

# IRON SULFIDE DISCOLORATION OF TUNA CANS<sup>1/</sup>

## No. 5 - Effect of Salt, Oil, and Miscellaneous Additives

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### ABSTRACT

Effect of additives as potential causative agents in the iron sulfide discoloration of tuna cans was investigated. Copper salts caused can corrosion but no iron discoloration. A series of chemical compounds at levels normally found in canned tuna did not cause discoloration. Source of salt or of vegetable oil added had no effect on discoloration.

### BACKGROUND

The formation of black iron sulfide deposits in certain batches of canned tuna has caused members of the tuna-packing industry much concern in recent years. This paper, the fifth in a series of six papers reporting the findings of an investigation into the factors associated with iron sulfide formation (Pigott and Stansby 1955), reports the effects of various additives on sulfide discoloration in tuna cans.

### EFFECT OF SALT AND OIL

About  $\frac{1}{8}$  ounce of salt and 1 to  $1\frac{1}{2}$  ounces of vegetable oil are added to each can of tuna ( $\frac{1}{2}$  can) before it is seamed and retorted. A series of experiments were carried out to investigate the effect of salt and oil on can discoloration and to determine whether different batches of salt or oil affect the formation of discoloration in different ways.

Table 1 - Acid Number and Free Fatty Acid Values Obtained with Various Vegetable Oils Used in Commercial Canning of Tuna

Type of Oil	Source of Oil	Acid Number		Free Fatty Acid	
		Received <sup>1/</sup>	Processed <sup>2/</sup>	Received <sup>1/</sup>	Processed <sup>2/</sup>
	Packer	..... (Number) .....		..... (Percent <sup>3/</sup> ) .....	
Olive .....	A	0.51	0.51	0.25	0.25
Soya .....	A	0.06	0.07	0.03	0.03
Soya (recovered) <sup>4/</sup> .....	A	0.06	0.06	0.03	0.03
Oil (stored) <sup>4/</sup> .....	B	0.09	0.09	0.04	0.04
Oil (as received) <sup>4/</sup> .....	B	0.03	0.04	0.01	0.02
Oil (recovered) <sup>4/</sup> .....	B	0.03	0.03	0.01	0.01
Olive .....	C	1.56	1.59	0.79	0.80
Soya (stored in tanks) <sup>4/</sup> .....	C	0.08	0.08	0.04	0.04
Soya (stored in drums) <sup>4/</sup> .....	C	0.07	0.07	0.04	0.04
Soya .....	D	0.06	0.06	0.03	0.03

<sup>1/</sup> Oil as received from cannery.

<sup>2/</sup> Same as in <sup>1/</sup> but oil processed for 75 minutes at 240° F.

<sup>3/</sup> Calculated as oleic acid.

<sup>4/</sup> By the packers supplying samples.

Rock salt and table salt from several commercial sources were used (1) in experimental solid packs of yellowfin tuna that normally formed discoloration in single-enamel cans<sup>2/</sup> and (2) in similar packs of albacore that did not normally form the discoloration. The amount of salt or the source of salt had no effect upon the extent of can discoloration in these studies. However, if no salt was added to the yellowfin packed with added vegetable oil, no discoloration was found whatever.

Vegetable oils for experimental packs were next obtained from several tuna packers. When used in these experiments, the oils had no effect on can discoloration

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<sup>2/</sup> Unless otherwise stated, all tuna canned throughout this investigation were canned in single-enamel cans like those that were used by industry when initial outbreaks of sulfide discoloration occurred.

in the packs of the yellowfin and albacore from the same lots used in the salt source studies. These oils were also analyzed for free fatty acid content, both before and after heat processing. No increase in free fatty acid content was found after the oils were processed 75 minutes at 240° F. These results are shown in table 1.

Oil from discolored and from normal packs of tuna were analyzed for free fatty acids (table 2). The results showed no important differences in free fatty acid content of normal, spoiled, and sulfide-discolored packs.

The yellowfin that normally caused can discoloration was packed using various combinations of soya oil, saturated brine (room temperature), and salt. If both salt and free oil, or salt and free water, or free water alone were present in the canned product, can discoloration took place (table 3). On the other hand, if a free liquid was not present, no iron sulfide was formed. Thus, free liquid seems to be necessary before can discoloration will occur. The effect of free liquid will be further discussed in the next paper of this series, where work on the effect of free liquid in flaked tuna pack is reported.

Source of Oil	Free Fatty Acid Content
	Percent <sup>1/</sup>
Packs from normal tuna . . . . .	0.101 to 0.272
Packs from badly-spoiled fish . . . . .	0.343 to 0.372
Discolored commercial packs . . . . .	0.129 to 0.486

<sup>1/</sup> Calculated as oleic acid.

#### EFFECT OF ADDING MISCELLANEOUS SUBSTANCES

Several substances that are known to be present in canned tuna, or that might possibly affect the formation of metal sulfide when introduced into the product, were added to experimental packs of yellowfin and albacore tuna. In each case, cans containing no additives were packed as controls. Fish that had a history of causing can discoloration as well as those that had never caused discoloration were used in the control packs.

Soya Oil	Additives		Discoloration
	Saturated Brine	Salt	
.....(Ounces).....			.....(Degree).....
1 <sup>1</sup> / <sub>2</sub>	0	1 <sup>1</sup> / <sub>8</sub>	Medium
1 <sup>1</sup> / <sub>2</sub>	0	0	None
0	1 <sup>1</sup> / <sub>2</sub>	0	Heavy
0	0	0	Medium <sup>3/</sup>
0	0	1 <sup>1</sup> / <sub>8</sub>	Medium <sup>3/</sup>
0	0	0	None <sup>4/</sup>
0	0	1 <sup>1</sup> / <sub>8</sub>	None <sup>4/</sup>

<sup>1/</sup> All packs were processed for 75 minutes at 242° F.  
<sup>2/</sup> Cumulative results of 3 experiments of 96 cans each. Total of 288 cans approximately evenly divided into the 7 groups.  
<sup>3/</sup> Considerable free water was present after retorting.  
<sup>4/</sup> No free water was present after retorting.

containing fish and in those containing only sodium sulfide and oil. However, the amounts that had to be added to obtain consistent discoloration in cans of tuna that normally did not cause the iron sulfide deposit were far above those found in the commercially-discolored tuna packs.

Trimethylamine and trimethylamine oxide have been shown to affect the amount of tin going into solution in cans of herring (Jakobsen and Mathieson 1946). These substances were added to packs of albacore and yellowfin in quantities up to 1 percent by weight. The addition of trimethylamine increased tin sulfide staining but neither substance showed any effect on can discoloration from iron sulfide formation.

coloration as well as those that had never caused discoloration were used in the control packs. Fatty acids were added to experimental packs of albacore and yellowfin to determine the effect of free fatty acid on can discoloration. Acetic acid, butyric acid, oleic acid, and stearic acid were added in various amounts from 0 to 1 percent by weight of can contents. These acids were also added to cans containing only vegetable oil and sodium sulfide. When large quantities of the acids were present, very extensive discoloration was produced, both in the cans

Glycerine, tartaric acid, sucrose, and glucose in quantities up to 1 percent by weight were added to yellowfin and albacore to see if polyhydroxy groups affected iron sulfide can discoloration. No consistent correlation of can discoloration to the presence of these substances was noted.

Monosodium glutamate, which is added by some tuna packers to enhance the flavor of the fish, was found to have no effect on can discoloration when added in amounts up to 1 percent of the total can contents.

Copper and tin ions have been considered important catalysts in the corrosion of can metal. Cuprous chloride, cupric chloride, and stannous chloride were added to albacore tuna packs in various amounts from 1 part per million to 1 part per hundred, by weight. It was found that these metals, when present in this experimentally canned albacore tuna, did not affect the ordinary type of can discoloration. However, cuprous or cupric ions, when added at a level of 100 parts per million or greater, caused corrosion within the cans resulting in hydrogen evolution and pinhole leaks.

### CONCLUSIONS

1. The presence of added salt was necessary before the yellowfin tuna solid packs (with added vegetable oil) used in this investigation would cause iron sulfide discoloration of the cans.
2. The source of the salt and vegetable oil samples when added to experimental packs had no effect upon the iron sulfide can discoloration.
3. Free fatty acids (at levels normally found in canned tuna), trimethylamine, trimethylamine oxide, glycerine, tartaric acid, sucrose, glucose, and monosodium glutamate, when added to the experimental packs did not foster or hinder can discoloration to any extent.
4. Cuprous and cupric salts, when added to the experimental packs, caused can corrosion, but not iron sulfide discoloration.

### LITERATURE CITED

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