiveness for sulphide-nonsulphide mineral separations, it is unlikely that they will be displaced by other reagents.

To date, separations of nonsulphide minerals, one from the other, are more difficult to effect. Various organic compounds have been proposed and utilized, both in the laboratory and in practice, as collectors for oxides, carbonates, silicates, and other minerals. Usually, such minerals have low unit value, and the high cost of some reasonably effective reagents automatically excludes them from use. Commercially, calcium phosphate is separated from quartz, fluorite from calcite and quartz, scheelite from associated silicates and quartz, baryte from silicates, and iron oxides (particularly hematite) from quartz. There are many other examples. In few cases, however, does the selectivity of the reagent employed equal that of the sulphydryl collectors for sulphide minerals.

The practical separation of the nonsulphide minerals dates back to the Christensen patent (U. S. pat. 1,467,354) in which fatty acids and their soaps were proposed as collectors. Since then, it has been shown that, with proper control of other factors, the fatty acids and their soaps, alkyl sulphates and sulphonates, alkylamines,

quaternary ammonium salts, and pyridinium salts can be utilized to make reasonably effective separations.

Of the foregoing substances, the fatty acids and their soaps are the cheapest. Therefore, provided that they will work as desired, the flotation engineer is predisposed in their favor. The selection of the collector is normally based on the economics of the situation. In the flotation of rhodochrosite (manganese carbonate), for example, cottonseed-oil foots is saponified and used directly as a collector. In other cases, the relatively inexpensive aliphatic acids derived from tall oil are in common use. Fish-oil fatty acids and their soaps have been used in the past, but for reasons unknown to the writer, they are not currently in favor.

It should be pointed out that, although the consumption of fatty acids in ore flotation is small in terms of pounds per ton of crude rock (ranging from 0.5 to 2.5 pounds per ton), the over-all consumption in the United States is impressive. The cement industry uses about 1,000,000 pounds of fatty acid annually; fluorspar flotation, about 500,000 pounds; and baryte, over 600,000 pounds. Iron-ore treatment has lagged behind other ores in this respect, primarily because of the relatively high cost of reagents, but two Michigan mills are currently treating approximately 3,400 tons of ore per day. The average annual consumption of crude oleic acid in these two plants is about 2,500,000 pounds. With the depletion of high-grade iron ores in the Lake Superior region, flotation is in the position of being a competitive means of concentration, and fatty acids and related materials will be used for this purpose. In view of the great tonnages that are to be treated, the consumption of fatty acid will be very large. This fact explains the preoccupation with iron-ore flotation in the contract with the U. S. Fish and Wildlife Service. The figures given above are conservative. Other ores use fatty acids in flotation, but the data regarding consumption are difficult to obtain.

MECHANISM OF COLLECTION: As a result of a very considerable amount of fundamental research, the generalization may safely be made that all water-soluble collectors are heteropolar in nature. When collection occurs, the polar grouping becomes attached to the surface of the mineral, and the nonpolar grouping then is oriented away from the mineral. Because the nonpolar group in chemical collectors is invariably a hydrocarbon radical, this is analogous to "coating" the mineral with a water-repellent surface. Gas then may partly displace water at the surface, the collector acting as a bond between the gas and the mineral. How the polar group of the collector is attached to the mineral surface still is disputed. If it is assumed that the mineral surface is the locus of ruptured bonds, and that for full coverage (that is, a monolayer) one collector ion is required per ruptured bond, then it has been demonstrated elsewhere that, for the ordinary sizes of minerals floated, only from $\frac{1}{2}$ to 10 percent full coverage is required.

The mechanism of collection of minerals by fatty acids is imperfectly understood. Clean quartz, a very common gangue mineral, is not collected by fatty acids if activating cations are absent from the pulp. At high pH, however, calcium ions are adsorbed by quartz. These ions then act as bonds between the quartz and the fatty acid ions, and the quartz becomes floatable. Using this process, the operator can quantitatively float quartz away from hematite, which is not collected by the acid at the pH employed.

On the other hand, hematite will respond to collection with fatty acid in the pH range from 5 to 8, and may be floated away from clean quartz in the absence of quartz-activating ions.

In fatty acid flotation, it is not even clearly established whether the free acid, the fatty acid ion, the acid soap ion, or combinations of any of these, or even all of them, is the cause of mineral collection. It seems most probably that the fatty acid ion is the effective collector.

Some reagents may play dual roles in flotation. The fatty acids and their soaps illustrate this principle, for they commonly are employed as both collectors and frothers. Oleic acid is a weak frother at low pH. As the pH is increased, the froth increases in volume and changes markedly in size of bubble. Overfrothing is as undesirable as underfrothing. In the former case, so much of the pulp proper may be occluded by the froth that selectivity is seriously impaired; in the latter, there is insufficient froth to remove the concentrate. Addition of a second frother (such as pine oil), in an effort to build up the froth, frequently results in complete destruction of the froth at certain relative levels of fatty acid and of independent frother. This situation adds another variable to the already complex system.

The saturated fatty acids and their soaps, from caprylic through stearic, are fairly effective collectors for hematite, the amount of reagent required for a given recovery decreasing with chain length. Saturated fatty acids with more than 18 carbon atoms are relatively ineffective. On the other hand, oleic acid is an excellent collector for hematite, very much less being required for a given recovery than any acid mentioned above. Linoleic and linolenic acids, in the order given, are decreasingly effective compared with oleic acid.

Mixtures of oleic acid with saturated aliphatic acids seem to be more effective than their content of oleic acid would indicate. The reason for this is obscure.

FLOTATION OF IRON ORE WITH FISH-OIL DERIVATIVES AS COLLECTORS: The purpose of the contract with the U. S. Fish and Wildlife Service is to study the applicability of fish-oil fatty acids and of their derivatives to the selective flotation of nonsulphide ores and mineral aggregates, with the purpose of ascertaining if such reagents are technologically competitive with fatty acids derived from other sources. Because of the local availability of iron ores and the writer's familiarity with their flotation, such ores were chosen for the initial portion of the investigation.

Preliminary work was carried out on a specularite ore similar to material currently being concentrated commercially by fatty acid flotation in Michigan. Most of the investigation has been confined, however, to a close study of the response of a Mesabi wash-ore tailing to various aliphatic acids. Oleic acid was used as a control and was of different degrees of purity, ranging from Eastman oleic acid (approximately 93 percent oleic acid) to pure oleic acid (99+ percent) furnished by the Hormel Institute. The acids investigated were various bulk unsaturated fatty acids derived from fish oils in laboratories of the University of Minnesota, a long series of unsaturated fatty acids separated from tuna and menhaden fish oils by the Hormel Institute under the direction of Dr.W. O. Lundberg, and a number of other fatty acids the behavior of which, as collectors for hematite, required investigation.

The Mesabi wash-ore tailing consisted of a mixture of hematite, goethite, magnetite, and relatively clean quartz. It was known to respond equally well to anionic (fatty acid) flotation and to cationic (alkylamine salt) flotation. It required very little grinding and very little scrubbing to remove superficial iron oxides from the quartz. By selecting this particular ore, we were able to reduce, if not to eliminate entirely, the effect of extraneous variables such as slime content, alkali-earth metal content, variation in hematite-geothite-magnetite ratio, and the effect of superficial iron oxide coating on the quartz. These are factors that change from ore to ore, and the elucidation of their effects on even a few types of material would tax much more extensive facilities than happen to be available here.

Primary slimes consist of near-colloidal or colloidal material released from ore during grinding, and are differentiated from secondary slimes in that the last-mentioned are a direct product of the comminuted minerals. Primary slimes are frequently a source of trouble in flotation, perhaps more so with iron ores than with others.

Our own past experience, which agrees with results obtained in other research laboratories, indicates that conventional flotation of iron ores containing primary slimes is a virtual impossibility because of excessive consumption of reagent by slimes and because selectivity is very low. This is true whether anionic collectors (generally fatty acids) or cationic collectors (generally alkylamine salts) are used. In the current investigation, a number of tests have been made using fatty acid collection on ores from which the primary slimes have not been removed. At room temperature, in no case was selectivity obtained between the iron minerals and the gangue; recoveries were invariably low; and frothing characteristics were extremely poor. For this reason, the current investigation was limited primarily to that fraction of the iron ores coarser than 20 microns.

Impure mixtures of fatty acids have been used in mineral flotation for many years, particularly crude oleic acid. There is a remarkable lack of published information, however, regarding the effects of even the most significant variables upon fatty acid flotation. Apparently, few if any systematic investigations have been made concerning (1) the behavior of pure or relatively pure fatty acids as collectors and frothers, (2) the effect of isomeric differences in structure upon function of the collecting agents, (3) the optimum pulp pH for specific mineral separations, or (4) the effect of elevated temperature upon efficiency of flotation. During the progress of the investigation, it has been found necessary to depart at times from the routine of scheduled testing to elucidate, if only in a most preliminary way, the effects of some of the variables listed above. These departures have served to improve our understanding of the mechanisms involved in fatty acid flotation and to give us a better understanding of the application of fish-oil fatty acids to flotation.

SUMMARY OF EXPERIMENTAL FINDINGS

As reported in an earlier article (Cooke and Stansby 1957), an empirical relationship exists between the iodine value of a number of fatty acids and the corresponding selectivity indices for an iron ore wash tailing, using 0.5 pound of collector per ton of ore, a pH of 6, and floating at room temperature. All of the unsaturated acids prepared by the Hormel Institute from menhaden and tuna oils, and a number of other acids have been tested under similar conditions; the relationship is of general application. Maximum selectivity index occurs between pH 6 and 7 for all except one or two nonfish-oil acids.

The unsatisfactory results given by acids with iodine values greater than about 115 were unexpected and are difficult to explain on the basis of present information. Because highly unsaturated acids are important constituents of fish-oil fatty acids, considerable thought has been given to this problem, and some short-term experimental work is being done to confirm or disprove a number of theories regarding their function in flotation.

Frothability, froth stability, bubble size, and wetness of froth differ with the degree of unsaturation of the fatty acid. All of these factors markedly influence the selectivity index, but not always detrimentally. For optimum flotation, there must be a proper balance between collecting and frothing.

Synthetic mixtures of stearic, oleic, linoleic, and linolenic acids, with iodine values averaging about 105, have been used for flotation at 0.5 pound per ton of ore, pH 6, and room temperature. It is significant that mixtures containing more than a certain proportion of either linoleic or linolenic acid give poor selectivity and excessive froths.

Spot flotation tests have been made on a scheelite ore containing 1 percent WO_3. One-half pound of pure oleic acid per ton of ore gave a poor froth and a low recovery. The same quantity of bulk menhaden fatty acid (I.V. = 217) at pH 10 gave excessive froth. Decreasing the level of addition of the acid to 0.25 pound per ton of

ore and floating at pH 9 gave good frothing characteristics and good flotation of the scheelite. In the case of iron ore, decrease in the level of addition of unsaturated fatty acid from 0.5 pound through 0.25 pound to 0.125 pound per ton of ore decreased the froth volume, gave a higher selectivity between the iron oxides and the quartz, but lowered the selectivity index owing to a sharp decrease in the weight of concentrate.

A general conclusion to be drawn from the work to date is that, at room temperature, the highly unsaturated fatty acids are potent frothers, and when present in moderate concentration in a mixture of fish-oil acids, they necessarily contribute to the excellence of a separation. The over-all effect of excessive concentration of such acids is detrimental. This statement should not be taken to mean that fish-oil fatty acids are precluded as flotation reagents, for in any use of fish oils for other purposes in which the highly unsaturated acids are required, the fatty acids of intermediate value would remain, and could be used for flotation.

Attention was directed earlier in this article to a number of variables that control selectivity of separation--among them temperature of conditioning and flotation. The work reported above was conducted at room temperature, but a few spot tests were made on iron ore, using 0.5 pound of oleic acid and of the relatively saturated fraction (I.V. = 116) of a menhaden oil bulk fatty acid. The results were so excellent that similar tests were made using linoleic and linolenic acids, and several of the fish-oil fatty acids with iodine values greater than 190 and which are listed on figure 4 of the report by Cooke and Stansby (1957).

Analyses of the products are not yet available, but the weights and remarkable cleanness of the products indicate extremely effective separations. Froths, with a given acid, are markedly different at elevated temperatures from those obtained at room temperature; flotation rates are greatly enhanced; and slime interference is reduced. Results to date indicate, for acids lying on or near the right-hand portion of the curve of figure 4 of the reference already cited, that elevated flotation temperature brings their performance close to that of oleic acid at the same temperature and gives results that are greatly superior to that of oleic acid at 25° C.

Although the economics of high-temperature flotation has not been investigated, it is known that one industrial plant is competitively floating fluorite using steam injection. As far as the flotation of iron ore is concerned, our work has opened a new and promising field of investigation, not only with regard to utilization of highly unsaturated acids, but also with respect to excellence of the separation *per se*.

An unexpected result of an investigation of a number of pure fatty acids is that the trans-isomers are more effective collectors than are the corresponding cis-isomers.

FUTURE WORK

Spot tests, using bulk fatty acids derived from fish oils, and the more promising of the unsaturated members isolated by the Hormel Institute, are being made on scheelite and hübnerite (tungsten) ores. Arrangements were made for a shipment of fluorite sink-and-float tailings, and work will be extended to this material. In view of the general excellence of the results obtained by flotation of iron ore at elevated temperatures with most of the fish-oil fatty acids, some isolated tests will also be made with these other ores at 50° C. or higher.

Certain fatty acids substituted in the double bond will be available from the Hormel Institute and will be used for similar tests.

LITERATURE CITED

COOKE, S.R.B., AND STANSBY, M.E.
1957. UTILIZATION OF FISH OILS IN ORE FLOTATION. COMMERCIAL FISHERIES REVIEW, VOL. 19, NO. 4A (APRIL SUPPLEMENT), P. 24.

NOTE: ACKNOWLEDGMENT IS MADE TO M. E. STANSBY FOR HIS INTEREST AND SUGGESTIONS; TO H.S. CHOI, WHO CARRIED OUT THE FLOTATION TESTS; TO K.V. BATRA, WHO MADE THE TUNGSTEN ASSAYS AND CERTAIN ORGANIC SEPARATIONS; AND TO H.H. WADE, DIRECTOR OF THE MINES EXPERIMENT STATION, MINNESOTA SCHOOL OF MINES AND METALLURGY, WHOSE LABORATORIES MADE THE IRON ANALYSES.

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DEVELOPMENT OF OBJECTIVE TESTS FOR QUALITY OF FRESH, FROZEN, AND PROCESSED FISH[1/]

(Nontechnical Summary)

The purpose of the research study was to develop objective chemical or physical tests by which the quality of fresh and frozen raw fishery food products could be determined. A suitable test would directly indicate the quality level of the fishery food product at the time tested and possibly provide a means of estimating the keeping quality of the product during subsequent iced or frozen storage. For such a test to be practical it must be reliable, simple, rapid, and relatively inexpensive.

The primary and most important value of the test would lie in its use as an aid to marketing throughout the distribution chain. The buyer and seller would know exactly the quality of the product involved in each transaction. Specific methods of application would be: (1) evaluation of the quality of fish landed at the dock (this would serve as a basis for sales between fishermen and packers); (2) evaluation of the quality of the manufactured or processed product (this would serve as a basis for sales between packer and broker, and it would also provide a basis for determining the market range and storage time for the particular product); and (3) as an objective measurement of quality it would serve as a legal basis in any court action and in State and Federal inspection and standardization programs at any stage in the distribution chain.

On June 1, 1955, a one-year contract was awarded to the Massachusetts Institute of Technology by the U. S. Fish and Wildlife Service to study the problem. The contract was renewed the second year to provide more complete data and to investigate additional approaches to the problem.

Iced fish spoil as a result of action of the bacteria present on the fish and from the enzymes normally present in the fish meat. This action results in the production of many degradation products. As these products begin to accumulate in the fish meat, undesirable odors and flavors are noted which in turn adversely affect the palatability or quality of the product.

Except for water, protein is the major component of most fishery products. The pattern for the spoilage of fish may usually be closely related to the production of degradation products from the protein fraction of fish. Realizing this the MIT researchers decided to investigate the degradation products of fish-meat protein as a means of developing an objective test for the quality of the fish. The problem, then, was to isolate and identify the various protein degradation products and to determine whether or not the progressive accumulation of these products in the fish meat would reliably indicate the quality of the fish at any given time. For comparison with the proposed objective tests, the actual quality of the fish was determined by use of a trained taste panel.

Another angle--the physical change--was also considered by the researchers. When degradation of protein occurs, certain changes develop in the physical condition of the fish. Some of the more obvious changes include (1) softening or development of stringiness of the meat, (2) clouding of the eyes, and (3) dulling of the color or sheen of the meat. Development of a physical objective test, then would involve a classification of the physical changes that take place, developing a method to evaluate or record progressive changes in the physical characteristics, and then relating these changes to the progressive change in quality of the fishery product.

1/THIS RESEARCH CONDUCTED BY THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY UNDER A CONTRACT WITH THE BUREAU OF COMMERCIAL FISHERIES, UNITED STATES FISH AND WILDLIFE SERVICE. FUNDS WERE PROVIDED BY THE SALTONSTALL-KENNEDY ACT OF 1954.

NOTE: ORIGINAL TECHNICAL MANUSCRIPT WRITTEN BY THE RESEARCH INVESTIGATORS: B. E. PROCTOR, J.T.R. NICKERSON, T. FAZZINA, L. RONSIVALLI, AND K. AMANO OF THE FOOD TECHNOLOGY DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

Degradation products of fish protein and compounds involved in biochemical reactions that were tested included piperidine, histamine, trimethylamine, creatinine, carbonyls, and amino acids. One or more tests were developed and applied to measure the amount of each of these products in the fish meat. Biochemical tests included measurement of the oxidation-reduction electrical potential of the fish meat and of the rheological (rheology is the science of flow dealing with the deformation of matter under certain specific conditions of stress) response of the tissue, such as measurement of the plasticity of the fish meat slurries. Physical tests included studies on changes in the tenderness of the meat, and in the viscosity and refractive index (light-bending properties) of the eye fluids of fish as spoilage progressed.

Of all the chemical, biochemical, and physical tests tried only one showed real promise. This was the physical test based on the refractive index of the eye fluids of the fish (haddock). When the various tests were first considered for the determination of the quality of fresh raw fish, it was concluded that any such test must be made on that portion of the fish which would not be subject to factors that would alter the reliability of the test. For example, use of certain chemical ices might affect the sheen or color of the skin but the resulting change taking place might not have any bearing on the condition of the fish. The eye fluids, since they were protected by the eyeball, would seem to meet such a requirement.

Visual observations of the eye fluids of the fish revealed that the fluid was crystal clear during the first few days the fish were held in ice. During continued storage the eye fluids became yellow and the intensity of the color increased with storage. After a certain point in storage, blood is liberated in the eye fluids and the yellow color is masked with a red color.

Although the changes in the eye fluids can be observed visually, this method does not provide a reliable basis of measuring and standardizing the changes which take place. A mechanical means of measuring such changes is necessary. Two methods were considered: (1) optical density and (2) refractive index of the eye fluids. Optical density refers to the relative transmittance of light and is measured with a colorimeter; refractive index refers to light-bending properties and is measured with a refractometer. When it was found that optical-density measurements did not give as promising results as the refractive index, stress was laid on the latter method.

The refractive index is a relatively simple test for a trained technician. Qualified laymen can be readily trained within a short period. The test is conducted as follows: The fluid of the eyes of several fish are collected. The fluid is transferred to a centrifuge to clarify the mixture, then filtered to remove and discard a gel-like component. Two to three drops of the clarified eye fluid is used to measure the refractive index in an Abbe refractometer.

Practical tests were run on board a commercial trawler on fish just after catching and followed through nine days of storage on ice. A typical "refractive index-storage time of fish" relationship for haddock stored in ice aboard a fishing vessel is shown in the table.

Time of Capture of Haddock (Fish Held in Ice)	Refractive Index of Eye Fluids 1/
0 hours	1.3347
3 hours	1.3347
1 day	1.3352
3 days	1.3355
5 days	1.3365
7 days	1.3369
9 days	1.3380

1/ REFRACTIVE INDICES ARE VERY PRECISE MEASUREMENTS. VARIATIONS IN THE THIRD PLACE BEYOND THE DECIMAL INDICATE SIGNIFICANT CHANGES IN THE REFRACTIVE INDEX.

As was pointed out in the first paragraph of this report, any objective test to be practical must be reliable, simple and easy to carry out, and relatively inexpensive.

The authors concluded from their data that the refractive index of the eye fluids correlated with the time of storage and the quality (as determined by a taste panel)

of haddock stored in ice or at refrigerator (above freezing) conditions. This conclusion on the reliability of the test is based on laboratory-scale experiments.

The test is rather simple and easy to carry out. It requires readily available basic laboratory equipment such as an Abbe refractometer, a centrifuge, and miscellaneous glassware. A qualified layman could be quickly trained to carry out the test. One single test could be made in about 20 minutes. The test lends itself to "mass-production" methods so that perhaps a half dozen or more tests could be run concurrently.

The test is relatively inexpensive. The major equipment required are the refractometer and centrifuge. Major and minor equipment costs would probably not involve more than $500.

It must be remembered, however, that the reliability of the test was based on laboratory-scale experiments. One more step in the study is required before the test can be considered commercially practical. This involves an application to commercial, dockside, and in-plant operations over a period of at least one full continuous year. It's a well-known fact that reliable results found in the laboratory or a pilot plant do not always work out on a practical basis under commercial conditions of operation. This final commercial test would provide the following information:

(1) Reliability of the test for fish caught in different areas;

(2) Reliability of the test for fish caught during different seasons of the year;

(3) Reliability of the test for different species of fish; and

(4) Cost of the test on a unit-test basis.

--THIS NONTECHNICAL SUMMARY BY FRANK T. PISKUR,
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TECHNICAL NOTE NO. 42 - KEEPING QUALITY AND RATE OF FREEZING OF COOKED DEEP-SEA LOBSTER MEAT FROZEN IN CANS

By John A. Peters* and Joseph W. Slavin**

ABSTRACT

REPORTS ON A SMALL-SCALE TEST CONDUCTED WITH COOKED LOBSTER MEAT PACKED IN CANS UNDER DIFFERENT CONDITIONS AND FROZEN. INFORMATION WAS OBTAINED ON: (1) EFFECT OF (A) THE AMOUNT OF VACUUM IN THE CAN, (B) ADDITION OF BRINE TO THE CANNED SAMPLE, AND (C) STORAGE TEMPERATURE ON KEEPING QUALITY; AND (2) RATE OF FREEZING OF CANNED LOBSTER MEAT IN A BLAST FREEZER.

BACKGROUND

A large quantity of deep-sea lobsters were fished in the Georges Banks area off the coast of New England by the U. S. Bureau of Commercial Fisheries exploratory fishing trawler Delaware during the spring of 1955 (Anonymous 1955). The finding of these lobsters has led to the development of a new lobster fishery in which several commercial fishing vessels are now engaged.

The deep-sea lobster is of the same species (Homarus americanus) as the smaller lobster found inshore along the coast of New England. However the size of the

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deep-sea lobsters (5 to 15 pounds) limits their sale in the retail live lobster market, which handles principally $\frac{1}{2}$- to 2-pound lobsters. Attention therefore is being given to other methods of marketing them.

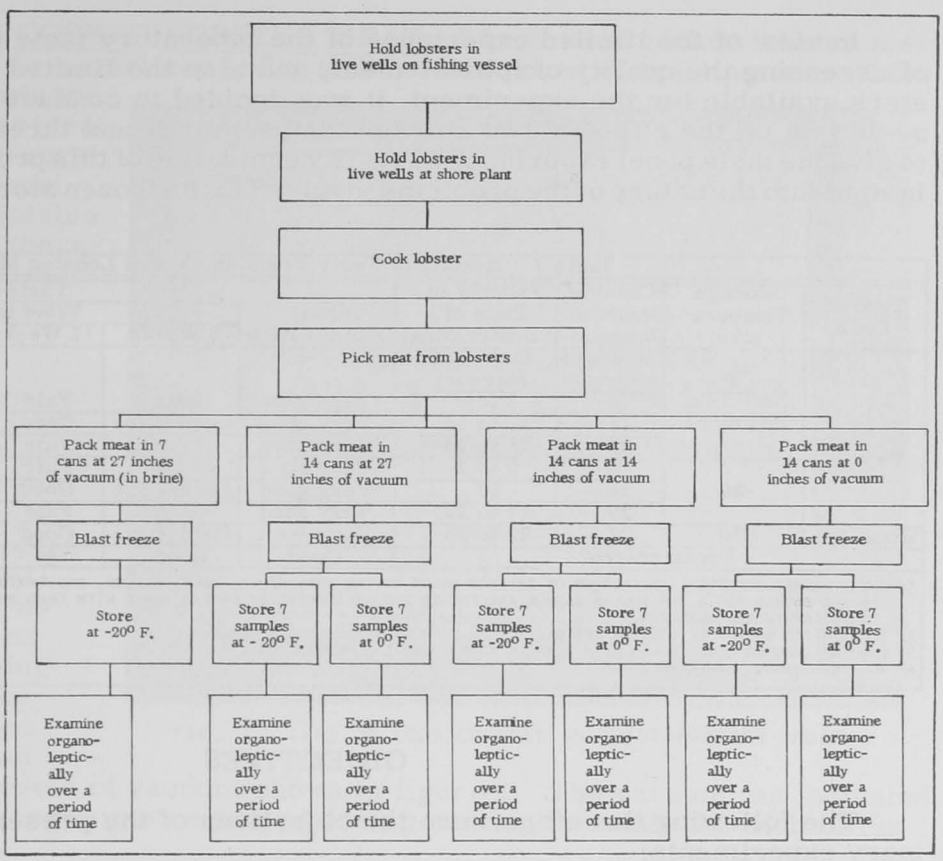

FIG. 1 - FLOW DIAGRAM SHOWING TREATMENT, PACKAGING, AND STORING OF LOBSTER MEAT.

Modern low-temperature refrigeration facilities in the frozen-food distribution chain of today make possible the freezing and distribution to inland cities of millions of pounds of frozen fishery products each year. A successful method of preserving lobsters by suitable refrigeration techniques therefore would be of value, since it would provide a greater market for the lobster meat. Accordingly, studies have been started at the Bureau's Fishery Technological Laboratory at East Boston, Mass., on the freezing and storing of deep-sea lobsters (Peters and Slavin 1956).

Stansby (1955) has reported that cans, being impervious to the transmission of moisture and oxygen, make an ideal package for frozen fishery products. Cans have not been used extensively as a package for frozen lobster meat; therefore, information on the effect of (1) various levels of vacuum in the can, (2) different storage temperatures, and (3) the addition of brine is necessary in order to furnish data that will enable processors to produce a high-quality frozen-canned product at minimum cost.

FIG. 2 - COOKING LOBSTERS IN BOILING SEA WATER.

Blast freezers provide rapid freezing and are commonly used in the fishing industry (Butler, Slavin, Patashnik, and Sanford 1956). Data on the freezing rates of lobster meat packed in cans consequently would be useful to plant operators contemplating the freezing of lobster meat in existing blast freezers and to engineers designing new equipment for freezing this product.

RESULTS AND DISCUSSION

KEEPING QUALITY: The results of the organoleptic examinations of the lobster meat by the taste panel are shown in table 1.

Analysis of the numerical scores for the various samples for significance of averages (Harrison and Elder 1950) shows that there was a significant preference for the fresh control sample over all the frozen samples except the sample packed under 27 inches of vacuum, and stored at -20° F. Although the sample packed under 27 inches of vacuum and stored at -20° F. was preferred over all other frozen samples, the difference between this sample and the one packed under 14 inches of vacuum and stored at -20° F. was not statistically significant. There was also an indication that all samples stored at -20° F. were preferred to those stored at 0° F. No consistent preference could be related to the vacuum in the can. Also, the cans of lobster meat that were filled with a brine containing 2.5-percent salt, packed under 27 inches of vacuum, and frozen and stored at -20° F. did not appear to be of better quality then were the samples without brine that otherwise were packed under the same conditions.

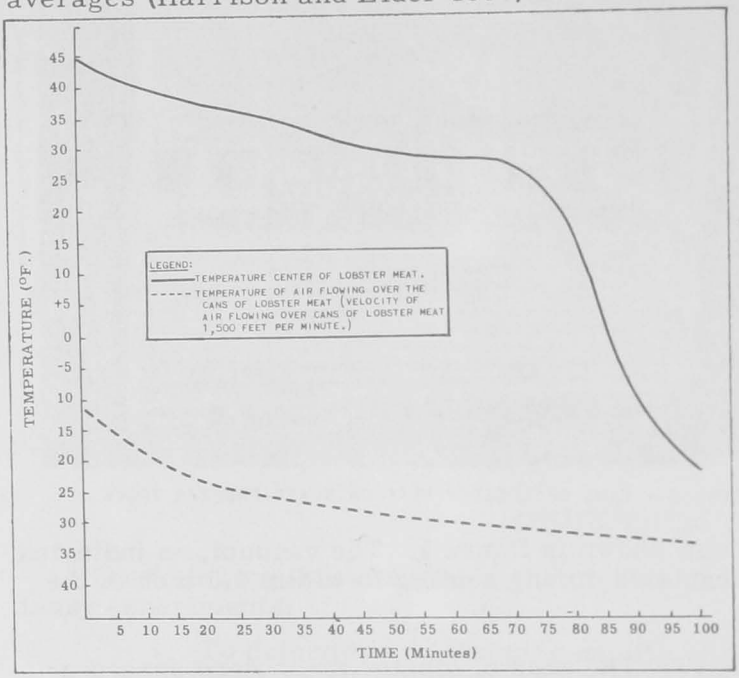

FIG. 4 - FREEZING RATE OF LOBSTER MEAT PACKED IN A NO. 2 CAN.

The negligible effect of the vacuum in the cans on the keeping quality indicates that frozen lobster meat might be suitably protected if packaged in a consumer-size package, overwrapped with a moisture-vapor-proof material, and stored at a temperature of -20° F. It is possible, however, that a longer period of storage would have shown differences that did not develop in the short period covered by these tests.

FREEZING RATE: The freezing curve for 1 pound of lobster meat packed in a No. 2 can and frozen in an air blast having a temperature of -10° F. to -35° F. and a velocity of 1,500 feet per minute over the cans is depicted in figure 4. It can be seen from this curve that about 50 minutes were required to cool the meat to its freezing temperature of about 28° F.; 25 minutes more to freeze the meat; 10 minutes more to cool it to 0° F.; and 15 minutes more to cool it to -20° F. In all, 85 minutes were required to cool the canned lobster meat from 45° F. to 0° F., and 100 minutes to cool it from 45° F. to -20° F.

SUMMARY

The discovery of large quantities of deep-sea lobsters off the coast of New England by the Bureau's trawler Delaware has led to the development of a new lobster fishery. Because of the large size of the deep-sea lobsters (5 to 15 pounds), however, the market for them in the live condition is somewhat limited. Since a successful method of preserving these lobsters by refrigeration would greatly extend the market for them, the Fishery Technological Laboratory in East Boston has started studies on the freezing and storage of them.

The present paper reports on a small-scale preliminary test conducted with cooked lobster meat frozen in cans to determine (1) the effect of (a) the amount of vacuum in the can, (b) the storage temperature, and (c) the addition of brine and (2) the rate of freezing of the canned lobster in a blast freezer. The findings were as follows:

1. Cooked lobster meat stored in cans for 18 weeks at -20° F. kept well and was apparently of better quality than was cooked lobster meat stored in cans for the same time at 0° F. The amount of vacuum in the can did not appear to affect the keeping quality appreciably. Samples of cooked lobster meat containing 2.5-percent salt brine, packed at 27 inches of vacuum, frozen, and stored for 18 weeks at -20° F. were at about the same level of quality as those not containing brine, but otherwise packed under the same conditions.

2. With lobster meat packed 1 pound per No. 2 can, 100 minutes was required to cool the cooked meat from 45° to -20° F. in an air blast having a temperature of -10° to -35° F. and a velocity of 1,500 feet per minute over the cans.

LITERATURE CITED

ANONYMOUS
1955. NEW ENGLAND EXPLORATORY FISHERY PROGRAM. COMMERCIAL FISHERIES REVIEW, VOL. 17, NO. 3, (MARCH), P. 34.

BUTLER, CHARLES; SLAVIN, JOSEPH W.; PATASHNIK, MAX; AND SANFORD, F. BRUCE
1956. REFRIGERATION OF FISH - PART ONE. COLD STORAGE DESIGN AND REFRIGERATION EQUIPMENT. FISHERY LEAFLET 427, U. S. FISH AND WILDLIFE SERVICE, WASHINGTON 25, D. C., JUNE, 146 PP.

HARRISON S., AND ELDER, L. W.
1950. SOME APPLICATIONS OF STATISTICS TO LABORATORY TASTE TESTING. FOOD TECHNOLOGY, VOL. 4, NO. 11, PP 434-439.

PETERS, JOHN A., AND SLAVIN, JOSEPH W.
1956. NEW TECHNIQUES FOR FREEZING AND STORING NORTH ATLANTIC LOBSTERS, COMMERCIAL FISHERIES REVIEW, WASHINGTON 25, D. C. VOL.18, NO. 7 (JULY), PP. 22-23 (ALSO SEPARATE NO. 443).

STANSBY, MAURICE E.
1955. PACKAGING FROZEN FISH IN TIN RESULTS IN SUPERIOR STORAGE. COMMERCIAL FISHERIES REVIEW, WASHINGTON 25, D.C., VOL. 17, NO. 7 (JULY), PP. 17-20 (ALSO SEPARATE NO. 407).

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TESTS ON STORAGE OF FROZEN SHRIMP SHOW THAT PROPER PACKAGING "PAYS OFF"

Frozen shrimp must be adequately protected, through the use of packaging or glazing techniques, or both, in order to minimize quality changes during frozen storage and marketing. Many investigators have found that poorly-packaged commercial samples of shrimp deteriorate rapidly during normal frozen storage at 0° F.

Information on the storage life of frozen shrimp afforded maximum protection through commercial packaging and glazing techniques would enable industry to take advantage of glut periods, level off production costs, and still market a high-quality product.

Realizing this, the Bureau of Commercial Fisheries Technological Laboratory at East Boston, Mass., is conducting studies to determine the frozen storage life of peeled and deveined and raw headless shrimp. These samples of shrimp were either (1) frozen individually, glazed and packaged in a $2\frac{1}{2}$-pound carton, which was

overwrapped with micro-crystalline waxed paper or (2) packed wet into a $2\frac{1}{2}$-pound carton, the carton overwrapped as above, and the shrimp frozen in the form of a block.

After six months of frozen storage at temperatures of 0° to -5° F., all samples are reported to be of very good to excellent quality. These tests are continuing.

Table 1 - Summary of Taste-Panel Scores on Frozen Shrimp Stored at 0° to -5° F.

Description of Samples of Frozen Shrimp	Product Score 1/ Months of Storage at 0° to -5° F.					
	1	2	3	4	5	6
Peeled, deveined, block frozen (packed wet)	8.7	8.6	8.7	8.6	7.8	7.7
Peeled, deveined, individually frozen (glazed)	8.7	8.4	8.7	8.1	8.0	8.0
Headed, not-peeled, block-frozen (packed wet)	8.8	8.7	8.7	8.6	8.3	8.3
Headed, not peeled, individually frozen (glazed)	8.6	8.6	8.5	8.4	8.1	8.1

1/ PRODUCT SCORE WAS THE AVERAGE VALUE FOR ODOR, FLAVOR, APPEARANCE, AND TEXTURE OF THE COOKED PRODUCT AS RATED BY THE TASTE PANEL. THE TASTE PANEL CONSISTED OF 8 TO 10 PEOPLE. SCORE BASED ON NINE-POINT SYSTEM OF: 9, EXCELLENT; 8, VERY GOOD; 7, GOOD; 6, FAIR; 5, BORDERLINE; 4, SLIGHTLY POOR; 3, POOR; 2, VERY POOR; AND 1, INEDIBLE.

Results of periodic examinations of the stored frozen shrimp are shown in table 1.

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HOW MANY DIFFERENT SPECIES OF FISHES IN THE WORLD?

According to the Curator of Fishes, Smithsonian Institution, there are 40,000 species and subspecies of fish in the entire world. The tropical Indo-Pacific region, which extends from the head of the Red Sea to Easter Island, is considered to be the richest in number of species of fish. containing over 9,000 species.