COMMERCIAL FISHERIES REVIEW

August 1960 Washington 25, D.C. Vol. 22, No. 8

CONTROL OF IRON SULFIDE DISCOLORATION IN CANNED SHRIMP (Xiphopeneus sp.) - PART 1

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ABSTRACT

The shrimp, seabob, has a short shelf life when canned, owing to discoloration of the can surface by iron sulfide. A study was made to determine whether a decrease in the pH of the can contents would prevent this discoloration. The pH was lowered in the experiments by the addition of either a lemon juice concentrate or a citric acid solution, the condition of the cans was noted after storage periods of varying lengths, and the data were interpreted in terms of efficiency of the additive and effectiveness of varying degrees of acidity in preventing the discoloration. Recommended canning techniques for seabob are discussed.

INTRODUCTION

For many years attempts have been made to utilize certain species of shrimp, commonly known as seabob, Xiphopeneus sp., for canning purposes, only to find that regardless of the freshness of the shrimp at the time of canning, the canned product had an extremely short shelf life. These shrimp cause an iron sulfide discoloration or blackening of the exposed metal surfaces of the can, which gradually spreads over the entire surface and eventually causes the shrimp themselves to discolor (Gallagher not dated).

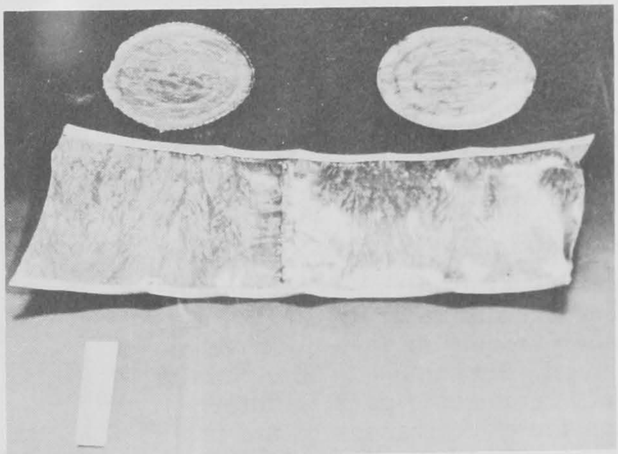

Fig. 1 - Severe iron sulfide discoloration present on can surfaces in control Lot No. 1 after a storage period of 360 simulated days.

Seabobs are found in commercial quantity in shallow waters of the Gulf of Mexico. The term seabob originated in the French name for this species, "six baub," which referred to the six sharp points on the rostrum of this species. The shrimp are of small size (70 to 80 count in the raw headless state) and are characterized by a very long upturned rostrum and long antennae, with the two posterior walking legs elongated into antennae-like filaments (Guest 1956).

In the Louisiana Delta area seabobs have long been salted and sun-dried. At various times they have been used to prepare shrimp meal. The supply of these shrimp far exceeds the demand for them, and consequently attempts have been made

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to process the seabobs in several types of cans when other shrimp are in short supply. However, the shelf life of the canned product has always been short, particularly at warm storage temperatures.

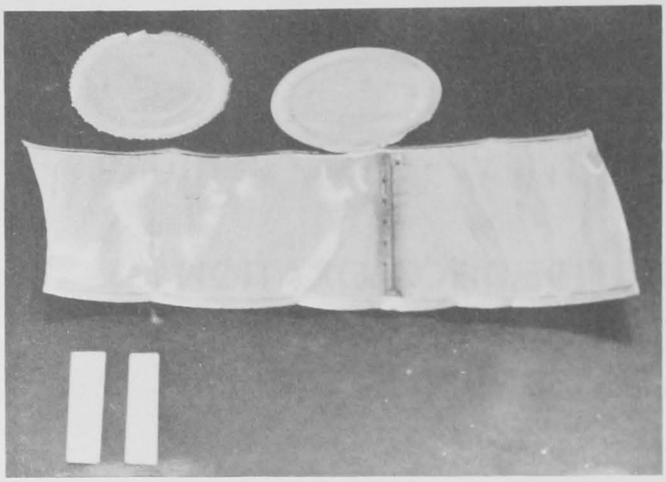

Fig. 2 - Absence of iron sulfide discoloration on can surfaces after a storage period of 360 simulated days.

The average pH of well-iced seabobs is 7.5 when measured immediately after picking, whereas the average pH of well-iced shrimp of other Gulf commercial species at that time is 7.0. In other commercial species of shrimp a pH of the canned product exceeding 7.2 will allow iron sulfide discoloration. The difference in the normal pH of the two types of shrimp in the raw state, and the corresponding difference to be expected in the canned product, has led to experimentation in the lowering of the pH of the canned product in an effort to reduce the iron sulfide discoloration of the can and its contents.

The present series of experiments were initiated to determine if pH was the primary factor involved in the case of seabobs, and if so, what additives could be used to prevent such blackening. In general, this discussion should be considered as the first part of a series of experiments, and later reports will deal with the effect of other additives upon the discoloration and comparisons of the effectiveness of the additives in dealing with this problem. Because both citric acid and lemon juice concentrate have been suggested as additives to control this discoloration, it was decided to test their relative effectiveness in the first experiment of the series. The present series of tests were conducted at higher storage temperatures; however, further storage studies at normal temperatures are contemplated. A secondary aim was to suggest a possible time limit on the shelf life of such products. In the course of these experiments, a satisfactory method of processing these smaller shrimp was also developed.

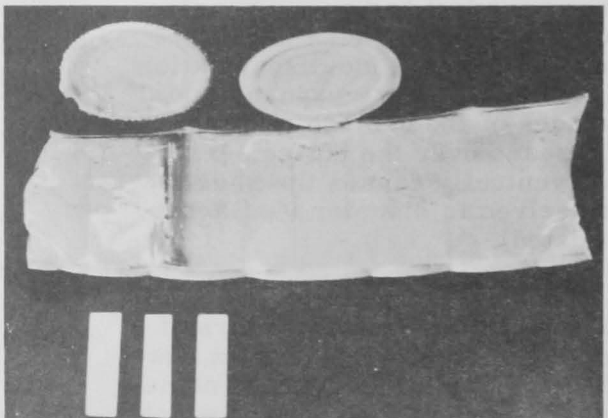

Fig. 3 - Iron sulfide discoloration present in slight amounts on can surfaces after a storage period of 360 simulated days.

The first portion of this paper deals with the initial experiments undertaken in an effort to find the proper amount of each additive to be used. Subsequently, the results of a larger-scale pack to determine the effectiveness of the two additives used, the increase in shelf life to be expected, and the effect of lowering the pH of the can contents is reported. Finally, the processing method developed for use with these smaller shrimp is outlined.

INITIAL EXPERIMENT

PROCEDURE: Processing Method: The following method was used in processing the shrimp in all of the experiments:

1. The shrimp were peeled, blanched in boiling 8-percent salt solution for 2 to 3 minutes, drained, and packed with 5.25 ounces of meats to the can. Number 211 x 300 shrimp cans, coated with C-enamel of the type commonly used by the shrimp canning industry, were used throughout. This method produced a drained weight of 4.75 ounces or more.

2. The can was filled to $\frac{1}{4}$-inch headspace (80 to 85 ml. of solution) with brine or brine plus additives and sealed at a temperature of 150° F.

3. The cans and contents were processed for 12 minutes at 250° F. and 15 pounds pressure, and water-cooled before storage.

<u>Scoring Method for Evaluating Discoloration</u>: The scoring method used in estimating the amount of iron sulfide discoloration is as follows:

(1) Score 0 - no iron sulfide discoloration

(2) Score 0+ - very slight iron sulfide discoloration (area of deposit - 4 mm.^{2} or less)

(3) Score 1 - slight iron sulfide discoloration (area of deposit - 4 to 36 mm.^{2})

(4) Score 2 - moderate iron sulfide discoloration (area of deposit 36 to 81 mm.^{2})

(5) Score 3 - heavy iron sulfide discoloration (area of deposit, more than 81 mm.^{2})

<u>Experimental Method</u>: Preliminary experiments were conducted with two levels of lemon juice concentrate and two levels of citric acid in an effort to determine the most effective concentration of each in retarding the iron sulfide discoloration. The shrimp were received well-frozen and headless, were thawed and peeled by hand, and were processed according to the method previously described. In this preliminary experiment, salt tablets were used instead of brine to follow local commercial practice. The tablet was later discarded in favor of brine, which was easier to handle under the conditions of this study. The pack was divided into the following classifications depending upon the type of solution used to fill the container:

1. Control - 4.8 g. salt plus water

2. Type 1 - 4.8 g. salt plus 1 part lemon juice concentrate No. 309 to 50 parts water

3. Type 2 - 4.8 g. salt plus 1 part lemon juice concentrate No. 309 to 25 parts water

4. Type 3 - 4.8 g. salt plus 0.26 g. citric acid (equivalent to a 0.33-percent citric acid solution)

5. Type 4 - 4.8 g. salt plus 0.33 g. citric acid (equivalent to a 0.41-percent citric acid solution)

This canned lot was stored at a constant temperature of 37.5° C. (98.6° F.) for 70 days. High storage temperatures, such as were used in these experiments, intensify chemical reactions in the can. The higher temperatures used in this study were the only known deviation from the normal commercial canning procedure. There is a rule of thumb that the rate of chemical reactions approximately doubles for every 10° C. increase in temperature. Thus, the changes which occur during a given storage time are effectively doubled if the product is stored at 37.5° C. (99.5° F.) rather than at usual warehouse temperatures of 27.5° C. (81.5° F.) For example, a lot with a storage period of 70 days under forced conditions is approximately equal to one with a 140-day period under normal conditions. Since there has not been a study of the kinetics of this particular reaction in relation to time and temperature, the figures used to indicate simulated storage days are only approximate ones based on the aforementioned rule of thumb. At the end of 140 and 280 simulated days the cans were opened, the amount of discoloration was noted, and the pH of the contents was determined with a pH meter.

RESULTS: Lemon juice in both concentrations was still effective at the end of 140 days and 280 days of simulated storage in retarding the discoloration. It appeared, however, that as discoloration was occasionally evident in the cans of 1:50 dilution, a slightly stronger concentration was needed, but one not as strong as the 1:25 dilution. At the same time, it appeared that neither the 0.26- nor the 0.33-gram concentrations of citric acid in the can were adequate to prevent discoloration. It was then decided to repeat the experiment on a larger scale, using a 1:40 dilution of lemon juice concentrate No. 309 and a concentration of 0.52 g. of citric acid per can.

PILOT-SCALE PACKING OF SHRIMP

PROCEDURE: It was necessary to process a large number of cans to determine the relative effectiveness of the proposed strengths of the two additives and to determine whether the relative acidity of the can contents, as indicated by the pH value, was a controlling factor in eliminating the discoloration.

One lot of seabobs was obtained from the Houma, La., area, where they had been peeled in an automatic shrimp peeler. They had been kept well-iced from capture until processing the following day, at which time the average pH of the raw shrimp was 7.5. The entire pack was divided into three smaller lots:

1. Lot No. 1 - Control, contained 80 to 85 ml. of 8.1 percent brine per can.

2. Lot No. 2 - Lemon juice, contained 80 to 85 ml. of 1 part lemon juice concentrate No. 309 to 40 parts of 8.1-percent brine per can.

3. Lot No. 3 - Citric acid, contained 80 to 85 ml. of 0.65-percent reagent-grade citric acid in 8.1-percent brine solution per can (0.52 g. of citric acid per can)

The cans were sealed, processed, and scored according to the general method outlined in the previous section. The 1:40 dilution of lemon juice concentrate No. 309 used, provides a concentration of citric acid in the can between 0.55 and 0.66 g. The pH of the 1:40 lemon juice solution was 2.8 and that of the citric acid solution was 2.7. Lots Nos. 1, 2, and 3 were stored at 47.5° C. (117.5° F.) for a 90-day period, which in effect was a simulated storage period of 360 days at normal temperatures. The day following that of processing, a can of each lot was cut, and a pH reading was taken to provide a base measurement. The pH of Lot No. 1 was 8.12; Lot No. 2, 6.42; and Lot No. 3, 6.40.

RESULTS: Since this was an experiment of a self-destructive nature in that when one can was cut it was lost as far as further storage studies were concerned, it seemed more valuable to simulate a storage period of approximately 1 year and to determine the condition of the cans and contents at the end of that time.

In order that an indication of the progress of the experiment could be provided, four cans from each lot were cut at the end of 220 simulated days. The results of this cutting are shown in table 1. The blackened condition of the cans in Lot No. 1, the control group, was marked, and the average pH was 7.57. The cans from Lot No. 2, 1:40 lemon juice, were not discolored and had an average pH of 5.96. Those cans from Lot No. 3, 0.65-percent citric acid, were slightly discolored and had an average pH of 6.42.

Table 1 - Condition and pH Values of Canned Shrimp Stored at 47.5° C. (117.5° F.)

Samples	220 Simulated Days					360 Simulated Days				
	No. Cans Opened	pH Range	pH Avg.	Score	Total No. Cans With Score	No. Cans Opened	pH Range	pH Avg.	Score	Total No. Cans With Score
					Percent					Percent
Control: Shrimp meats, 8.1-percent brine	4	7.50-7.60	7.57	3	100	47	7.29-7.52	7.37	3	100
Lemon Juice: Shrimp meats, 8.1-percent brine, 1:40 lemon juice concentrate No. 309	4	5.80-6.12	5.96	0	100	22	5.62-6.24	6.01	0	51
						6	6.11-6.21	6.18	0+	14
						15	6.10-6.30	6.19	1	35
Citric Acid: Shrimp meats, 8.1-percent brine, 0.65 percent citric acid	4	6.35-6.50	6.42	1	100	7	6.18-6.59	6.41	0	17
						16	6.19-6.51	6.35	0+	38
						16	6.15-6.51	6.38	1	38
						3	6.60-6.69	6.63	2	7

At the end of 90 actual days, or 360 simulated days, the remainder of the cans in each of the lots were cut, the discoloration evaluated, and the pH measured. The results of this cutting are also shown in table 1. In control Lot No. 1, totaling 47 cans, all of the cans were heavily discolored. The pH ranged from 7.29 to 7.52 and averaged 7.37. In 68 percent of the cans this discoloration was so heavy that it permeated the shrimp meats.

In Lot No. 2 (1:40 lemon juice), totaling 43 cans, 51 percent of the cans showed no discoloration, 14 percent showed very slight discoloration, and 35 percent showed slight discoloration. The pH of those cans with no discoloration ranged from 5.62 to 6.24, average 6.01; those with very slight discoloration ranged from 6.11 to 6.21, average 6.18; and those with slight discoloration ranged from 6.10 to 6.30, average 6.19.

In Lot No. 3 (0.65-percent citric acid), totaling 42 cans, 17 percent of the total showed no discoloration, 38 percent of the cans were very slightly discolored, 38 percent were slightly discolored, and 7 percent were heavily discolored. The pH of those cans with no discoloration ranged from 6.18 to 6.59, average 6.41; those with very slight discoloration ranged from 6.19 to 6.51, average 6.35; those that were slightly discolored ranged from 6.15 to 6.51, average 6.38; and the heavily discolored cans ranged in pH from 6.60 to 6.69, average 6.63.

DISCUSSION: Discoloration was present on the can surface either in the headspace or beneath the surface of the contents. The blackening appeared first at those places where there was evidence of a break in the C-enamel. Kohman and Sanborn (1928) noted that in cans with enameled surfaces, the actions on the can surfaces are enormously concentrated at the point where the enamel has been pierced. As reactions take place in the can, the entire amount of tin plate is removed from this small surface area, allowing the sulfides present in the canned product to react with the exposed steel surface and produce the black iron sulfide discoloration. Since beginning discoloration surrounds a break in the enamel, it starts most often at the can seam or junction of the can lid and can body. As discoloration becomes more pronounced, the blackening extends under the enamel until it almost entirely covers the inside surface of the can. Since the cans were kept in one position throughout the entire storage period, it appeared that the discoloration could take place either in the headspace or on surfaces directly in contact with the can contents. This would indicate that the unwanted chemical reactions are taking place in the can's contents, as well as in the headspace of the can, contrary to previous experience with some other seafoods. The corrosion mechanism of tin plate is believed to be a function of the particular food product being dealt with, however, and results cannot always be extrapolated from one product to another (Frankenthral 1959).

The initial area of blackening of the cans in control Lot No. 1 was apparent, in some cases, the day after they were processed. These control cans were heavily discolored within a period of 360 simulated days as were those experimental, Lot No. 3, cans in which the pH exceeded 6.6. Thus it can be seen that the addition of the proper concentration of lemon juice or citric acid will prevent severe discoloration of the cans.

In comparison of Lot No. 2 and Lot No. 3, it can be seen that at the end of 360 simulated days, 51 percent of the cans of Lot No. 2 containing the 1:40 lemon juice were entirely free of discoloration, whereas only 17 percent of the cans containing the 0.65-percent citric acid were free of blackening. This appears to indicate that an added controlling effect was obtained by using lemon juice. It must be noted, however, that in none of the cans in either Lot No. 2 or Lot No. 3, except in the three cans in Lot No. 3 with a pH exceeding 6.6, was the blackening excessive.

It was apparent from the range of pH values in the cans with a 0, 0+, or 1 rating, whether containing lemon juice or citric acid, that there was a considerable overlap in the values. Therefore, a statistical analyses of variance, called the F test[1/], was applied to the pH values regardless of the amount of discoloration and regardless of the additive. The F value did not exceed the 5-percent level of probability, and it was concluded that these groups did not differ significantly in their pH values. Although the pH of the can apparently should be lowered to less than 6.6 for effective control, once it falls below this point the degree of effectiveness of the additive is dependent upon other characteristics of that additive rather than the acidifying characteristic alone.

SUGGESTED PROCESSING METHOD

The processing procedure, employed in these experiments is commonly used in the Gulf of Mexico area to process other types of shrimp. The texture of the canned seabobs was firm, and no evidence of crumbling was observed in either Lot No. 2 or Lot No. 3. There was no evidence of spoilage, other than the iron sulfide discoloration present in some of the cans. This indicated that the processing time, temperature, and pressure were adequate. There appeared to be too much salt present, however, for maximum taste appeal. The cans in Lot No. 3 also appeared to have a slight aftertaste, which could have been due to the citric acid. For these reasons it was decided to pack a small number of cans with varying salt and citric acid concentrations and subject them to organoleptic analysis by a trained panel.

PROCEDURE: Cans were packed with salt concentrations varying from 0.0 to 4.9 g. per can and citric acid varying from 0.0 to 0.65 g. per can. The pack was processed as before, stored until the following day, and subjected to organoleptic evaluation.

RESULTS: Upon evaluation it was found that the optimum pack contained 3.6 g. of salt. At a concentration of citric acid greater than 0.52 grams per can an aftertaste not present in the cans containing 0.52 grams or less, was discerned by some members of the panel. This indicated that it was not practical to increase the amount of citric acid used in the previous experiment in order to attempt to attain the level of protection afforded by the lemon juice. A 1:40 concentration of lemon juice concentrate No. 309, as used in the previous experiment, did not appreciably affect the taste of the shrimp.

SUMMARY

1. A trial pack of shrimp (Xiphopeneus sp.) was processed to determine the optimum level of lemon juice concentrate No. 309 or citric acid needed to prevent iron sulfide discoloration of the canned product.

1/ A statistical test used to determine if differences between measurements may be considered as real.

2. Three large lots were processed: (a) a control lot using no additives; (b) a lot containing 80 to 85 ml. of 1:40 lemon juice concentrate No. 309 in brine per can; and (c) a lot containing 80 to 85 ml. of a 0.65-percent citric acid in brine per can (0.52 g. of citric acid per can). These were stored at 47.5° C. (117.5° F.) for 90 days (360 simulated days). At the end of this period the cans were cut, the discoloration evaluated, and the pH of the contents measured. The following conclusions were obtained from these data:

When the pH was adjusted to a value below 6.6, only slight discoloration of the cans occurred after a storage of 360 simulated days.

Fifty-one percent of the cans in the lot containing lemon juice were entirely free of blackening, whereas only 17 percent of the cans in the lot containing citric acid were free of discoloration. This disparity in percentage of cans free of discoloration would seem tc indicate that some factor in addition to acidification of the can contents was active in reducing the iron sulfide discoloration.

In an evaluation of the pH of cans scoring 0, 0+, and 1, regardless of additive or score, no significant difference was found between the lemon-juice lot and the citric-acid lot, further indicating an additive effect obtained in using lemon juice. The only significant difference in pH values obtained was between the pH values of the cans graded 0, 0+, and 1 and those graded 3 (heavily discolored).

3. A third pack was processed to determine the optimum concentration of the ingredients. The trained organoleptic panel preferred the shrimp processed with 3.6-percent brine. It was felt that the organoleptically maximal concentration of citric acid was 0.52 g. per can. A concentration of 1:40 lemon juice concentrate No. 309 did not appreciably affect the taste of the shrimp.

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AUTOMATIC DEVICE PROTECTS DRIFT NETS FROM STORM DAMAGE

The Leningrad Designing Institute of the Fishing Fleet of the U. S. S. R. is stated to have devised an automatic installation for the protection of drift nets from breaking under the strain of a storm. When the length of the nets is more than 2 miles, the strains are enormous and the new device consists of a winding drum and an electric motor which so responds to tension that it automatically pays out more cable as the strain increases and takes in slack when the tension is lowered. (Australian Fisheries Newsletter, July 1958.)