TECHNICAL NOTE NO. 22--A NEW LIQUID MEDIUM FOR FREEZING ROUND FISH

INTRODUCTION

As one phase of the project dealing with the freezing of fish at sea now being conducted by the Boston Laboratory of the U. S. Fish and Wildlife Service, commercially-important New England species of groundfish (cod, haddock, and ocean perch) are being frozen at sea "in the round," that is ungutted, on board the experimental trawler Delaware for later processing into frozen fillets ashore. The fish, immediately after removal from the trawl, are frozen by immersion (Magnusson, H. W.; Pottinger, S. R.; and Hartshorne, J. C.; 1952) in a strong sodium-chloride (23 percent by weight) brine maintained, as nearly as possible, at a temperature of 5° F. (-15° C.). The fish are then stored in the vessel's cold-storage compartments at 0° to 5° F. (-17.7° to -15° C.) until the trawler returns to port.

Subsequent experience on the Delaware indicates that although sodium-chloride brine is a good immersion-freezing medium it imposes two limitations on operations of freezing fish at sea: (1) restriction of the freezing operation range from 5° to 10° F. (-15° to -12.5° C.) with the concentration of brine used to avoid freezing-out of water or precipitation of salt in the tubes of the heat-exchanger in the refrigerating system, and (2) rises in temperature above the safe maximum (about 10° F.) for negligible penetration of the salt into the meat of the fish when gluts of fish are being frozen.

Immersion freezing utilizes the relationship between the concentration and freezing point of a solution. Water, which normally freezes at 32° F. (0° C.), freezes at a lower temperature if a soluble substance is added to it. Since the degree of depression of the freezing point of a solution is related to the concentration of the substance added, a strongly concentrated solution may freeze at temperatures well below 0° F. (-17.7° C.). Refrigeration of such solutions results in formation of a cold bath or immersion-freezing medium. Immersion of a relatively warm object in the solution causes a rapid flow of heat from the object to the cold solution. The intimate over-all contact and large temperature differential enables freezing of the object to be accomplished in a fraction of the time necessary for other methods of freezing.

Foods may be successfully frozen in such freezing baths if the soluble substance added to the water is carefully chosen. Brines composed of sodium chloride and sugar (Goldsmith and Bartlett 1948) have been proposed for the freezing of meats. Sugar syrups (Taylor and Ferris 1939; Bartlett 1941 and 1942; Woodroof 1939) are used in the freezing of fruits and vegetables. Sodium-chloride brine has long been advocated as a liquid medium for the freezing of fish (Ottesen 1915 and 1925).

Ideally, an immersion-freezing medium designed to be used for freezing fish at sea should have the following characteristics. It should:

1. Remain liquid below 0° F. and allow freezing operations at or below that temperature.

2. Produce no adverse effect on the frozen product.

3. Exhibit high specific heat and thermal conductivity.

4. Have a low viscosity.

5. Be relatively inexpensive and easy to reclaim and re-use.

6. Exhibit a progressive decrease in freezing point with increase in concentration, that is, should evidence a straight-line relationship when concentration is graphed against freezing point.

A search of the literature did not yield information on a liquid medium that entirely suited the particular needs of the freezing-fish-at-sea project. Brines or syrups used industrially for freezing of foods other than fish are maintained at or slightly above 0° F. (-17.7° C.). Moreover, the products to be frozen are, in general, uniform in size and shape and the rate at which they are delivered to the freezer is regulated. Under such ideal conditions, few gluts occur and temperature variations in the freezing media are minimized. There has been, until the present, little incentive and need for research and development of better liquid-freezing media which could be adapted to the freezing of fish.

EXPERIMENTAL

During the past year, as a part of the freezing-fish-at-sea project, a large number of chemical compounds, organic and inorganic, alone or in combinations, were tested at this laboratory as possible materials for new liquid-freezing media. The great majority of these materials were rejected from further consideration for reasons of high cost, toxicity, penetration into the meat of the fish, or high viscosity. Research then centered around those showing the most promise, such as a few inorganic and organic salts, alcohols, glycerols, glycols, and various sugars. Combinations of sugars with inorganic salts for reasons of cost, availability, and lack of toxicity appeared to be best.

Goldsmith and Bartlett (1948) reported on media containing mixtures of the sugars (glucose and sucrose, and of glucose, sucrose) and sodium chloride. They showed that both of these media evidence a straight-line relationship between concentration and freezing point. These media were tested in the routine manner in this laboratory. They were all characterized by high (40 to 60 percent by weight) sugar content and high viscosities.

To lessen the viscosity and to reduce the expense of the above media, the sodium chloride content was raised from the recommended 3 percent to about 12 percent and the glucose and sucrose contents were reduced, respectively, to about 34 and 3 percent (by weight). At these concentrations the medium was capable of remaining fluid at a temperature of -10° F. (-23.3° C.). By using such a solution, the freezing operation range could be extended by only 2° F. while operating 13° F. above the freezing point as a safety factor. Though an improvement, such a small extension of the operating temperature range over that of sodium-chloride brines could not justify the use of relatively expensive sugar.

There are, however, several other features of such sugar-sodium chloride mixtures which recommend them. The first is the enhanced appearance of the frozen product due to a glistening sugar glaze left upon it. The second is the markedly lower salt penetration into the round fish during freezing due, apparently, to the two factors of the lowered temperature and decreased (as compared to a 23 percent sodium-chloride brine) salt concentration. Finally, there appears to be formed at low temperatures what Noyes (1940) reported to be "double-compounds" of the glucose and sodium chloride which render the medium only very slightly sweet. These "double-compounds" may also be a factor in reducing salt penetration of the flesh by osmosis.

Calcium-chloride solutions, of varied concentrations, had previously been tested as possible freezing media. The high solubility of calcium chloride and its extreme range of freezing-point depression (to -59.8° F. or -51° C.) made it a very desirable component of a freezing solution. As the single component, other than water, of a freezing medium, it had caused very noticeable deterioration of the surface membrane of the fish. In combination with sodium chloride, the solubility of each was limited and the maximum added depression of the freezing-point of the mixed brine was only about 3° to 4° F.

The experiments had indicated that calcium chloride, in a concentrated solution, is more than twice as effective per chemical-unit weight in reducing the freezing-point of water as is sodium chloride. It was reasoned that substitution, in whole or in part, of calcium chloride for sodium chloride in the above mentioned sugar-sodium chloride solution might result in a medium requiring less glucose, no sucrose, evidencing little or none of the typical calcium chloride surface effect on the fish and yet capable of attaining a much lower freezing temperature. All these suppositions were upheld by subsequent experimentation. Furthermore, calcium chloride, while dissolving, gives off much heat. The heat raises the temperature of the liquid and greatly facilitates the subsequent solution of glucose.

A series of experiments were performed to determine the minimum proportions of glucose to calcium chloride necessary to prevent the deteriorative effect of the calcium chloride on the surface membrane of the fish. The composition of the solution was varied radically. It was found that a minimum of one part glucose to one part calcium chloride was necessary. With decreasing quantities of glucose, the adverse effect on the surface of the fish became more and more apparent. Increase of the glucose content to or beyond the 1:1 ratio completely eliminated the surface effect.

Fish were frozen in an unagitated bath consisting of 34 percent glucose and 20 percent calcium chloride, in water, at a temperature of -20° F. (-28.8° C.). Visual and organoleptic testing of the fish failed to reveal any adverse effects. When subsequently stored in a plate-freezer (-50° F. on the plates and about -30° F. in the ambient air) a wholly transparent and apparently durable glaze was formed which greatly enhanced the appearance of the fish. Woodroof (1939), in referring to such glazes on fruits, reports them to be of two millimeters in thickness and apparently unchanged after six months of storage.

Although the refrigerating capacity of the compressor serving the immersion-freezer at the laboratory was highly inadequate for operations at temperatures approaching -20° F. (-28.8° C.), it was decided anyway, to attempt some preliminary studies of freezing rates of fish in the medium. A solution, consisting of 25 percent each (by weight) of calcium chloride and glucose was prepared. These concentrations were selected since they appeared in small-scale tests to afford a solution which satisfied the requirements previously listed for a medium for use in freezing fish at sea. The solution freezes at a temperature of about -24° F. (-31.1° C.). It has a low viscosity and is the least expensive. It affords ample excess of dissolved calcium chloride and glucose to eliminate concern over freezing out of the medium due to dilution of the brine. Such dilution occurs when large quantities of fish, carrying considerable adsorbed water, are placed in the medium to be frozen.

The temperature of the medium, in an open tank refrigerated by direct expansion of a gas in surrounding coils, was reduced to about -18° F. (-27.8° C.). Since the capacity of the compressor was inadequate to maintain this temperature and, at the same time, absorb the heat released to the solution by a pump used to circulate and agitate the medium, it was necessary to study the freezing rates in still brine. Scrod haddock (3 pounds in weight and about 2½ inches in cross-section at the widest point) were frozen in a period of 40 to 45 minutes. Large-size haddock (5 pounds in weight and 3 to 4 inches wide) required 90 minutes to freeze. Magnusson and Hartshorne (1952), reporting on rates of freezing of scrod and large haddock at 0° F. (-17.7° C.), found them to be, respectively, 80 and 110 minutes in agitated brine. The rates at 10° F. (-12.5° C.) in agitated brine were reported to be, respectively, 125 minutes and 170 minutes.

Metal corrosion, somewhat of a problem with sodium-chloride brines, is lessened in calcium-chloride brines and should be still less of a problem due to the anti-corrosive effect of sugar.

Taste-panel members, when served portions of unseasoned, steamed fish, previously frozen in the glucose-calcium chloride medium, were unable to distinguish between them and control samples of fish frozen in sodium-chloride brine.

Fish, from both lots, were then stored for one week in a household refrigerator (about 40° F.) and again served, after steaming, to the taste panel. Other than the normal decline in quality for both lots, no adverse comments were made by the panel. Fish, identically frozen in the experimental medium but differing in that some were air-thawed and the others water-thawed, when served as before to the taste panel, were judged to be of good quality and indistinguishable one from the other. It is apparent that, under laboratory conditions, the quality of the fish is not affected by immersion-freezing in the new medium. As a test for the development of off-flavors over an extended period of storage, several hundred pounds of fish frozen in this medium will be placed in a commercial cold storage and sampled at regular intervals.

DISCUSSION

It would seem that the limitations imposed upon the freezing-fish-at-sea project might be overcome by the use of sugar-calcium chloride brine. Since there is a progressive decrease in freezing point with increasing concentration, the effective freezing temperature of the medium may be extended from a range of about 5° to 10° F. (-15° to -12.5° C.) to a range of from -18° to +10° F. (-17.5° to -12.5° C.)--an increase of at least 23 degrees F. Such an extended range would render unimportant any temporary increase in temperature of the medium due to large loads of fish. Further, dilution of the brine by water adsorbed on the surface of immersed fish would no longer be a source of concern since, due to the high concentration, the effect of dilution on the freezing-point depression would be very slight. The necessity for constant supervision of the machinery would be eliminated.

Rates of freezing of fish, due to the lower temperatures attainable in the new medium, were faster than in sodium-chloride brines during the preliminary studies. The resultant shorter immersion period necessary for freezing the fish has, at least, a theoretical advantage in the preservation of quality.

Penetration of the calcium chloride into the meat of the fish should be minimized by the rapidity of freezing of the outer layer of meat, by the apparent formation of the "double-compounds" of salt and sugar with resultant decrease in quantity of salt subject to osmosis, and by the shortened immersion periods. Tests, so far performed, have indicated this to be the case.

SUMMARY

It is felt that an immersion-freezing solution peculiarly well adapted to the requirements of freezing fish at sea may have been developed.

The straight-line relationship between concentration and freezing point appears to insure safer operating conditions without need for constant attention.

Freezing rates were faster than in sodium-chloride brines in the tests so far performed, due to the lower temperatures attained.

Temperature increases in the freezing medium, induced by gluts of fish, should not be of such magnitude as to rise above the desired freezing temperature maximum of 10° F. (-12.5° C.). The freezing-operation range has been extended from a temperature range of 5° F. to 10° F. to a range -18° F. to +10° F.

No adverse effects on the frozen product were noted during organoleptic testing of fish frozen in the medium.

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