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IRON SULFIDE DISCOLORATION OF TUNA CANS[1/]

No. 6 - Experiments to Elucidate Mechanism of the Reaction

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ABSTRACT

Experiments which were conducted to elucidate and render inoperative the mechanism whereby tuna cans are discolored by iron sulfide formation were partially successful. The catalytic factor was found to be heat-stable and present in the meat of certain batches of tuna. Repacking of the tuna from discolored cans into new cans with a second retorting did not prevent discoloration. Neither oil nor brine from such cans, when repacked, caused discoloration. Headspace gases did not show any significant differences between control and discolored packs. Acids were found not to be the cause of the discoloration though they did cause corrosion of the cans. Inversion of the cans soon after retorting prevented the formation of iron sulfide. Discoloration does not occur in cans containing no free liquid.

BACKGROUND

Certain batches of tuna fish, when canned, cause an iron sulfide discoloration n the can area adjacent to the headspace. The present investigation has been a tudy of iron sulfide formation and the variables that affect it (Pigott and Stansby 955).

The five preceding papers in this series of articles designed to report the work f the project have dealt with the effect of processing variables on can discoloration. he objective of this paper, the last in the series, is to discuss various experiments hat were carried out to elucidate the mechanism of the reaction causing the iron ulfide discoloration.

EXPERIMENTAL WORK

GENERAL: Previous work in this investigation has shown that the iron sulfide iscoloration is formed from hydrogen sulfide that is produced by tuna meat during etorting, and iron in the tin can that has been converted to the ferrous state. The olution to the problem now lies in determining the mechanism whereby iron is conerted to the ferrous form by a substance present only in certain batches of tuna. A eries of experiments were carried out to study the mechanism of this reaction.

REPACKING CANNED TUNA: A repacking experiment was undertaken in an ffort to determine if the factor causing discoloration was in the meat or in the liqid. The experiment was as follows: After cans of discolored and normal tuna were pened, the oil was drained, and the meat was repacked into new single-enamel cans. he drained oil from both the discolored and the normal packs was added to a fresh- precooked albacore pack that had never caused can discoloration. Results of this ork are shown in table 1.

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1/ This investigation, which was carried out at the Seattle Technological Laboratory, U. S. Fish and Wildlife Service, was jointly sponsored by the Continental Can Company and the U. S. Fish and Wildlife Service.

Table 1 - Effect of Repacking and Reprocessing Tuna Upon Can Discoloration						
Species of Tuna	Original Pack[1]		First Repack of Original Fish[1]		Second Repack of Original Fish[1]	
	Additive	Degree of Discoloration	Additive	Degree of Discoloration	Additive	Degree of Discoloration
Yellowfin	Oil, salt	Medium	Soya oil	Medium	Soya oil	Light
	Oil, salt	Medium	Brine	Medium	Brine	Light
Albacore	Oil, salt	None	Soya oil	None	Soya oil	None[2]
	Brine	None	Soya oil	None	Soya oil	None[2]
	Brine	Medium	Brine	Medium	Brine	Light
	Oil, salt	Medium	Soya oil	Medium	Soya oil	None[3]
	Oil, salt	None	Soya oil from discolored pack	None	Soya oil from discolored pack	None
	Oil, salt (flake pack)	None	Soya oil	None	-	-

1/SOLID PACK UNLESS OTHERWISE STATED.
2/THIS PACK SHOWED MEDIUM DISCOLORATION WHEN THE SECOND REPACK WAS INCUBATED AT 37° C. FOR 14 DAYS.
3/THIS PACK SHOWED LIGHT DISCOLORATION WHEN SECOND REPACK WAS INCUBATED AT 37° C. FOR 14 DAYS.

The tuna that caused discoloration in the original packs again caused discoloration when repacked into a new can. The oil that was drained from the original discolored packs did not cause discoloration in the albacore packs. Brine packs gave the same results, when repacked, as did oil packs. Thus, the factor favoring discoloration seems to be present in the tuna meat, since the factor causing can discoloration is carried by the previously processed tuna meat into a new can even when the oil or brine from the preceding stage is removed and fresh oil or brine is added.

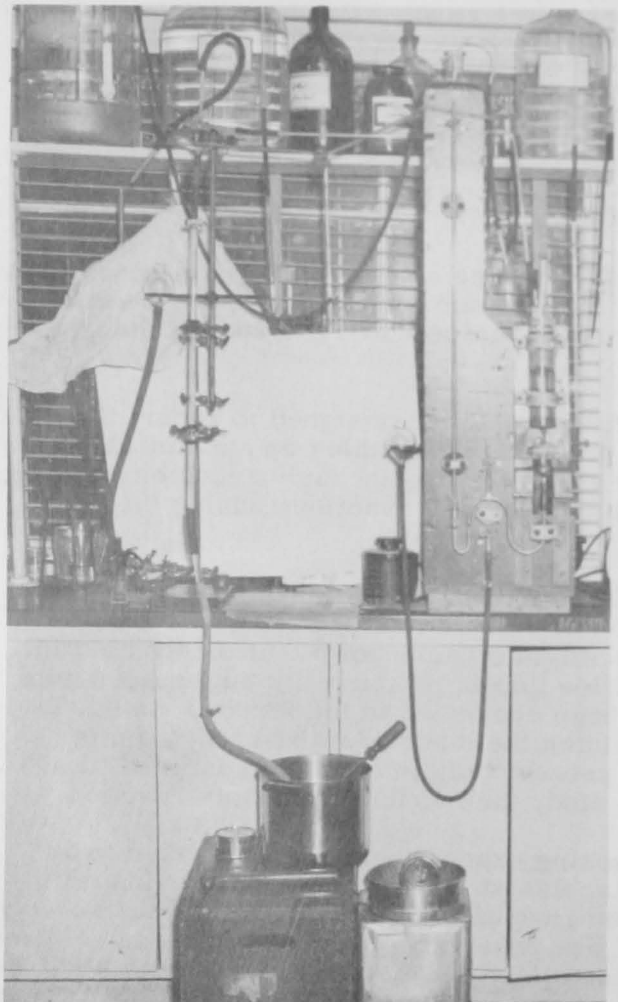

Fig. 1 - Apparatus used in determination of quantity and chemical composition of head-space gases in canned tuna.

COMPOSITION OF HEADSPACE GASES: Headspace gases in various experimental and commercial solid packs of tuna were analyzed for volatile acids, volatile bases, oxygen, and hydrogen to see if a difference in composition between normal and discolored packs could be detected (table 2). In general, no significant differences were detected between the various packs. The variation in composition for the constituents measured was just as great in cans from the same pack as it was between different packs, normal or discolored.

EFFECT OF pH: With the exception of one discolored commercial albacore pack that had a pH of 5.6, all of the packs inspected in this investigation ranged from a pH of 5.85 to 6.1. The acid content of experimental packs was varied to determine the effect of pH of the meat on can discoloration. Both acetic and hydrochloric acids were used to adjust the pH of the can contents just before sealing and retorting.

At pH values of 5 or above no can discoloration was produced in experime al packs of albacore that normally did not cause can discoloration. When the pH was adjusted below 5, the cans were attacked, but the corrosion was not of the same ype as that found in cans discolored under normal processing onditions. Futhermore, owing o the buffering capacity of the una meat, such a large amount f acid had to be added that the neat became inedible.

Table 2 - Composition of Headspace Gases in Solid-Pack Tuna		
Constituent	Volume of Gas[2/]	
	Range	Average
	. . . . (Cubic Centimeters)	
Total headspace gas[1/]	6.75-27.5	15.0
Volatile acid	0.23- 2.28	0.72
Volatile base	0.23- 1.42	0.72
Oxygen	0- 0.45	0.18
Hydrogen	3/	0

1/THE INERT GAS (MOSTLY NITROGEN) DETERMINED BY DIFFERENCE WAS 80 TO 95 PERCENT BY VOLUME.
2/70° F., ATMOSPHERIC PRESSURE.
3/FOUND IN MINUTE QUANTITIES IN FOUR CANS ONLY.

EFFECT OF FREE LIQUID: Discoloration reported in commercial packs occurs in solid-pack tuna but not in flake packs. The two main differences between solid packs and lake packs are the particle size and the amount of free liquid that is in the can. The lake pack absorbs much more oil than does the solid pack so that commercially-canned flake tuna has no free oil in the can. The effect of having free oil or brine n flake packs was thoroughly investigated using albacore and yellowfin tuna that ormally cause can discoloration in solid packs.

It was found that normal flake packs will not cause can discoloration when the mount of oil that is normally used is present. However, if enough excess oil is dded so that free oil is present in the can, the same amount of discoloration is ound in flake packs from lots of tuna causing discoloration as is found in solid packs rom the same lots of tuna. The presence of free brine in brine flake packs from he same lots of tuna also produced sulfide discoloration. A slight amount of can liscoloration was found in some flake packs not containing free liquid when canned. This was due to free liquid being cooked from the brine packs during retorting. Thus, hese results indicate that there is a substance in some tuna that will cause can discoloration if a medium such as oil or brine is free to wash over the can surface during retorting. Results of this work are shown in table 3. In these experiments it was again found that salt must be present if discoloration is to take place.

Table 3 - Effect of Type of Pack[1/] and Additives on Discoloration of Tuna Cans				
Type of Pack[2/]	Additives			Discoloration
	Soya Oil	Saturated Brine	Salt	
	. . . . .	. (Ounces) .	. . . .	Degree
Solid	1½	0	⅛	Medium
	1½	0	0	None
Flake	1½	0	⅛	None
	3[3/]	0	⅛	Medium
Solid	0	1½	0	Heavy
	0	0	0	None[4/]
Flake	0	1½	0	None[4/]
	0	3[3/]	0	Medium

1/THESE PACKS WERE MADE FROM LOTS OF TUNA THAT HAD A RECORD OF CAUSING CAN DISCOLORATION.
2/ALL PACKS WERE PROCESSED 75 MINUTES AT 240° F.
3/APPROXIMATELY 3 OUNCES OF OIL OR BRINE WERE ADDED TO THESE PACKS TO INSURE COMPLETE COVERAGE OF THE MEAT. THEREFORE, FREE LIQUID WAS PRESENT IN THE CAN.
4/IF THE PRECOOKED FISH WAS MOIST ENOUGH SO THAT FREE LIQUID WAS COOKED OUT OF THE FISH DURING RETORTING, CAN DISCOLORATION WAS FOUND.

These results were followed by experiments to determine whether or not can discoloration would occur if the free liquid were kept from contacting the surface of the lid during retorting. When the tuna and liquid that ordinarily caused discoloration were placed in sausage kins and then canned and processed, can discoloration was prevented.

INVERTING CANS AFTER RETORTING: Iron sulfide discoloration never occurs here meat or liquid is in contact with the can during the cooling period after retorting. Tin sulfide frequently forms in this area in both normal and discolored acks. Since cans that will be discolored apparently have ferrous iron being formed in the headspace during the cooling period, it seemed that ferrous sulfide might e prevented if the cans were inverted during cooling, just before the deposit occurred. At this time, enough of the liquid might adhere to the bottom, so that when the an was inverted, stannous ions would continue to form in the new headspace. Also, e original top end would be covered with the liquid that prevents ferrous ions from eing formed.

Packs of yellowfin and albacore that ordinarily produce can discoloration were retorted for 75 minutes at 240° F. Cans from the packs were then inverted at intervals from 0 to 60 minutes after retorting. Cans that were inverted between 5 and 20 minutes after retorting showed no discoloration on the top or bottom, whereas the tops of control cans (not inverted) were discolored. After the cooling period the cans could be turned right-side up for labeling and handling.

In a very few tuna canneries, the cans are placed in orderly fashion on trays and retorted. The cans on these trays could readily be inverted after removal from the retort. However, in the vast majority of tuna canneries, the cans are placed in baskets in a jumbled fashion, with most cans standing on edge. In such plants it would be quite impossible to invert cans after they are retorted as a method of preventing can discoloration.

CONCLUSIONS

1. The factor that caused can discoloration was relatively heat stable and was present in the meat of certain batches of tuna.

2. No significant differences in the gross headspace gas composition of normal and discolored tuna were detected.

3. The pH of the tuna was not found to be an important factor in determining the extent of can discoloration.

4. Discoloration did not occur in canned tuna unless free liquid (oil or brine) was present in the can. This accounts for the fact that flake packs, which absorb the amount of oil normally added commercially, do not show can discoloration.

5. Discoloration did not occur where meat or liquid was in contact with the can during cooling.

RECAPITULATION OF ENTIRE INVESTIGATION

The object of this entire investigation was to study the reaction mechanism whereby iron sulfide is formed during the canning of some batches of tuna. Of course, the ultimate aim of any such project is to supply information that will lead to a commercially-feasible solution of the problem. The most important conclusions that have been reached during this investigation and reported in this series of papers are as follows:

1. Formation of black iron sulfide in canned tuna depends upon the presence of ferrous iron.

2. All cans of tuna contain sufficient hydrogen sulfide to give can discoloration if any exposed iron in the can is in the ferrous state.

3. Sulfide discoloration occurs only in cans that have free liquid in the can.

4. Sulfide discoloration occurs after the cans are retorted, during the cooling period.

5. Increasing the length of time the fish are in cold storage prior to canning increases the tendency for tuna to cause can discoloration.

6. Sulfide discoloration is much worse in cans of tuna that are allowed to remain at elevated temperatures after the retorting period.

7. The factor that causes iron in the can to be converted to the ferrous state in certain batches of canned tuna is present in the meat of the fish.

Currently, the senior author is undertaking an investigation 2/ of the tin-iron ouple in tuna cans during processing and cooling. It is hoped that the factor that auses ferrous ions to be present in the can area adjacent to the headspace in certain batches of tuna can be found by this approach. If this factor can be defined, a ong step will have been taken toward the control of iron sulfide discoloration of tuna ans.

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/ This investigation is being carried out in the Department of Chemical Engineering, University of Washington, Seattle, Wash., as the basis for a Ph. D. thesis.

TUNA FOR BREAKFAST

"Eat a Better Breakfast"--the slogan of National Better Breakfast Month in September--was intended to point up the need for improving breakfast eating habits.

Various government, medical, and nutritional leaders have stated that from many standpoints breakfast is the most important meal of the day. Yet, in many households it is the "neglected meal."

Surveys show that a consistent feeling of well-being is maintained after eating a high-protein breakfast. This maintains the proper blood sugar level and increases the physical and mental efficiency of the young and old alike.

Canned tuna with its high-quality protein is a natural ingredient for a breakfast "delight" made by combining tuna with scrambled eggs, Served with a fruit, toast, and a beverage, you have a perfect start for a busy day.

Join the bandwagon for a better breakfast by serving "Tuna and Egg Scramble" as recommended by the home economists of the U. S. Fish and Wildlife Service.

TUNA AND EGG SCRAMBLE

1 CAN (6 OR 7 OUNCES) TUNA
$\frac{1}{2}$ CUP CHOPPED ONION
3 TABLESPOONS BUTTER OR OTHER FAT, MELTED
7 EGGS, BEATEN
$\frac{1}{3}$ CUP MILK

1 TABLESPOON LEMON JUICE
1 TEASPOON WORCESTERSHIRE SAUCE
$\frac{1}{2}$ TEASPOON SALT
DASH CAYENNE PEPPER
CHOPPED PARSLEY
TOAST POINTS

Drain tuna. Flake. Cook onion in butter until tender. Combine eggs, milk, lemon juice, seasonings, and tuna. Add to onion mixture and cook until eggs are firm, stirring occasionally. Garnish with parsley sprinkled over the top. Serve on toast points. Serves 6.