BLACKENING OF CANNED PRAWN AND ITS PREVENTION

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The paper gives an account of the types of blackening associated with canned prawn in brine and their control. It was found that blackening caused by iron sulphide could be controlled by maintaining proper titratable acidity of fill brine in cans. The paper also elaborates on the factors responsible for or governing this critical titratable acidity. In regard to copper sulphide blackening, control was found to be difficult by maintaining the acidity or by additives such as EDTA when the copper content in the material went above the critical level.

INTRODUCTION

Among the various technical problems associated with seafood canning industry, product blackening and sulphur staining of can interior are considered to be the most important. Canned crustaceans, particularly prawns, though packed in special lacquered cans are not free from these phenomena. Sulphur staining is of two types, one caused by tin sulphide and the other by iron sulphide. Apart from the mere staining, deposition of iron sulphide at break points of the can interior is also often observed. There have been several studies on the latter problem throughout the world among which the most note worthy are those of Davis(1955); Piggot and Stansby (1955, 1956 a, c, 1957 a, b) and Thompson and Waters (1960). In the case of canned shrimp products, sporadic outbreaks of iron sulphide discolouration have been reported by Landgraf (1956) and Thompson and Waters (1960). The effect that such an outbreak can have on the shrimp export trade was evidenced in India in the first half of 1967 when more than 84% of the total detention in preshipment inspection was due to blackening of the material or the can interior. In the case of canned tuna it is known that the formation of iron sulphide deposits is not favoured by the mere presence of hydrogen sulphide and exposed iron in the vapour phase, but, is greatly influenced by the presence of either volatile acids or bases released at the time of heat-processing and cooling of the cans (Pigott *et al*, 1964). According to

Kohman and Sanborn (1928) removal of tin from solution in a canned product tends to increase the removal of tin from the steel plate thereby increasing the area of iron exposed to sulphides present in can.

Addition of citric acid in various forms in moderate concentrations, is recommended for reducing iron sulphide discolouration (Thompson and Waters, 1960). These authors further noted that addition of lemon juice gives greater protection against blackening than citric acid alone at the same pH but is not fully effective. The full merits of these additives on the different types of blackening have however not been elucidated although their protective effect has been explained as due to their capacity to supply Sn^{++} ions to the canned product (Thompson, 1963). In the present study, an attempt has therefore been made to explain the types and causes of blackening in canned prawns and methods of its control with particular reference to the quality of the material used.

Materials and methods

All the experiments were carried out with two important species of prawn, *M. dobsoni* and *M. affinis* available locally unless otherwise specified.

Volatile sulphides released from prawn were estimated by the method of Pigott and Stansby (1959 b) with slight modification. The released sulphides from samples kept in a boiling water bath were trapped in saturated lead acetate solution acidified with acetic acid, for 1 hour.

Titratable acidity of brine in processed cans was estimated as per method given in I. S. 2236—1968. The result is expressed as % of citric acid (w/v) obtained by multiplying the ml of decinormal sodium hydroxide required to titrate 10 ml of brine by the factor 0.07.

Excepting the studies made on the influence of the size of the can on titratable acidity, all the canning experiments were made employing 301 x 206 S. R. lacquered cans as described by Nandakumaran *et al* (1969).

The estimation of copper in the samples was made by the sodium diethyldithiocarbamate method (I. S 2168—1962, 1963). The method of Sandell (1944) was used for the estimation of iron.

Results and discussion

A. Types of blackening:

Analysis of commercial wet-pack canned prawn revealed that blackening of canned meat took place by direct interaction between sulphur and copper or iron, or by secondary reaction through iron sulphide deposits. In the former case there existed a linear relationship (Nandakumaran *et al.*, 1969) between the intensities of blackening and the copper content of the material. Slightly blackened products usually showed above 15 ppm of copper in the meat on dry weight basis (DWB) while moderately and heavily blackened samples contained 28 to 64 ppm of copper (DWB). Meat containing 200 ppm of iron (DWB) or above showed a deep brownish discolouration which was distinct from blackening caused by copper. Iron sulphide blackening as against discolouration was characterised by deposition of black spots initially along the vertical seam-joint spreading slowly along the internal seam curvature and imparting black discolouration to the meat in the can.

B. Source of contaminants.

(i) *Copper and Iron*:

The main source of copper and iron was the prawn tissue itself which after canning was found to contain 3 to 12 ppm of copper and 12 to 64 ppm of iron (DWB) (Nandakumaran *et al.*, 1969). Water, salt, ice, copper- and iron-base utensils with

TABLE I DISTRIBUTION OF COPPER & IRON IN THE RAW MATERIALS

Raw materials	No of samples	Iron (ppm)	Copper (ppm)
Water	150	0.049 — 0.193	0.0017 — 0.064
Ice	85	1.22 — 6.49	0.0090 — 0.043
Brine	60	0.199 — 0.256	0.003 — 0.004
Citric acid (commercial)	25	6.17 — 6.90	0.23 — 0.25
Raw meat at different stages of handling	65	20.0 — 260*	9.0 — 75*

* Dry weight basis

which the meat came into contact during the various stages of canning and repeatedly used blanching brine in 'continuous blanching' (the use of same blanching brine for a number of batch-wise blanching operations) might also individually or collectively, contribute to the mineral contamination. The ranges of heavy metals associated with water, ice, brine, citric acid and meat at various stages of handling are shown in Table I. The accumulation of heavy metals in the blanched meat during continuous blanching is evident from the figures in Table II.

TABLE II RETENTION OF IRON AND COPPER IN THE BLANCHED MEAT IN CONTINUOUS BLANCHING

No. of blanching	Iron (ppm, dry weight basis)	Copper (ppm, dry weight basis)
1	20.37	2.96
2	33.33	2.96
3	37.51	3.27
4	43.74	3.87
5	50.08	3.87
6	68.28	3.87
.	...	...
9	83.23	3.87
.	...	...
18	117.28	3.87

Inert type of utensils such as stainless steel or plastic vessels or others which form white metallic sulphides such as aluminium, may be used for handling the material for canning.

Iron being the most abundent mineral in the world, the chances of contamination are more. However, blackening caused by iron-sulphide is less as its deposition is not favoured under standard conditions of canning and usually the iron content of the meat does not exceed its critical limit. But canners very often drift from the standard technique of processing befitting their need and facility only to face some difficulties. Though the most modern 'inert-lacquer' is used for coating the interior of the tin-plated iron-base container, it does not completely prevent the transmission of iron from the body of the can to the contents during storage.

Experimental samples containing more than 200 ppm of iron in the meat (DWB) show some discolouration of meat which is usually uncommon in commercial cans. However, the effect of these higher levels of iron could be controlled by the incorporation of certain chelating agents such as salts of EDTA. Table III reveals that the nature of discolouration/blackening is related to pH. When the pH value of the brine is almost neutral or alkaline, the addition of 60 ppm of iron in brine, for example, gives deep black discolouration to the meat and brine which is considerably reduced by the incorporation of 0.5% Na_2 EDTA. But under acidic pH (6.4) the colour formed by the same level of iron is only brownish which can be controlled effectively by the addition of even 0.1% Na_2 EDTA. The table also indicates that blackening induced by

TABLE III INFLUENCE OF DISODIUM - EDTA ON BLACKENING OF CANNED PRAWN ARTIFICIALLY DEVELOPED BY IRON/COPPER

EDTA in fill brine %	60 ppm Iron				EDTA in fill brine %	15 ppm Copper			
	pH 8.0 Nature of		pH 6.4 Nature of			pH 8.0 Nature of		pH 6.4 Nature of	
	Meat	Brine	Meat	Brine		Meat	Brine	Meat	Brine
0.00	H.B	H.B	B.D	B.D	0.00	H.B	B.T	H.B	B.T.
0.05	H.B	H.B	S.B.D	S.B.D	0.05	"	"	"	"
0.10	↓	↓	N.D	N.D	0.10	"	"	"	"
0.20	↓	↓	"	"	0.20	"	"	"	"
0.30	↓	↓	"	"	0.30	"	"	"	"
0.40	↓	↓	"	"	0.40	"	"	"	"
0.50	M.B	B.D	"	"	0.50	"	"	"	"

H.B — Heavy blackening
B.D — Brownish discolouration
M.B — Moderate blackening
B.T — Blackish Tint
S.B.D — Slight brownish discolouration
N.D — No discolouration

copper cannot be controlled or even reduced by EDTA in both acidic and alkaline pH ranges.

(ii) *Volatile sulphides :*

Besides the heavy metals, volatile sulphides are also necessary for the formation of black copper and iron sulphides. The main sources of these sulphides are the sulphur containing amino acids of the tissue and the sulphides sometimes found in water. The release of sulphides from the tissue depends on:

a) quality of the meat. The poorer the quality the more is the release of volatile sulphides (Table IV). During ice storage of the meat, the volatile sulphides show an initial increase followed by gradual fall probably due to loss of solubles by leaching.

b) retorting conditions: The higher the retorting time and temperature the more is the release of volatile sulphides (Table V) due to breakdown of tissue.

c) concentration of brine in the can: The lower the concentration of salt ($< 2\%$) the more is the release of sulphides (Table VI).

TABLE IV RATE OF RELEASE OF VOLATILE SULPHIDES FROM RAW MEAT WITH RELATION TO QUALITY OF THE RAW MATERIAL

Sample	Species	Quality	Volatile sulphides as H_2S (μg/100g meat)
A	M. dobsoni	fresh	47.66
	-do-	slightly spoiled	185.10
B	P. indicus	fresh	35.65
	-do-	spoiled	973.80
C	P. stylifera	fresh	33.28
	-do-	slightly spoiled	205.20
D	M. dobsoni	ice-stored	
		Days of storage	
		1	20.98
		2	37.81
		3	84.70
		4	45.37
		5	42.35
		6	30.25

d) pH of the contents: The higher the pH of the packed contents the more is the release of volatile sulphides. It is known that cystine is the main precursor of sulphides in muscle (Mecchi *et al*, 1964), its breakdown

TABLE V INFLUENCE OF TIME AND TEMPERATURE OF PROCESSING ON THE RATE OF RELEASE OF VOLATILE SULPHIDES FROM CANNED PRAWNS *(P. Indicus)*

Processing condition		Volatile sulphides as H_2S (μg per can *)
Time (Minutes)	Steam pressure (lbs/sq. inch)	
20	10	226.9
30	10	824.9
40	10	1100.0
12	15	30.0
15	15	412.5

*100 g blanched meat packed with 100 ml brine

TABLE VI INFLUENCE OF CONCENTRATION OF SALT IN FILLING BRINE IN CANS ON THE RELEASE OF VOLATILE SULPHIDES

Salt concentration (% of NaCl)	Volatile sulphides as H_2S (μg per can*)
0.5	769.1
1.0	769.1
1.5	714.2
2.0	604.3
3.0	604.3
4.0	604.3
5.0	604.3

*100 g blanched meat packed with 100 ml brine

TABLE VII INFLUENCE OF pH ON THE RATE OF RELEASE OF VOLATILE SULPHIDES FROM CANNED PRAWN *(M. dobsoni)*

pH of the canned material	Volatile sulphides as H_2S (μg per can)*
3.30	16.48
3.50	16.48
4.00	19.68
4.60	21.96
5.35	164.80
5.85	461.41
6.50	494.40
6.80	582.40
6.90	659.40
7.50	2473.00
8.20	5824.00
8.85	6483.00
9.15	8241.00

*100 g blanched meat packed with 100 ml brine

(at 100°C) occurring only in alkaline medium (Naka *et al*, 1957).

C. Relationship between pH and titratable acidity:

Control of acidity in canned prawn is very important in order to maintain its storage life and also to keep it free from undesirable influence of contaminants. Analyses of commercial cans indicate that deposition of iron sulphide takes place even at pH levels 6.4 to 6.6 which are usually taken as ideal, but not in cans having titratable acidity of 0.06% level or above. On the other hand, different levels of acid added to cans under identical conditions of processing, also show the same pH values. The correlation between the change of pH and acidity of brine for commercial cans was worked out to be −0.156 which is not significant at 5% level indicating its non-linear relationship. Emphasis has therefore to be made on the titratable acidity of the fill-brine in the processed can, rather than pH.

Generally, acidity of brine in can is controlled by addition of citric acid in the blanching or filling brine or both. Addition of (upto 0.5%) citric acid in blanching brine and finally packing the blanched meat in simple brine is a common commercial practice. In such cases it has been found that final acidity in the can varies significantly depending on the number of blanchings carried out in the same liquor without replenishment of the acid. Generally after each blanching about a gallon of liquid is removed with simultaneous addition of some quantity of fresh water and salt, but no care is taken for the maintenance of acidity. So, with continuous blanching, the acidity of the blanching brine and consequently the titratable acidity of the fill-brine decrease gradually. A typical example is shown in Table VIII. As the number of blanchings using the same brine increases there is reduction in

TABLE VIII INFLUENCE OF CONTINUOUS BLANCHING (WTHOUT REPLENISHMENT OF CITRIC ACID) ON THE ACIDITY OF PROCESSED MATERIAL

No. of blanching	Blanching brine: Change in NaCl concn (% NaCl)	Blanching brine: Change in Titratable acidity (% C.A)*	Filled brine: Change in NaCl concn (% NaCl)	Filled brine: Change in Titratable Acidity* (% C.A)
1	10.50	0.156	3.68	0.050
2	8.75	0.109	3.33	0.050
3	7.88	0.093	2.86	0.032
4	7.58	0.067	2.95	0.032
5	7.30	0.067	2.57	0.029
6	7.30	0.067	2.80	0.029
7	6.72	0.065	3.27	0.029
8	7.00	0.065	2.97	0.027
9	7.00	0.064	2.85	0.027
10	6.42	0.064	2.63	0.026
11	6.40	0.064	2.93	,,
12	7.00	0.063	2.80	,,
13	6.72	,,	2.80	,,
14	6.78	,,	2.92	,,
15	7.00	0.062	2.95	,,
16	7.00	,,	2.98	,,
17	7.00	,,	2.98	,,
18	7.00	,,	2.86	,,
19	7.27	,,	2.85	,,
20	7.00	,,	2.85	,,
21	6.57	,,	2.81	,,
22	6.43	,,	2.81	,,

* C. A = Citric acid

the final acid content in the can upto the tenth blanching whereafter it tends to be almost constant. The observation indicates that in order to control the acidity it is desirable to add required quantity of acid to the filling brine depending upon the period of pre-processing ice-storage of the prawn, size of the can etc.

D. Maintenance of titratable acidity.

(i) *Period of ice-storage of prawn in relation to acidity.*

In the standard methods adopted by the trade, levels of acid to be used in the blanching and filling brines are fixed by convention irrespective of the condition of freshness of raw material. It has been found that this invariably results in fluctuations in the titratable acidity. The quantity of acid to be added to the filling brine was found to be more in the case of raw material preserved for longer periods in ice. This may probably be due to the leaching out of water soluble fraction and consequent shrinkage caused to the blanched meat during the later stages of ice-storage. Table IX reveals that a four-day iced material requires almost three times the acid of that required by fresh prawn to maintain the same level of titratable acidity in the finished product.

TABLE IX QUANTITY OF CITRIC ACID TO BE ADDED IN FILLING BRINE FOR THE MAINTENANCE OF MINIMUM DESIRABLE TITRATABLE ACIDITY (0.06 TO 0.15% IN THE FILLED BRINE) WITH RELATION TO THE PERIOD OF PRE-PROCESSING ICE-STORAGE OF PRAWN

Days of storage in ice	Citric acid to be added in filling brine after blanching the meat in brine containing 0.2% citric acid.
1	0.1 – 0.15
2	0.15 – 0.20
3	0.25 – 0.30
4 and above	0.30 – 0.40

(ii) *Size of can:*

In India prawn is usually packed in cans of the following dimensions: 301 x 109, 301 x 206, 301 x 307 and 401 x 411. Experiments showed that the minimum desirable level of acidity can be maintained so long as the correct ratio of meat and brine is maintained. Prawns packed in the can-sizes of 301 x 109, 301 x 206 and 301 x 307 maintain an average ratio of 1.54, but in 401 x 411 size it is 2.34 (Table X). So, in order to maintain the same level of acidity in

TABLE X QUANTITY OF ACID TO BE ADDED WITH RELATION TO CHANGE IN SIZE OF THE CAN

Can Size —>	301 x 109				301 x 206				301 x 307				401 x 411			
Citric Acid in filling Brine %	pH	T. A	Nature of Brine	Meat/ Brine Ratio	pH	T. A	Nature of Brine	Meat/ Brine Ratio	pH	T. A	Nature of Brine	Meat/ Brine Ratio	pH	T. A	Nature of Brine	Meat/ Brine Ratio
Control	6.85	0.042	S.C		6.85	0.042	S.C		6.85	0.042	S.C		6.85	0.032	S.C	
0.1	6.65	0.049	S.C		6.55	0.055	C		6.35	0.050	C		6.45	0.042	S.C	
0.2	6.65	0.063	S.C		6.45	0.066	C		6.40	0.067	C		6.45	0.056	C	
0.3	6.45	0.068	C	1.44	6.25	0.077	H.C	1.55	6.20	0.078	C	1.64	6.40	0.061	C	2.34
0.4	5.95	0.081	H.C		6.00	0.089	H.C		...	...	...		6.40	0.065	C	
0.5	5.70	0.087	H.C		...	...				...	...			...	...	

T.A — Titratable acidity to phenolphthalein. S.C — Slightly Colloidal. H.C — Highly Colloidal. C — Colloidal.

401 x 411 cans, it is necessary to add 1.5 times more acid than that required by the other sizes. But canners under standard conditions of canning usually add the same filling brine with or without acid in all cases irrespective of can size. Iron sulphide deposition is thus likely to be more in the 401 x 411 cans.

(iii) *Size grade and species of prawn:*

Work carried out mainly with the commercially important species of prawns indicate that most of the species viz., *M. dobsoni*, *M. affinis* and *P. indicus* have no influence on the quantity of acid to be added for maintaining the acidity while the size of the prawn exhibits significant effect, smaller size grades requiring more acid in filling brine compared to bigger size grades. It has been observed that the quantity of salt and acid absorbed during blanching by different size grades (Tiny, Cocktail and Broken) of *M. dobsoni* is independent of size, but the amount of salt released in the filling medium is proportionately more to size grades in the order shown above while in the case of acid release after retorting the trend is found to be reversed (Tables XI and XII). The latter is manifested by greater shrinkage of meat in the smaller size grades than in the bigger, under identical conditions of canning. It is therefore necessary to blanch the smaller size grades in lower percentage of acid (0.1%) and then pack in 0.2 to 0.25% acid (in fill brine) rather than the reverse conditions which are commercially practised.

P. Stylifera behaves in a totally different manner from the other commercial species mentioned. This will be discussed in a separate communication.

RECOMMENDATIONS

Material used for canning should be fresh and should have minimum level of heavy metal contamination. Only potable

TABLE XI ANALYSIS OF VARIANCE SHOWING DECREASE OF TITRATABLE ACIDITY WITH INCREASE IN SIZE GRADE OF CANNED PRAWN PREPARED UNDER IDENTICAL CONDITONS OF CANNING

Source	SS	D.F	M.S	F
Total	0.00045525	11		
Between sizes	0.00028456	2	0.00014228	66.48**
Between concentrations	0.00015787	3	0.00005262	24.59**
Error	0.00001282	6	0.00000214	

** Indicates significance at 1% level.

TABLE XII ANALYSIS OF VARIANCE SHOWING INCREASE IN SALT CONTENT WITH INCREASE IN SIZE GRADE OF CANNED PRAWN PREPARED UNDER IDENTICAL CANNING CONDITIONS

Source	SS	D.F	M.S	F.
Total	0.2561	11		
Between sizes	0.2556	2	0.127800	1907.46**
Between concentrations	0.0001	3	0.000030	0.45
Error	0.0004	6	0.000067	

** Indicates significance at 1% level.

TABLE XIII EXPORT FIGURES SHOWING THE QUANTITY OF CANNED PRAWN DETAINED BY INSPECTION AGENCY DUE TO BLACKENING BEFORE AND AFTER THE ADOPTION OF RECOMMENDATIONS MADE TO THE INDUSTRY

Month		Quantity Inspected x 10^3 Kg	Total quantity detained x 10^3 Kg	Detention due to blackening x 10^3 Kg	Percentage detained due to blackening
A. Before the adoption of the recommendations					
January,	'67.	233.35	4.06	4.06	100.00
February	,,	233.69	8.57	7.66	89.3
March,	,,	170.52	11.11	9.88	88.9
April	,,	128.64	3.48	1.64	47.0
May,	,,	138.96	0.17	0.02	11.10
B. After the adoption of the recommendations					
June,	'67.	123.73	1.40	Nil	Nil
July,	,,	150.31	2.53	0.28	1.13
August,	,,	182.70	1.31	Nil	Nil
September,	,,	133 12	0.33	,,	,,
October,	,,	148 90	1.96	,,	,,
November	,,	91.28	0.92	,,	,,
December	,,	131.64	0.56	0.01	1.8
January	'68.	163.65	1.85	Nil	Nil
February	,,	165.29	7.63	,,	,,
March,	,,	191.77	6.1	,,	,,

(Compiled from data on Preshipment Inspection: January 1967 — March 1968) water free from copper and iron as far as practicable but not containing more than 0.1 and 0.3 ppm respectively should be used for all requirements in the various stages of canning. Direct use of iron and copper utensils particularly the latter should be avoided.

Cans should be processed at a lower temperature for a longer period (22 min. at 115°C) rather than at higher temperature for a shorter period (12 min. at 121°C). Higher temperatures and prolonged retorting should be avoided.

Titratable acidity (0 06 to 0.15%) of brine in the processed cans should be maintained by the incorporation of specified quantity of citric acid in the filling brine depending on the period of preprocessing ice-storage of the prawn.

The above recommendations are generally followed by the trade in India since the middle of 1967 with spectacular results. The percentage of incidence of of blackening and consequent detention from export is almost non-existant now as may be seen from data in Table XIII.

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