IRON SULFIDE DISCOLORATION OF TUNA CANS[1/]

No. 4 - Effect of Retorting and Cooling Canned Fish

By George M. Pigott* and M. E. Stansby**

ABSTRACT

Investigations were made on the effects of retorting and cooling on the formation of black ferrous sulfide discoloration in canned tuna. Free sulfide was not found in the unprocessed fish but appeared in all canned tuna after processing. The amount of free sulfide was found to increase with longer retorting periods. Free sulfide did not form a black precipitate of ferrous sulfide unless the free iron in the ferrous state was available. Discoloration occurred in the cans during the cooling period and was greater in cans held, while cooling, at elevated temperatures.

INTRODUCTION

Certain batches of tuna when canned cause an iron sulfide deposit to form on the can area adjacent to the headspace. The deposit is caused by a reaction between sulfide from the fish and iron in the can. This paper is the fourth in a series of six papers in which a study of the reaction between ferrous iron in tuna cans and sulfide in tuna meat is reported (Pigott and Stansby 1955).

Previous work showed that precooked tuna contains no free sulfide. Therefore, the sulfide in the canned product that is available for reacting with iron must be produced during retorting. Any discoloration formed could also be materially affected by the conditions of time and temperature under which the cans are cooled. The object of this paper is to report experimental work on the effect of retorting and cooling on the sulfide content, and subsequent discoloration, of canned tuna.

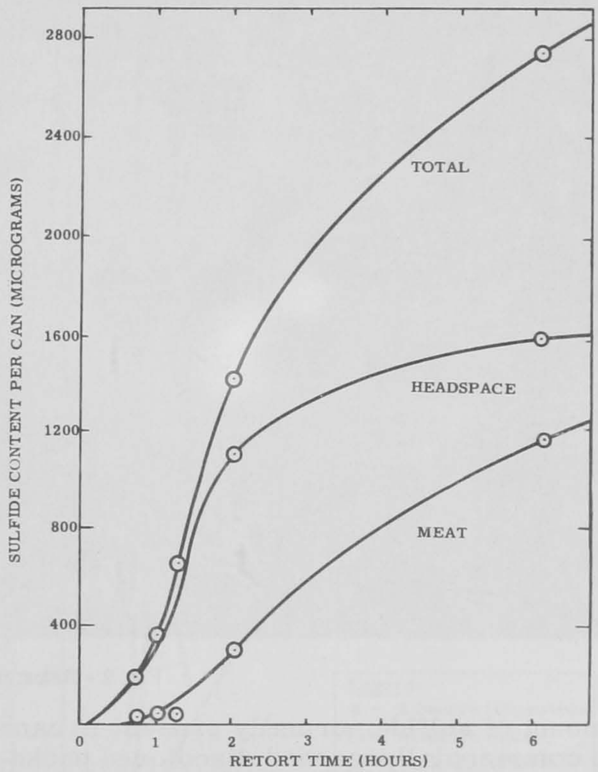

Fig. 1 - Sulfide content of can vs. retort time.

RETORTING CANNED TUNA

If the amount of discoloration in canned tuna depends on the amount of sulfide present and the amount of sulfide produced is dependent on the length of the retorting period, a slight variation in the cooking time might be the deciding factor in can discoloration. In order to investigate the formation of sulfide as a function of retorting time, local albacore tuna that had been in cold storage at -20° F. for 10 months was canned and retorted at 240° F. for various periods of time up to 6 hours. The headspace gases and meat (including liquid) in composites containing 5 cans each were then analyzed for sulfide content. The precooked fish contained no free sulfide when placed into the cans.

The sulfide content became appreciably larger in amount as the retorting time was increased. The results (fig. 1) showed that the free sulfide formed during

* Formerly Chemical Engineer, Continental Can Company, Seattle, Wash.
** Chief, Pacific Coast and Alaska Technological Research, Fishery Technological Laboratory, Branch of Commercial Fisheries, U. S. Fish and Wildlife Service, Seattle, Wash.

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 Fish and Wildlife Service.

retorting was found mostly as hydrogen sulfide gas in the headspace of the can, although significant amounts were found in the meat. Tin sulfide staining was found in cans that were processed one hour, and this staining also became larger in amount with increased retorting time. However, even though the sulfide content of the cans became far greater than that found in normal packs, no ferrous sulfide discoloration was formed in this particular batch of tuna.

The above results showed that sulfide in canned tuna is released during the retorting period (fig. 2). A series of analyses were carried out to determine the

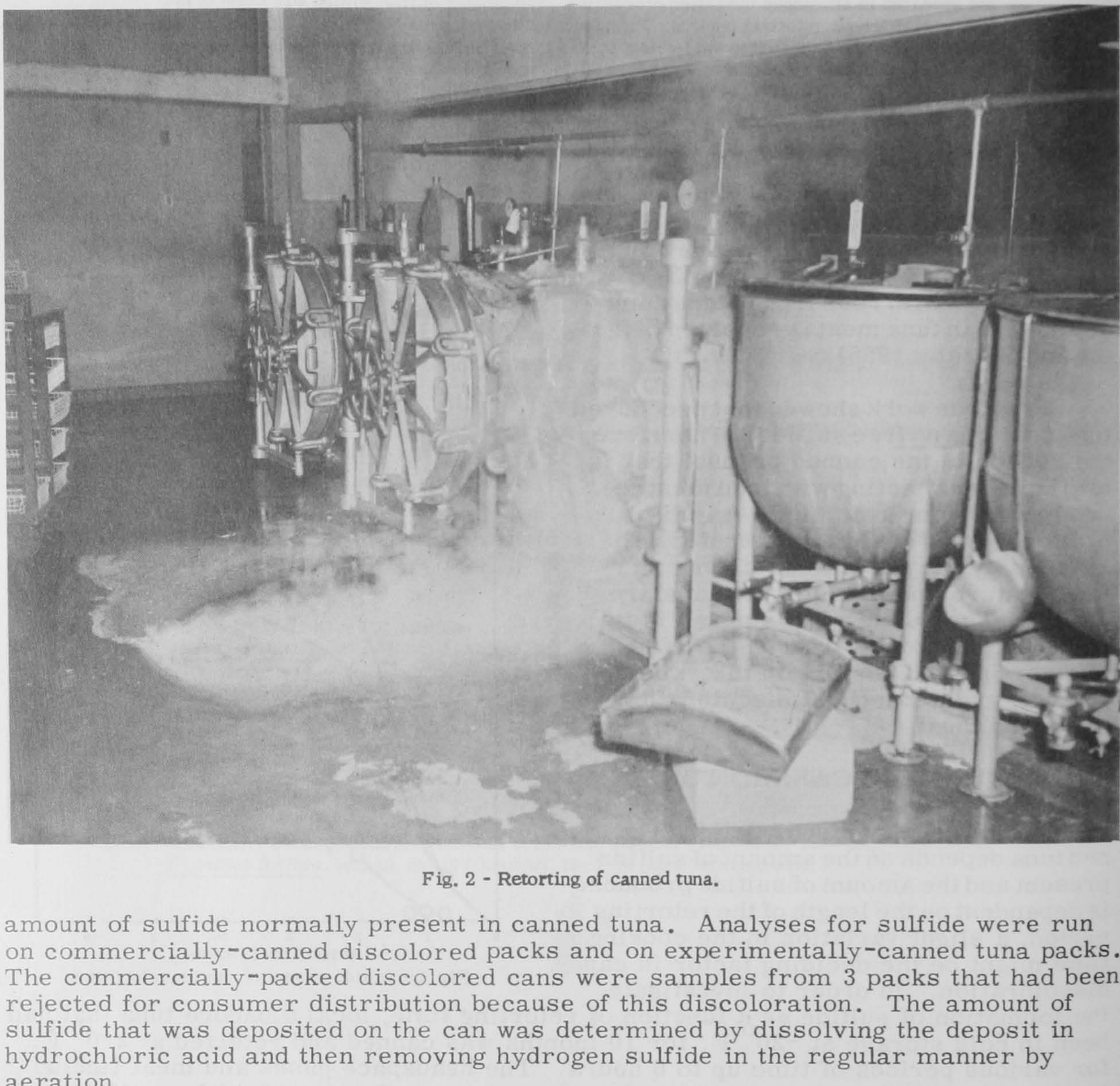

Fig. 2 - Retorting of canned tuna.

amount of sulfide normally present in canned tuna. Analyses for sulfide were run on commercially-canned discolored packs and on experimentally-canned tuna packs. The commercially-packed discolored cans were samples from 3 packs that had been rejected for consumer distribution because of this discoloration. The amount of sulfide that was deposited on the can was determined by dissolving the deposit in hydrochloric acid and then removing hydrogen sulfide in the regular manner by aeration.

It was found that appreciable sulfide is present in both normal and discolored tuna cans. The distribution of sulfide in various packs is shown in table 1. Experimental pack 1 is from the same experiment in which the amount of sulfide formed during retorting was determined. An exploration for the hydrogen sulfide being much higher in this pack is that the fish used were from the group of local albacore that were slightly spoiled when frozen and hence the fish tissue was more easily broken down by thermal processing.

Sulfide was added to experimental packs in quantities varying from 100 micrograms to 1 gram. Even when 1 gram of sodium sulfide was added--as shown in

Table 1 - Distribution of Sulfide in Various Packs of Tuna

Packs From Which the Cans Were Obtained				Sulfide Deposited on Can[1]		Sulfide Still Available in Can (as H_2S)[1]			Total Sulfide in Can
Designation of Pack		Species of Tuna	Type of Pack	Amount Deposited (as H_2S)	Degree of Discoloration	Amount in Meat, Including Liquid	Amount in Headspace Gas	Total Amount	
Type	Lot								
	No.			Micrograms per Can [2]		.... (Micrograms Per Can [2])			
Commercial	1	Yellowfin	Flake	Trace	Slight	18	38	56	56
	2	Yellowfin	Solid	55	Moderate	29	15	44	99
	3	Albacore	Solid	30	Moderate	57	64	121	151
Experimental	1	Albacore	Solid	0	None	66	582	648	648
	2	Albacore	Solid	0	None	24	104	128	128
	3	Yellowfin	Solid	0	None	15	101	116	116
	4	Albacore	Solid	0	None	-	-	-	[3] 10^6
	5	Albacore	Solid	0	None	-	-	-	[4] 10^6

1/The values given are the averages obtained in the examination of 48 cans or more from each pack, except for Commercial Pack No. 1 from which 12 cans were examined.
2/Size 307 x 113, one-half pound tuna can. 3/Sulfide artificially added as Na_2S.
3/Sulfide artificially added as Na_2S. A few drops of dilute HCl were added to insure liberation of H_2S.

table 1, experimental lots 4 and 5--iron sulfide did not form. However, when ferrous salts were suspended in water and painted on the lids used in the experimental packs, extensive deposits of ferrous sulfide formed in all experimental packs after retorting. Thus, it is the presence of ferrous iron and not the amount of sulfide that is the controlling factor in can discoloration.

COOLING CANS AFTER RETORTING

A series of experiments were carried out to determine when discoloration actually takes place in canned tuna. Albacore and yellowfin from batches of tuna that had a history of causing can discoloration were packed and retorted for 75 minutes at 240° ± 2° F. The pack, which was allowed to cool at room temperature, was sampled at time intervals up to 24 hours. The sampled cans were opened and the area of sulfide discoloration was measured. In all cases, no discoloration was found immediately after the cans were retorted. The first specks of iron sulfide were detected after about 1 hour and continued to grow in size and number until about 10 hours after the retorting period. In all cases the maximum discoloration was reached before 24 hours after retorting. The results of this experiment are shown in figure 3.

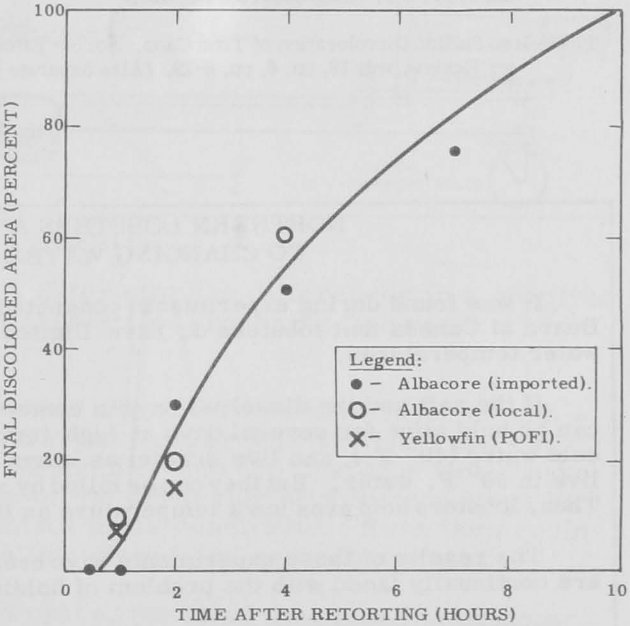

Fig. 3 - Development of can discoloration after retorting.

An investigation of the effect of various cooling temperatures was carried out using yellowfin tuna from the above experiments. Albacore tuna that had shown no history of can discoloration was also used. Immediately after the retorting period the canned fish were placed in constant-temperature oil baths ranging from 64° F. to 216° F., for a period of 21 hours. After removal from the baths, the cans were placed at room temperature storage. Upon inspection of the cans "cooled" at the various temperatures, can discoloration was found to be at a maximum after the 21-hour period. Iron sulfide discoloration was found in cans of both the yellowfin and albacore that were held at temperatures above 135° F. In all cases, can discoloration became progressively worse with increased cooling temperatures.

CONCLUSIONS

(1) Formation of black iron sulfide in canned tuna was found to depend upon the presence of ferrous iron.

(2) All cans of tuna contained sufficient hydrogen sulfide to give can discoloration if any exposed iron in the can was in the form.

(3) Sulfide discoloration occurred after the cans were retorted, during the cooling period.

(4) Sulfide discoloration in packs that commonly showed the discoloration was made much worse if the cans were allowed to remain at elevated temperatures while cooling.

(5) The free sulfide formed during retorting was found mostly as hydrogen sulfide gas in the headspace of the can, although significant amounts were found in the meat.

Note: Also see Commercial Fisheries Review; Oct. 1955, p. 33, for "Background" and "No. 1 - Theory of Iron Sulfide Formation in Cans;" Feb. 1956, p. 5, for "No. 2 - Analytical Methods;" June 1956, p. 8, for "No. 3 - Effect of Variables Introduced by the Fish."

LITERATURE CITED

Pigott, George M., and Stansby, Maurice E.

1955. Iron Sulfide Discoloration of Tuna Cans. No. 1 - Theory of Iron Sulfide Formation in Cans. Commercial Fisheries Review, vol. 17, No. 10, pp. 34-39. (Also Separate No. 418.)

1956a. Iron Sulfide Discoloration of Tuna Cans. No. 2 - Analytical Methods. Commercial Fisheries Review, vol. 18, no. 2, pp. 5-9. (Also Separate No. 429.)

1956b. Iron Sulfide Discoloration of Tuna Cans. No. 3 - Effect of Variables Introduced by the Fish. Commercial Fisheries Review, vol. 18, no. 6, pp. 8-12. (Also Separate No. 439.)

NORTHERN LOBSTERS ADJUST THEMSELVES TO CHANGING WATER TEMPERATURE

It was found during experiments conducted by scientists of the Fisheries Research Board of Canada that lobsters do have limited ability to adjust themselves to changing water temperatures.

If the salt and the dissolved oxygen content of the water are favorable, the lobsters can be held alive for several days at high temperatures. Those lobsters acclimated to cold water (40° F.), can live in water as warm as 75° F.; those used to 80° F. water can live in 90° F. water. But they can be killed by a sudden lowering of the water temperature. Thus, lobsters held at as low a temperature as 60° F. died when placed in water of 40° F.

The results of these experiments have been of great value to commercial interests who are continually faced with the problem of holding lobsters alive for shipment to markets.

In the waters where the lobster (*Homarus americanus*) is found, the temperature range is about 45° F., from 30° F. in winter to 75° F. in certain areas during the summer months.

--*Sea Secrets*, The Marine Laboratory, University of Miami, Coral Gables, Fla.