A UNITED STATES DEPARTMENT OF COMMERCE PUBLICATION

U.S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NATIONAL MARINE FISHERIES SERVICE

Blueing of Processed Crab Meat. II. Identification of Some Factors Involved In the Blue Discoloration of Canned Crab Meat (*Callinectes sapidus*)

1971

SPECIAL SCIENTIFIC REPORT–FISHERIES No. 633

NOTE

Until October 2, 1970, the National Marine Fisheries Service, Department of Commerce, was the Bureau of Commercial Fisheries, Department of the Interior.

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, *Secretary*

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
Dr. Robert M. White, *Administrator*

NATIONAL MARINE FISHERIES SERVICE
Philip M. Roedel, *Director*

Blueing of Processed Crab Meat. II. Identification of Some Factors Involved in the Blue Discoloration of Canned Crab Meat (*Callinectes sapidus*)

By

MELVIN E. WATERS

Special Scientific Report—Fisheries No. 633

Seattle, Washington
May 1971

CONTENTS

Page

Introduction 1

I. Determining the cause of blue discoloration 2
  A. Dead or decaying crab hypothesis 2
    1. Processing dead crabs 2
    2. Discarded crabs from debacking line 2
  B. Processing hypothesis 3
    1. Effect of parchment liners 3
    2. Effect of method of obtaining a vacuum 3
    3. Effect of plant water used in processing 3
  C. Chemical ion hypothesis 3

II. Remedial treatments 6
  A. Addition of organic acids 6
  B. Addition of chelating agents 6
  C. Addition of buffer solution 7
  D. Extraction of the blue colored complex 7

III. Need for additional research 7

Literature cited 7

Blueing of Processed Crab Meat.
II. Identification of Some Factors Involved in the Blue Discoloration of Canned Crab Meat *(Callinectes sapidus)*

By

MELVIN E. WATERS, Research Food Technologist
National Marine Fisheries Service Fishery Products Technology Laboratory
Pascagoula, Mississippi 39567

ABSTRACT

An outbreak of blue discoloration in canned crab meat occurred during 1969. This paper reports the result of a study we made to pinpoint the cause of blueing and suggest a remedy. Factors found not to affect the color of canned crab meat are (1) method of obtaining a vacuum, (2) the use of a parchment liner, (3) plant water used in processing, (4) the use of dead and/or partially dead crabs, and (5) several metal ions reported as the cause of blueing in other products.

Results showed that iron was involved in the discoloration. It was further shown that a buffered solution of citric acid (pH 6.5-6.8) prevented formation of the blue-colored complex.

INTRODUCTION

In early summer of 1969 during the beginning of the canned crab meat production season on the Gulf coast, a local processor experienced an outbreak of severe blue discoloration in his canned product. The discovery was made some 72 hr after processing and was the first noted for the season. A close examination of the product revealed that (1) the blue discoloration was typical of that occasionally found in canned crab meat, (2) the discoloration was not limited to any particular area of the can, (3) there was no evidence of can corrosion at the seams, (4) not all fibres of meat were affected nor was the entire fibre always affected, and (5) the pH of the meat was considerably higher than that normally found in routine production when additives were used.

After the discovery of this discoloration, a check made of subsequent production showed (1) no evidence of discoloration and (2) a lower pH than that in the affected crab meat. The outbreak in this producer's pack was confined to one day's production. We concluded that someone inadvertently left out the additives (or a portion thereof) normally added to prevent blueing.

A survey of other processors in the area showed that several of the processors were experiencing discoloration of the product. The raw material used was supplied from a wide geographical area. The blue discoloration was particularly prevalent in claw meat taken from Texas crabs. We also learned that a severe outbreak, such as that described above, had not occurred for some 7 or 8 years. The industry as a whole is affected at one time or another; consequently, it asked our help in determining the cause and suggesting a remedy.

The development of blue discoloration in various fishery products has been reviewed many times, most recently by Waters (1970). The cause(s) have been only suggested and have never been positively identified. The presence of copper ions has usually been implicated in the appearance of the blue color. Ammonia, sulfur, ferrous, and ferric ions have also been suggested as causes. Since ammonia appears to be involved, freshness of the meat is all important. Corrosion of the can's seams may supply the Fe^{++} and Fe^{+++} ions involved in blue discoloration, as the literature suggests.

The remedial treatments proposed are mainly organic acids such as ascorbic, lactic, and citric. Citric acid is widely used in the shrimp and crab processing industry to inhibit certain naturally occurring enzymes and sequester trace minerals which can act as pro-oxidant catalysts. The purpose of this paper is to (1) report on our efforts to determine the cause of blue discoloration in canned blue crab meat and (2) recommend an approved food additive that will eliminate blue discoloration in canned crab meat.

I. DETERMINING THE CAUSE OF BLUE DISCOLORATION

A. Dead or Decaying Crab Hypothesis

If a production manager is asked what is causing the blue discoloration in his canned crab meat he will probably say his supplier is picking some dead crabs. It is true that meat from crabs that had expired prior to processing is darker and the texture is somewhat different. In fact, in the debacking process the employee is asked to discard a crab suspected of being dead using these criteria for rejection. The "dead crab theory" of the processors was only a hypothesis and was not based on experimental facts. The idea, however, seemed to have merit, particularly in that both ammonia and pH have been thought to play a part in the blueing phenomenon. The ammonia would be formed as a product of the breakdown of proteins and the pH of the crab meat would be raised.

The following experiment was designed to test this theory:

1. **Processing dead crabs.** — One hundred lb of very active crabs were selected for this study. They were randomly divided into two lots. One of the lots was processed without further treatment. The method we used consisted of removing the meat from the boiled crabs, placing the meat in 307 × 113 C-enamel cans, and adding about 100 ml of brine. The cans were closed under a 10- to 15-inch vacuum and heat processed for 45 min at 240° F. This method is a laboratory reproduction of an often used commercial procedure.

The second lot was exposed to the sun (75-95° F) for 24 hr without the aid of a cooling water spray or any other cooling effect. We hoped that this unusual treatment would cause the crabs to die. After 24 hr exposure to the sun, the crabs were examined to determine their condition. Only 40% of the crabs had actually died but the remainder were somewhat less than active. The lot was processed using the commercial method described above.

Representative cans from both lots were examined after 1, 2, and 4 days of storage. There was no detectable discoloration of the crab meat. Generally, when blueing appears in canned crab meat, it occurs within 24 hr after processing. After studying the results of this experiment, we thought that perhaps the crabs had not been dead long enough for degradation products to be present. Consequently, we conducted another experiment.

2. **Discarded crabs from debacking line.** —Fresh crab meat was obtained from the processing line of a commercial crab meat plant. This lot was processed by our usual method and served as the control. Discarded crabs that were found dead prior to boiling were obtained from the debacking line. The dead crabs were from the same lot of crabs. The color of the meat removed from the carcass was a light grey and entirely different in color from the meat picked from fresh, live crabs. This meat was also processed in the usual manner. The processed samples were stored and examined as above.

The results showed that heat processing did not cause any added discoloration over that present in the nonprocessed discarded crabs. We concluded that processing dead crabs, in itself, was not the cause of blueing. However, it is possible that this condition is contributing when other factors are present.

B. Processing Hypothesis

Plant conditions and/or methods of preparing crab meat for canning vary from plant to plant. For example, one processor may use a parchment liner while another may not. Commercial methods for obtaining a vacuum are (1) mechanical evacuation of the air prior to sealing the cans and (2) heating the open cans prior to sealing. Another variable is the composition of the inplant water as water in the coastal areas sometimes contains high levels of minerals that could affect the processed product. These variables were examined to determine if they contribute to the blueing problem. Figure 1 describes the experimental design.

1. **Effect of parchment liners.** — Approximately 40 cans of crab meat were prepared and divided into two lots. Parchment liners were added to the first lot while the second lot without liners served as the control. The cans of crab meat were then processed. Examination of the two lots after 3 days of storage revealed no difference in color between the two lots.

2. **Effect of method of obtaining a vacuum.**—Cans of crab meat were prepared as in experiment 1 above and the two lots were further divided into two lots each, making a total of four lots (Fig. 1). Two lots (with and without parchment liners) were processed using mechanical means for vacuum production while the second two lots were heated to 140° F prior to sealing the cans in order to produce the vacuum. Examination of the stored product showed no discoloration in any of the lots.

3. **Effect of plant water used in processing.**—An experiment was conducted whereby water from three sources was used in processing crab meat. A brine solution was made from (1) water used in the plant where the crab meat was picked (primary), (2) water used in the canning plant where the blueing outbreak occurred (secondary), (3) Pascagoula city water (known to contain a high level of certain minerals), and (4) a distilled water control. Cans of crab meat were prepared as in experiment 2 (four lots) with each lot being further divided four ways. Brine solutions prepared from the various water sources were added as shown in Figure 1. The cans were processed, stored, and examined as before. No difference in color existed among the different lots.

We concluded that the use of parchment liners, the method used to produce vacuum, and the source of the processing water did not influence the development of blue discoloration.

C. Chemical Ion Hypothesis

Many theories have been proposed relative to the role chemical ions play in the blue discoloration of crab meat. A majority of the reports found in the literature suggest that copper ions are responsible (Oshima, 1932; Fellers and Harris, 1940; Dassow, 1963; Groninger and Dassow, 1964). Others report that iron, ammonia, and sulfur contribute to the problem.

Heretofore, we had not been able to reproduce the blueing experienced in the commercial lots. We decided, therefore, to add chemical compounds containing the ions mentioned above to cans of crab meat to determine if the blueing could be produced in this manner.

Dilute solutions of the following compounds were added to cans of crab meat: cuprous chloride [$CuCl$], cupric nitrate [$Cu(NO_3)_2$], ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$], and ammonium hydroxide [NH_4OH]. Distilled water was used for the control. Salt was added to the solutions to give the desired brine concentration. The cans were processed by our commercial method and examined after 3 days of storage. Table 1 shows the results.

The ferrous ammonium sulfate solutions produced blue discoloration typical of that found in canned crab meat. Neither copper compound caused significant blueing nor did the dilute solutions of NH_4OH. The control was negative. Thus, the foregoing results showed that one of the ions in $Fe(NH_4)_2(SO_4)_2$ was responsible for blueing.

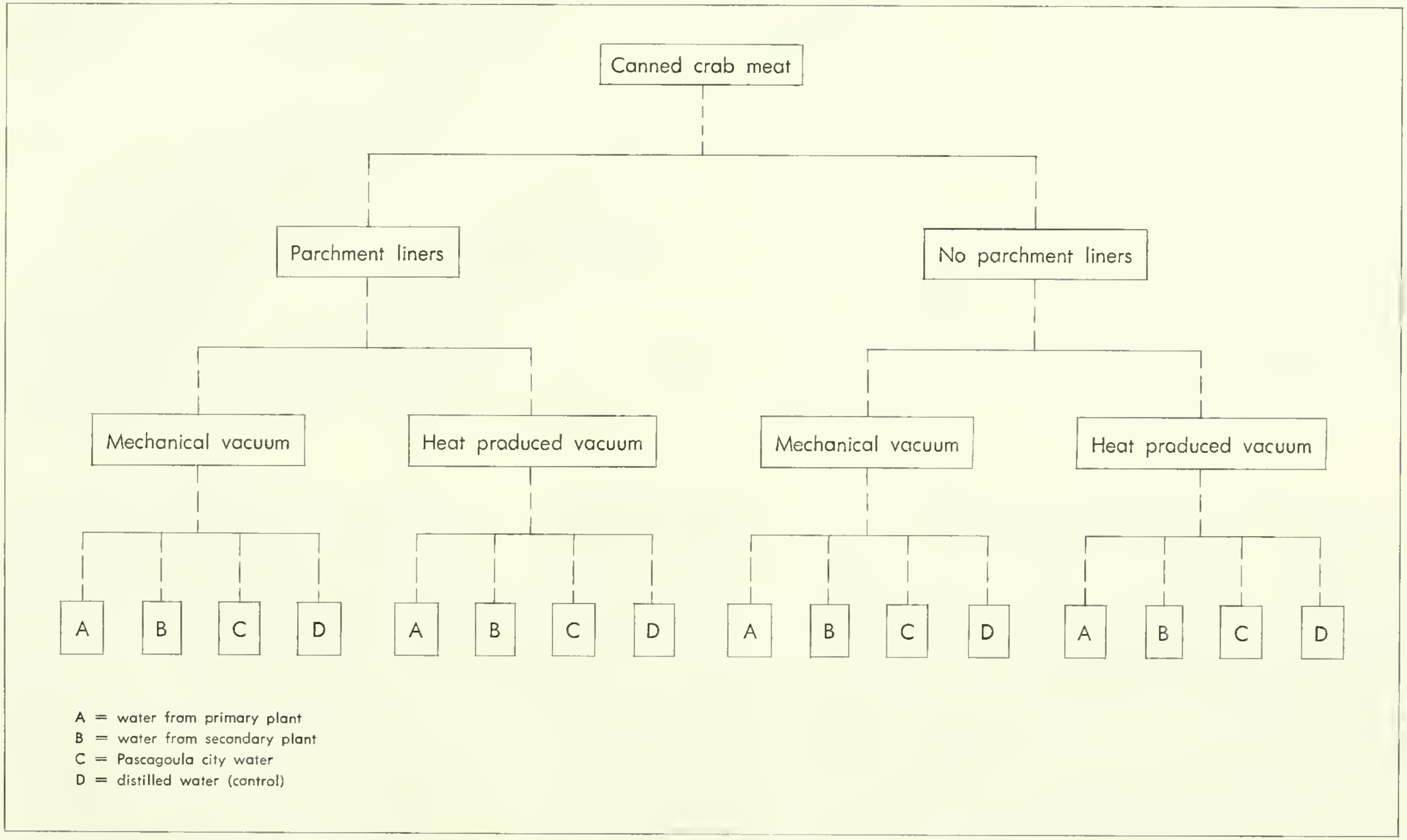

Figure 1.—Flow sheet describing experimental procedure used to determine if varying processing techniques contribute to blue discoloration in canned crab meat.

Table 1.—Results of adding chemicals to canned crab meat to determine the responsible agent involved in blue discoloration.

Additive	Concentration	Visual rating[1]
NH_4OH	0.01 M	+
	.005 M	+
	.001 M	0
$Fe(NH_4)_2(SO_4)_2$	.01 M	++++
	.005 M	++++
	.001 M	+++
CuCl	.05 M	+
	.01 M	+
	.005 M	0
$Cu(NO_3)_2$	.05 M	+
	.01 M	+
	.005 M	+
Distilled water (control)	..	0

[1] 0 = no visible blueing
+ = very slight blueing
++ = slight blueing
+++ = moderate blueing
++++ = heavy blueing

A second experiment was designed to include different compounds containing Fe^{++} and/or Fe^{+++}, NH^+, and $SO_4^=$ ions alone.

Dilute solutions of the following chemicals were added to cans of crab meat as before: ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$], ferric chloride [$FeCl_3 \cdot 6H_2O$], ammonium citrate [$(NH_4)_2HC_6H_5O_7$], ammonium nitrate [NH_4NO_3], ammonium chloride [NH_4Cl], ammonium sulfate [$(NH_4)_2SO_4$], cuprous chloride [CuCl], cupric sulfate [Cu_2SO_4], and ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$]. Distilled water served as the control. After processing and 3 days of storage, cans of each variable were examined. Results are shown in Table 2.

The copper compounds were included again to positively determine if copper could be incriminated in the blueing reaction. The results show that every lot containing Fe^{++} and Fe^{+++} ions had considerable blueing. Each Fe^{++} and Fe^{+++} compound displayed about the same degree of blueing when added at the same concentration. Compounds (exclusive of $Fe(NH_4)_2(SO_4)_2$) containing either $SO_4^=$, NH_4^+, Cu^+, or Cu^{++} ions did not discolor the crab meat appreciably. Several additional experiments were conducted adding

Table 2.—Results of adding chemicals containing $SO_4^=$, NH_4^+, Cu, and Fe^{++} and Fe^{+++} ions to canned crab meat.

Additive	Concentration	Visual rating[1]
Cu_2SO_4	0.1 M	++
CuCl	.1 M	++
$(NH_4)_2C_2O_4 \cdot H_2O$	.1 M	0
$Fe(NH_4)_2(SO_4)_2$	.005 M	++++
$FeCl_3 \cdot 6H_2O$	.1 M	++++
	.05 M	++++
	.01 M	++++
$(NH_4)_2HC_2H_5O_7$	.1 M	+
	.01 M	+
NH_4NO_3	.1 M	+
	.01 M	+
NH_4Cl	.1 M	+
	.01 M	+
$(NH_4)_2SO_4$	.1 M	+
	.01 M	0
Distilled water (control)	..	0

[1] 0 = no visible blueing
+ = very slight blueing
++ = slight blueing
+++ = moderate blueing
++++ = heavy blueing

$Fe(NH_4)_2(SO_4)_2$ to crab meat obtained from various processing plants and on every occasion the meat turned blue. These results demonstrated beyond any reasonable doubt that Fe^{++} and/or Fe^{+++} ions are responsible for blue discoloration in canned crab meat.

Apparently, at some time during the life of the crab or during the processing procedure, the meat is exposed to or contaminated with a relatively high concentration of iron. Whether the contamination comes from processing techniques or is inherent to the crab is open to conjecture. One possible source is through airborne contamination. Thompson and Farragut (1969) determined that airborne metallic particles were responsible for green discoloration in frozen raw breaded shrimp. Iron processing baskets are often used. Pollution of the waters which the crabs inhabit cannot be ruled out. Whatever the cause, blueing occurs spontaneously and sporadically.

II. REMEDIAL TREATMENTS

Before a comprehensive study could be undertaken to prevent blueing, we first had to be able to produce the condition in the laboratory since its natural occurrence was unpredictable. We were able to do this in the preceding experiments and now we could move on to the area of preventive measures.

A. Addition of Organic Acids

The literature suggested that various organic acids would prevent blueing of crab meat. We had determined that increasing the pH would influence the degree of blueing slightly. We proceeded to add dilute solutions of the following acids to cans of crab meat containing iron: citric acid, ascorbic acid, lactic acid, and tartaric acid. The crab meat was processed and examined as previously described. Results are shown in Table 3.

Table 3.—Results of adding organic acids to canned crab meat to prevent blueing.

Additive	Concentration	Visual rating[1]
Citric acid	2%	++
	3%	0
	5%	0
Ascorbic acid	1%	++++
	3%	++++
Lactic acid	1%	++++
	3%	+++
Tartaric acid	1%	++
	2%	++
Ferrous ammonium sulfate	0.005 M	++++
Distilled water (control)	..	0

[1] 0 = no visible blueing
+ = very slight blueing
++ = slight blueing
+++ = moderate blueing
++++ = heavy blueing

Results shown that when a 3% and a 5% citric acid brine solution were added to the cans, no blue discoloration occurred even in the presence of iron. A 2% citric acid solution, however, allowed some discoloration to develop. Unfortunately, a 2, 3, and 5% citric acid solution imparted a very unpleasant flavor to the crab meat. Varga, Dewar, and Anderson (1969) reported that the association between the concentration of citric acid added and the appearance of blue discoloration in crab meat bore a statistically significant inverse relationship. A 1% and 2% solution of tartaric acid did not completely prevent blueing. Both concentrations seemed to be about as effective as the 2% citric acid solution. Lactic acid and ascorbic acid appeared not to prevent blueing.

These results indicated that a lowering of the pH contributes, at least in part, to the effectiveness of citric acid in preventing blueing. Citric acid, however, is also known for its antioxidant effect and chelating ability. Ascorbic acid is a good antioxidant but proved useless in the above experiments. We decided to determine if chelation of essential metal ions by citric acid produced the anti-blueing effect by experimenting with other chelating agents.

B. Addition of Chelating Agents

Ethylenediaminetetraacetic acid (EDTA) and several of its salts have proven effective in chelating troublesome metal ions such as magnesium, iron, copper, etc. Since we had found earlier that iron was responsible in part for blue discoloration, we thought that this group of compounds might prove beneficial in correcting the blue discoloration. The disodium salt of EDTA is already approved by the Food and Drug Administration for use in vegetables, fruits, and dressings. The calcium disodium salt is approved for use in several seafoods, vegetables, soft drinks, and dressings. The following experiment was conducted using various salts of EDTA.

Disodium EDTA, disodium calcium EDTA, and tetrasodium EDTA, at a level of 250 ppm in brine, were added to cans of crab meat containing iron. The 250 ppm level was selected because this is the present upper allowable limit of any salt of EDTA. The cans were processed, stored, and examined after 3 days. The results showed that no difference in the intensity of blueing occurred between the various salts of EDTA and/or between the salts and the control. It is not entirely clear why EDTA salts did not deter blueing. It is known, however, that the effectiveness of EDTA in eliminating certain metal ions depends on (1) the pH of the system and (2) the order of complexation of the metals present.

C. Addition of Buffer Solution

As mentioned earlier in this paper, one of the companies whose product was affected in the blueing outbreak in the summer of 1969 used a chemical formula to prevent blueing. This preservative was formulated by a consultant and is patented. It consists of a phosphate buffered citric acid solution added with the brine solution. This solution decreases the pH of the canned crab meat to 6.8 or less.

Our work confirmed that the addition of the company-supplied phosphate-citric acid brine solution to cans of crab meat containing added iron ions prevented blueing. pH thus appeared an all-important factor in blue color inhibition; however, the chelation of iron ions by citric acid at pH 6.5-6.8 cannot be ruled out.

D. Extraction of the Blue Colored Complex

We wished to extract the blue colored complex in order to further study the blue phenomenon. Several attempts were made using organic solvents such as hexane, acetone, chloroform-methanol, acetone-chloroform, ether, and trichloroacetic acid (TCA). None of these solvents would extract the complex nor did they affect the color. A dilute solution (0.01 N) of HCl was employed with little success. The acid tended to cause the blue color to dissipate rather than to extract the responsible compound. No further attempt was made to study the blueing complex.

III. NEED FOR ADDITIONAL RESEARCH

Data obtained during the course of this work probably posed more questions than they answered. Although the objectives of this work were achieved, questions regarding the blueing reaction abound: (1) what other condition(s) or compound(s) must be present in addition to iron? (2) is the iron bound and, if so, to what constituent of the crab meat? (3) where does the iron come from? (4) what can be used to extract the color complex in order to better study its formation? and (5) how may the processor avoid the conditions necessary for blueing? All must be answered if a clear understanding is to be forthcoming.

LITERATURE CITED

DASSOW, J. A. 1963. The crab and lobster fisheries, p. 193-208. *In* M. E. Stansby (ed.) Industrial fishery technology. Reinhold Publishing Corp., New York.

FELLERS, C. R., and S. G. HARRIS. 1940. Canned Atlantic crab meat, a new American food. Ind. Eng. Chem. 32: 592-594.

GRONINGER, H. S., and J. A. DASSOW. 1964. Observations of the "blueing" of king crab, *Paralithodes camtschatica*. U.S. Fish Wildl. Serv., Fish. Ind. Res. 2(3): 47-52.

OSHIMA, K. 1932. Studies in crab canning. [U.S.] Bur. Fish., Invest. Rep. 8. 8 p.

THOMPSON, M. H., and R. N. FARRAGUT. 1969. Problem of "green" frozen raw breaded shrimp. U.S. Fish Wildl. Serv., Fish. Ind. Res. 5. 1-10.

VARGA, S., A. B. DEWAR, and W. E. ANDERSON. 1969. Effect of citric acid on quality of heat processed crab meat. Can. Fish. Rep. 13: 169-174.

WATERS, M. E. 1970. Blueing of processed crab meat. 1. A Study of processing procedures that may cause a blue discoloration in pasteurized crab meat. U.S. Fish Wildl. Serv., Fish. Ind. Res. 6: 173-183.

UNITED STATES
DEPARTMENT OF COMMERCE
NATIONAL OCEANIC & ATMOSPHERIC ADMINISTRATION
NATIONAL MARINE FISHERIES SERVICE
SCIENTIFIC PUBLICATIONS UNIT
BLDG. 67, NAVAL SUPPORT ACTIVITY
SEATTLE, WASHINGTON 98115

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE

PERIODICALS LIBRARIAN E
MARINE BIOLOGICAL LABORATORY
LIBRARY
WOODS HOLE, MA 02543