THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

IX. Method for Preventing the Formation of the Crystals during the Processing of the Cans

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I. Formation of the crystals in canned foods to which gelatine, agar or S.L.D. were added in order to raise the viscosity of the juice

In the previous paper, I of this series[1], the authors have suggested a relationship between the viscosity of the juice of canned foods and formation of the crystals. Also in paper VI[2], observations were reported on the formation of the crystals in the solution of chemical components of the crystal to which gelatine or agar was added in order to raise the viscosity. According to the observations, the higher the viscosity of the juice is, the slower the crystallization becomes, but over a long period the crystals will surely be formed; when the crystals once begin to form, they are likely to grow to large ones having regular surfaces.

The authors have here observed the formation of the crystals in canned crab or canned salmon to which gelatine, agar or S. L. D. were added in order to raise the viscosity of the juice. S. L. D. is the commercial name of a powder of the hydrolyzate of starch, made by Mimatsu Co. Ltd.

1. In the case of canned crab

(1) *Sample and experimental method*

When the canned crab was prepared from the raw material caught off Nemuro, the meat was packed with gelatine or agar of 0.45~0.075% of the total quantity of the content. The cooling of the cans was done in a water tank. The sample cans were brought to the laboratory and opened after 50 days; the formation of the crystals in the cans was observed. Experiment was carried out following the same methods as were described in paper VIII[3].

(2) *Experimental results*

Results obtained are shown in Tables 1 and 2.

As seen in these two tables, the higher the specific viscosity became as a result of the addition of gelatine, the smaller the size became of the crystals formed in the cans. When the specific viscosity was above or below a boundary of 2.4, the crystals formed were small or large respectively. In the case of the addition of agar, the specific

Table 1. Formation of the crystals in canned crab to which gelatine was added

			0.45	0.38	0.30	0.23	0.15
Concentration of gelatine (%)			0.45	0.38	0.30	0.23	0.15
Color of meat			Good	Good	Good	Good	Good
Taste of meat			Good	Good	Good	Good	Good
State of juice		Viscosity (η/η_0)	2.7	2.6	2.4	2.3	2.1
		V.B.-N (*mg%*)	26.1	23.5	24.1	22.8	9.4
		Tot.-N. (%)	1.11	1.13	1.16	1.10	1.21
		Soluble Mg (*mg%*)	1.6	1.8	1.2	0.5	0.2
Crystal in juice	Regular crystal	Number (per *cc*)	56×10^4	56×10^4	12×10^4	8×10^4	8×10^4
		Size (μ)	25×5	26×9	21×6	80×38	38×2
	Amorphous	Number (per *cc*)	80×10^1	100×10^4	56×10^4	80×10^4	80×10^4
		Size (μ)	12×3	13×3	13×3	6×3	6×3
Size of crystals on parchment paper		Top (μ)	250×60	250×65	3×3	1000×2000	660×170
		Side wall (μ)	200×45	250×65	2×2	1000×2000	660×160
		Bottom (μ)	250×65	250×65	40×10	1000×2000	660×170

Table 2. Formation of the crystals in canned crab to which agar was added

Concentration of agar (%)			0.30	0.24	0.15	0.075
Color of meat			No good	No good jelly state	No good jelly state	No good
Taste of meat			Good	Good	Good	Good
State of juice		Viscosity (η/η_0)	10	5.2	3.3	2.3
		V.B.-N. (*mg%*)	34.2	33.9	32.2	39.0
		Tot.-N. (%)	1.08	0.93	0.10	—
		Soluble Mg (*mg%*)	5.2	4.5	3.0	3.4
Crystal in juice	Regular crystal	Number (per *cc*)	8×10^4	—	8×10^4	20×10^4
		Size (μ)	9×6	—	38×12	70×12
	Amorphous	Number (per *cc*)	80×10^4	80×10^4	22×10^4	80×10^4
		Size (μ)	25×25	25×25	25×25	12×12
Size of crystals on parchment paper		Top (μ)	—	—	—	—
		Side wall (μ)	190×60	190×60	430×200	120×250
		Bottom (μ)	600×250	250×100	820×220	120×250

viscosity increased considerably. When the specific viscosity became over 5.2, numerous and irregular crystals tended to form in the cans, but some difference was observed only in size of the crystals formed. In such cans, the content is jellified and has poor merchandise value.

According to the results obtained, a relation between state of the crystallization and the amount of added materials was observed respectively to be different in each of the cans to which gelatine or agar was added. Size of the formed crystals became small in accordance with the increasing of the specific viscosity or the amount of added gelatine. In the cans to which were added various amounts of agar, difference in the size of formed crystals was not observed, but difference in shape was observed. The number of irregular crystals increased with larger amount of added agar. However, in the juice the soluble magnesium which has not reacted with other components of the crystal remained in large quantity in those cans to which the larger amount of gelatine or agar was added. This happens, because the supersaturated solution is stabilized with the added high polymer; then, the crystal will grow over a long time with probability of growing to a large size. However, the growing velocity of the formed crystals will be reduced considerably because of the larger number of crystals formed as a result of the addition of the larger amount of these substances.

2. In the case of canned salmon

(*1*) *Sample and experimental method*

When the canned salmon has been prepared as customarily from the raw materials (*keta* salmon) caught in the northern sea (Hokuyō), the meat was packed with gelatine of 0.48~1.88% or S. L. D. of 0.04~0.80% of the total quantity of the content. The cooling of the cans was done as usual. The cans prepared by the method described above were employed for experiment as the sample, and opened after one and a half years; the formation of the crystals in the cans was observed in the same manner as that described in paper VIII[3].

(*2*) *Experimental results*

Results obtained are shown in Tables 3 and 4.

As seen in Tables 3 and 4, the larger the amount of the added gelatine or S. L. D. was the less became the number of large crystals formed in the cans. When the added amount of gelatine was over 3.5 *g* per a can (1.4%), visible crystals of over 1 *mm* size were not formed. In such can, the content is jellified and has poor merchandise value.

In the cans to which S. L. D. was added, the pH values declined toward the acidic side owing to the larger amount of added S. L. D. When the added amount of S. L. D. was over 1 *g* per a can (0.4 %), the formation of large crystals were not observed. In

Table 3. Formation of the crystals in canned salmon to which various amount of gelatine was added

Sample No.	Added amount of gelatine (*g/can*)	Color of meat	Vis-cosity (η/η_0)	Crystals on meat: Visible crystals		Crystals in juice: Visible crystals		Microcrystals	
				Size (μ)	Number (*/can*)	Size (μ)	Number (*/can*)	Size (μ)	Number (*/cc*)
1	0	Good	2.9	1000~3500×800	30	500~3000×200~1000	20	32~98×16	7×10⁴
2	1.2	Rred brown	4.4	2000×1000	2	1000~2000×200~1000	8	50~160×16~32	30×10⁴
3	2.4	Yellow brown	6.1	3000~3500×800~1000	6	3000~3500×800~1000	3	65~190×16~32	17×10⁴
4	3.5	Brown jelly-state	7.0	—	None	—	None	32~110×16	30×10⁴
5	4.7	Brown jelly-state	7.7	—	None	—	None	32~65×16	3×10⁴

Table 4. Formation of the crystals in canned salmon to which various amount of S.L.D. was added

Sample No.	Added amount of S.L.D. (*g/can*)	Color of meat	pH	Vis-cosity (η/η_0)	Crystals on meat: Visible crystals		Crystals in juice: Visible crystals		Microcrystals	
					Size (μ)	Number (*/can*)	Size (μ)	Number (*/can*)	Size (μ)	Number (*/cc*)
1	0	Good	6.2	2.9	2000~5000×200~1000	10	3000~6000×800~1000	9	32~64×16	3×10⁴
2	0.1	Good	6.0	3.5	2000~7000×1000	92	650~820×160~250	2	—	None
3	0.2	Good	5.9	3.8	1000~5500×200~1000	90	1500~3100×160~650	8	—	None
4	0.5	Good	5.7	3.7	1000~4000×200~900	58	820~1200×320~570	6	—	None
5	1.0	Good	5.7	4.3	—	None	—	None	—	None
6	2.0	Good	5.1	4.6	—	None	—	None	—	None

such cans, the reduction of the formation of crystals will be considered to be caused not only by the increased specific viscosity, but also by the decreasing of pH value. As seen in the results described above, if comparatively larger amount of agar, gelatine or S. L. D. were added in order to rise the specific viscosity of the juice in the cans, the formation of the larger crystals may be prevented. But, in such cans, the content will have poor merchandise value in appearance.

II. The addition of complex ion-making agents as a method for preventing the formation of the crystals

In order to prevent the formation of scales which are an accumulation of Ca or Mg salts in a boiler from boiler water, antiscales have been used. The practice is based on the principle that antiscales unite with Ca or Mg of divalent metallic ion to make soluble complex salt and thus prevent the precipitation of Ca or Mg salts. In the U. S. A., to prevent the formation, in canned sea foods, of glass-like of struvite, which consists of Mg, NH_4 and PO_4 ions, certain antiscales, *e. g.* sodium hexametaphosphate have been used. However, the use of antiscales in canned foods must be examined, because such foods with added antiscales have unfavourable taste or comparatively worse quality from the health point of view.

Sodium hexametaphosphate combines with Mg in the canned foods as a soluble magnesium complex salt according to the following formula.

$$[Na_{2n}(PO_3)_{3n}] + nMg \rightarrow Na[Mg_n(PO_3)_{3n}]$$

This soluble magnesium complex does not precipitate in the can. The authors have used sodium hexametaphosphate for preventing the formation of $MgNH_4PO_4 \cdot 6H_2O$ crystals in the canned crab.

1. Test tube experiments on the influence of the addition of sodium hexametaphosphate upon the formation of the crystals

In order to determine the adequate dose of sodium hexametaphosphate, solutions of various concentrations of the reagent were respectively added to the mixed solution of the chemical constituents of $MgNH_4PO_4$, magnesia mixture and sodium phosphate solutions, and the formation of the crystals was observed.

(*1*) *Experimental method*

Each 0.01 Mol solution of magnesia mixture and sodium phosphate solutions was instantly mixed in separate test tubes, to which various concentrations of 1~0.1% of sodium hexametaphosphate were added. Then the formation of the crystals was observed.

(*2*) *Experimental results*

Results obtained are shown in Table 5.

As seen in Table 5, when the chemical constituents were instantly mixed after the addition of sodium hexametaphosphate, the crystals having regular surface did not appear even after 24 hours, and the size of the crystals which were formed was smaller than that in material to which no agent had been added. After long storing of the test tubes to which a small quantity of the complex ion-making agent (below 0.5 %) had been added, the crystals came to have regular surface. This is perhaps owing to the formation of Mg-complex and to the increase in the viscosity of the solution. This was also suggested from the results reported in the previous paper, VI[2]. However those crystals formed were microscopic and invisible. The amount of Mg in the mixed solution of magnesia mixture and sodium phosphate was 0.0122 % and the amount of Mg in the

Table 5. States of the formation of the crystals in the solution to which various amount of sodium hexametaphosphate were added

Concentration of sodium hexametaphosphate (%)		0	1	0.5	0.25	0.1
Leaving time 5 (min.)	Form	C	E	E	E	E
	Size (μ)	380×19	1×1.5	1×1	1×1	3×2
24 (hrs.)	Form	C	E	E	E	E, C
	Size (μ)	540×50	No change	No change	1.5×2	6×2
48 (hrs.)	Form	C	E	C, E	C	C
	Size (μ)	No change	No change	——	10×2	6.5×2

Note: Singns which are described in this table show the states of the formed crystals as follow. C=columnar crystal, E=amorphous

juice of canned crab is 0.008%[1]; the amount of Mg in the mixed solution agrees with the amount of Mg in the juice of canned crab. In order to form only microscopic crystals, additon of 0.5~1.0% of sodium hexametaphosphate is considered to be adequate.

2. The influence of the addition of sodium hexametaphosphate upon the formation of the crystal in canned foods

1. In the case of canned crab

(1) Sample

When the cans were prepared in customary manner from the raw material caught off Nemuro, the meat was packed with sodium hexametaphosphate (Mascolin S, made by Taiheiyō Kagakukogyō Co. Ltd.) or tablet of sodium hexametaphosphate made by Scientific Salting Co. in the U. S. A. The added amount of the complex ion-making agent is shown in Table 6.

The cans containing various of the reagent were processed as customary and opened after 50 days.

(2) Experimental method

By the method described in a previous paper[3], determinations of the qualities of the contents, specific viscosity, amounts of volatile basic nitrogen, total nitrogen and the soluble magnesium in the juice were carried out. Also, the shape, number and size of the crystals formed in those cans were observed microscopically.

(3) Experimental results

Results obtained are shown in Tables 7 and 8.

Table 6. Added amounts of sodium hexametaphosphate for canned crab

Sample	Added amount of tablet of sodium hexametaphosphate (made in U.S.A.) (g/can)	Added amount of sodium hexametaphosphate (g/can)	Added rate of sodium hexametaphosphate for the amount of the contents (%)
1	1.5	0.45	0.23
2	0.90	0.30	0.15
3	0.69	0.23	0.11
4	0.45	0.15	0.075
5	0.27	0.09	0.045
6	0.09	0.03	0.015
Sample	**Mascolin "S"**	**Added amount of sodium hexametaphosphate**	**Added rate of sodium hexametaphosphate for the amount of the contents**
1	0.45	0.45	0.23
2	0.30	0.30	0.15
3	0.23	0.23	0.11
4	0.15	0.15	0.075
5	0.09	0.09	0.045
6	0.03	0.03	0.015

Table 7. States of the formation of the crystals in canned crab to which various amounts of sodium hexametaphosphate tablets were added

Concentration of sodium hexametaphosphate (%)		0.23	0.15	0.11	0.075	0.045	0.015
States of meat	Color	White pale yellow	White pale yellow	Good	Good	Good	Good
	Taste	Bitter	Bitter	Good	Good	Good	Good
Viscosity (η/η_0)		3.0	2.5	2.4	2.5	2.5	2.3
V. B-N. (mg%)		29.7	32.8	——	35.4	34.3	24.7
Total-N (%)		0.999	1.12	1.06	1.09	0.453	1.03
Mg (%)		0.0018	0.0049	0.0054	0.0037	0.0033	0.0054
Crystals in juice	Number(/cc)	80×10^4	80×10^4	80×10^4	8×10^4	24×10^4	40×10^4
	Size (μ)	3.8×3.8	3.8×3.8	13×9	10×12	31×5	45×13
	Form	E	E	E, C	C	C	C
Crystals on parchment paper	Top	—	—	—	—	—	+
	Side wall	—	—	—	—	+	+
	Bottom	—	—	+	+	+	+

Note: Singns which are described in this table show the states of the formed crystals as follow. + = crystals of above 150μ, − = no crystal, C = columnar crystal, E = amorphous

Table 8. States of the formation of the crystals in canned crab to which various amounts of sodium hexametaphosphate made by Taiheiyō Kagaku Co. were added

Concentration of sodium hexametaphosphate (%)		0.23	0.15	0.11	0.075	0.045	0.015
States of meat	Color	Yellow	Yellow	Yellow	Good	Good	Good
	Taste	Bitter	Bitter	Sour	Good	Good	Good
Viscosity (η/η_0)		1.9	2.1	1.9	2.1	2.0	2.5
V. B-N. (*mg%*)		31.5	38.2	35.4	36.2	33.9	31.5
Total-N (%)		0.984	1.011	1.02	1.07	1.04	1.09
Mg (%)		0.0081	0.0023	0.0029	0.0023	0.0088	0.0045
Crystals in juice	Number (/*cc*)	100×10^4	——	22×10^4	50×10^4	22×10^4	22×10^4
	Size (μ)	4×4	4×4	38×25	25×13	57×19	110∼210×20
	Form	E	E	C	C	C	C
Crystals on parchment paper	Top	—	—	—	—	−, +	+
	Side wall	—	—	—	—	+	+
	Bottom	—	—	—	−, +	+	+

Note: Singns which are described in this table show the states of the formed crystals as follow. + = crystals of above 150μ, − = no crystal, C = columnar crystal, E = amorphous

As seen in Tables 7 and 8, in the cans to which sodium hexametaphosphate was added in various concentrations, the formaticn of the crystals was varied with the added amounts of the reagent. When the added amount was 0.3 g per one can and was above 0.15 % of the amount of the contents, the crystals formed in the cans were irregular shaped, large in number and 3∼8 μ in size. If the amount of sodium hexametaphosphate was less than 0.15 *g* (0.075 % of the content), crystals generated having a more regular surface and larger size. No intimate relation was observed among the added amount of sodium hexametaphosphate and specific viscosity or the amounts of volatile basic nitrogen, total nitrogen and soluble magnesium. But, remarkable relation was observed between the commercial qualities of the content of the cans and the added amounts of the reagent. The larger the added amount of the reagent, the worse were the color and the taste of the contents. When the amount of the reagent added to the cans was over 0.15 %, the contents of the canned food became pale yellow in color and bitter in taste. In order to prevent the formation of the crystal in the canned crab, the amount of sodium hexametaphosphate added per a can must be limited commercially below 0.11 % of that content (0.23 *g*. per one can).

2. In the case of the canned salmon

(*1*) *Sample*

On the floating cannery, when the cans were processed in customary manner from the *keta* salmon caught at the northern sea (Hokuyō), the meat was packed with tablets of sodium hexametaphosphate, Mascolin "M" ($M_n + 2P_nO_{3n+1}$) and Mascolin "T" ($M_n + 2P_nO_{3n+1}$) which are kinds of sodium hexametaphosphate. The amounts of the complex ion-making agent are shown in Table 9.

Table 9. Added amounts of sodium hexametaphosphate for canned salmon

Sample	Added amount of tablet of sodium hexametaphosphate (made in U. S. A.)	Added rate of sodium hexametaphosphate for the amount of the contents
P 1	0 *g/can*	0 %
P 2	0.7	0.28
P 3	1.18	0.47
P 4	1.88	0.75
P 5	2.35	0.94
P 6	3.53	1.41
Sample	Added amount of Mascolin "M"	Added rate of Mascolin "M" for the amount of the content
M 1	0.24 *g/can*	0.096 %
M 2	0.70	0.28
M 3	1.18	0.47
M 4	2.35	0.94
M 5	3.53	1.41
M 6	4.70	1.88
M 7	7.05	2.82
Sample	Added amount of Mascolin "T"	Added rate of Mascolin "T" for the amount of the content
T 1	0.24 *g/can*	0.096 %
T 2	0.70	0.28
T 3	1.18	0.47
T 4	2.35	0.94
T 5	3.53	1.41
T 6	4.70	1.88
T 7	7.05	2.82

The cans containing various amounts of the reagents were seamed, cooled as customarily after sterilization, and opened after one year.

(2) *Experimental method*

The state of the formed crystals in the cans to which the reagents were added was observed by the same method described in the previous paper[3)].

(3) *Experimental results*

Results obtained are shown in Tables 10, 11 and 12.

As seen in these tables, the state of the formation of the crystals in the cans to which the complex ion-making agents were added varied with the added amounts of the reagent.

Table 10. States of the formation of the crystals in canned salmon to which various amounts of tablets of sodium hexametaphosphate were added

Sample No.	Added amount of tablet	pH	State of juice	States of crystals in juice						Crystals on meat	
				Amorphous		Microcrystal		Macrocrystal		Macrocrystal	
				Size (μ)	Number	Size (μ)	Number (/cc)	Size (μ)	Number (/can)	Size (μ)	Number (/can)
P 1	0.0	6.2	Good	24×16	Many	16~48×16	5×10^4	240~3300×32~510	52	1500~5500×1000~1500	7
P 2	0.7	6.4	Good	16×16	Many	48×16	2×10^4	1000~5000×500~2000	26	1000~3000×500~1500	24
P 2	0.7	6.4	Good	16×16	Many	32×16	2×10^4	1000~12000×500	20	1000~1200×500~800	18
P 3	1.18	6.4	Good	16~32×16	Many	48×16	1×10^4	1000~2500×200~1000	15	——	None
P 3	1.18	6.4	Good	32×16	Many	32×16	1×10^4	1000~1150×200~500	14	500~1200×200~800	3
P 4	1.88	6.5	Good	16×16	Many	16× 8	1×10^4		None		None
P 4	1.88	6.5	Good	16× 8	Many	32×16	1×10^4		None		None
P 5	2.35	6.5	Muddy	16×16	Many	——	None		None		None
P 5	2.35	6.5	Muddy	16×16	Many	——	None		None		None
P 6	3.53	—	Muddy	16×16	Many	16× 8	1×10^4		None		None
P 6	3.53	—	Muddy	16×16	Many	——	None		None		None

Table 11. States of the formation of the crystals in canned salmon to which various amount of Mascolin "M" were added

Sample No.	Added amount of Mascolin "M" (g/can)	pH	State of juice	State of meat	Crystals on meat		States of crystals in juice			
					Visible crystal		Microcrystal		Visible crystal	
					Size (μ)	Number (/can)	Size (μ)	Number (/cc)	Size (μ)	Number (/can)
M 1	0.24	6.0	Good	Good	——	None	32~160×16~32	2×10^4	——	None
M 2	0.70	5.4	Good	Pale brown	——	None	32~150×16~32	2×10^4	——	None
M 3	1.18	6.4	Good	Pale brown	——	None	32~100×16~32	1×10^4	——	None
M 4	2.35	6.0	Muddy	Pale brown	——	None	32×16	1×10^4	——	None
M 5	3.53	6.0	Muddy	Pale brown	——	None	——	None	——	None
M 6	4.70	5.8	Muddy	Pale brown	——	None	——	None	——	None
M 7	7.05	5.3	Muddy	Pale brown	——	None	——	None	——	None

Table 12. States of the formation of the crystals in canned salmon to which various amount of Mascolin "T" were added

Sample No.	Added amount of Mascolin "T" (*g/can*)	pH	State of meat	State of juice	Crystals on meat: Visible crystal Size (μ)	Number (*/can*)	States of crystals in juice: Microcrystal Size (μ)	Number (*/cc*)	Visible crystal Size (μ)	Number (*/can*)
T 1	0.24	6.0	Good	Good (yellow)	—	None	32~65×16~32	3×10^4	—	None
T 2	0.70	5.6	Discolor	Good (yellow)	—	None	32~65×16~32	5×10^4	—	None
T 3	1.18	6.3	Discolor	Muddy brown	—	None	32~65×16~32	1×10^4	—	None
T 4	2.35	6.4	Discolor	Muddy brown	—	None	32×16	1×10^4	—	None
T 5	3.53	6.3	Discolor	Muddy brown	—	None	—	None	—	None
T 6	4.70	6.3	Discolor	Muddy brown	—	None	—	None	—	None
T 7	7.05	5.7	Discolor	Muddy brown	—	None	—	None	—	None

When the tablet of sodium hexametaphosphate was added in quantity over 0.94 % of the content of the can (2.35 *g* per one can), neither the microcrystals, nor macrocrystals (visible) were formed.

In the cans to which the reagent of 1.88 *g* (0.75 % of the content in the can) was added, a few microcrystals were formed, but no visible crystal generated which would be commercial obstacles. However, when the added amount of the reagent was below 0.75 % of the content of the can, the formed crystals were not only microcrystals, but also macrocrystals. In the cans to which various amounts of the reagents were added, the relation between the qualities of the juice of the can and the added amounts of the reagent was observed.

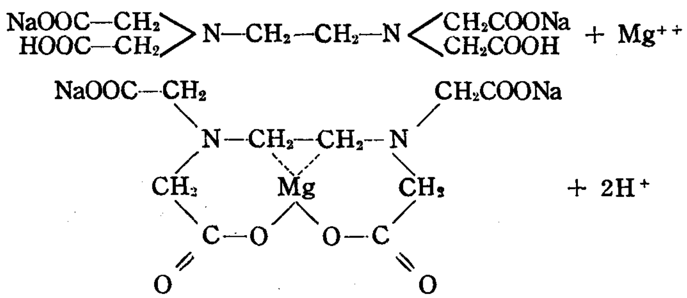
When the added amount of reagent was over 0.94 % (2.35 *g* per one can), the juice of the can became muddy and was whitish turbid. On the contrary, when the added amount of the reagent was below 0.75 % (1.88 *g* per one can), no difference between the cans and blank one was observed in the quality of the juice. In the manufacture of canned salmon, in order to prevent the formation of crystals without loss of commercial merchandise value, the added amount of the tablet of sodium hexametaphosphate should be 0.75 % of the content of the can (1.88 *g* per one can).

As seen in Tables 11 and 12, in the cans to which the added amount of Mascolin "M" or "T" was over 0.09 % of the content of the can (over 0.24 *g* per can), visible crystals were not formed. In the cans to which the added amount of Mascolin "M" or "T" was above or below 0.94 % as a boundary for the content of the can, visible crystals or microcrystals were not formed in the former, but microcrystals were formed in the later respectively. In such cans, the pH values declined toward the acidic side dependent upon the larger amount of Mascolin "M" or

"T" added. When Mascolin "M" or "T" was added to the cans, the state of the content of those cans differed. In the cans to which Mascolin "M" was added, the juice was pale yellow and transparent. In the cans to which Mascolin "T" was added, juice of the canned food was brown and muddy. Also, remarkable differences in the color or appearance of the meat content of the cans were observed. It is interesting that in the cans to which Mascolin "M" was added, the larger the added amount of the reagent, the stronger was the elasticity of the meat in the cans, also the color of the meat became brown. In the cans to which Mascolin "T" was added, the elasticity of the meat was not changed in proportion to the added amounts of the reagent, but the color of meat became pale, and the meat was discolored. According to these results, it is evident that Mascolin "M" or "T" is available to prevent the formation of the crystals, and the amount of the reagents is considered to be adequate at 0.24 ~ 0.7 *g* per can (0.096 % ~ 0.28 % of the content of the can).

III. The influence of the addition of E.D.T.A. (Ethylendiamine tetraacetate) upon the formation of the crystals

Recently, in the field of inorganic analysis, E. D. T. A. has been generally employed in accordance with the chemical action in which the disodium salt (disodium dihydrogen ethylen diamine tetraacetate dihydrate) form quantitatively a stable complex salt with calcium ion (Ca^{++}) or magnesium ion (Mg^{++}) as described in the following.



Here, the authors will report the observations on the influence of the addition of E. D. T. A. upon the formation of the crystals, the quality of the content of canned foods and the empty cans.

1. The influence of the sheet iron of an empty can upon the reactivity of E. D. T. A. reagent

(1) Experimental method

One-fiftieth N E. D. T. A. solution and N/50 magnesium sulfate solution were prepared. Twenty *cc* of N/50 E. D. T. A. solution was diluted to 250 *cc*. In order to know the reactivity of the diluted E. D. T. A., 10 *cc* of the solution was titrated with

N/50 magnesium sulfate solution. The remaining volume, 240 *cc*, of the diluted E. D. T. A. solution was poured into an empty can (half pound, flat). This can was seamed, heated at 5 *lbs* for 85 minutes and then was cooled in running water. The can was left for 40 days. The change of the reactivities of the processed E. D. T. A. solution was estimated by titrating with N/50 magnesium sulfate solution.

(2) *Experimental results*

Results obtained are shown in Table 13.

Table 13. The change of the reactivities of the processed E.D.T.A. solution

Reactivity of non-processed solution	2.31 *mg* Mg/100 *cc* E. D. T. A.
Reactivity of processed solution after 40 days	0.91 *mg* Mg/100 *cc* E. D. T. A.
Reducing rate of reactivity of processed solution (%)	60.5

Table 14. Added amount of E. D. T. A.

Sample No.	Amount of crab meat	Amount of juice	Added amount of N/50 E.D.T.A. solution	Added amount of dist. water
1	5 *g*	0 *cc*	5 *cc*	0 *cc*
2	5	0	10	0
3	5	0	15	0
4	5	0	20	0
5	5	0	0	10
6	5	2	10	0

As seen in Table 13, the reactivity of E. D. T. A. solution which was poured in the can and was processed as in usual canning declined to 39.5 % in comparision with the reactivity of the non-processed solution.

2. The influence of E. D. T. A. upon the formation of the crystals in test tubes

(1) *Sample and experimental method*

In a can of crab (*Erimacrus isenbeckii*) which was prepared in the author's laboratory, the ratio of meat and juice was determined to be 5:2. Here, as shown in Table 14, each 5 *g* of the meat taken from that can was placed in six empty test tubes, and 2 *cc* of the juice separated was poured into one of the test tubes. Various amount of N/50 E. D. T. A. solution were poured into all the test tubes.

All those test tubes were closed with cotton stopper and heated at 5 *lbs* for 85 minutes as usual, cooled and then left for 40 days. After the leaving, the changes in the color of the contents in the test tubes were observed. The juice separated from those test tubes was diluted with dist. water to 50 *cc*. Several drops of 1 % Na_2S solution was added to 10 *cc* of the dilute in order to counteract the obstacles to complex-making with $Fe^{++}$and Cu^{++}. Then 1 *cc* of the buffer solution was added to make pH 10.0, accompanied with indicator solution (alcoholic solution of eryochrome black "T"). The remaining amount of Mg^{++} which did not form E. D. T. A.–complex was estimated with N/50 E. D. T. A. solution and the amount of E. D. T. A. was beforehand back titrated with N/50 $MgSO_4$.

(2) *Experimental results*

Results obtained are shown in Table 15.

Table 15. Amount of E. D. T. A. required to prevent the formation of crystals in canned crab

Sample No.	1	2	3	4	5	6
Color of meat	No-change	No-change	No-change	No-change	No-change	No-change
Presence of free Mg ion which did not form complex-salt	+	+	−	−	+	+
Amount of E.D.T.A. required to the complex-salt	18.8 (*mg*)	24.3	26.1	37.2	15.6	32.4
Amount of E.D.T.A. required per one can of canned crab	0.34 (%)	0.43	0.47	0.67	0.28	0.51

As seen in Table 15, the dose of E. D. T. A. to be used for canned crab is clarified to be 0.34~0.67 % of the amount of the content of the can. In No. 5 sample can in which distilled water was added in place of E. D. T. A. solution, the amount of magnesium which dissolved into the juice in the can was slight. This is owing to the formation of complex salt from E. D. T. A. and magnesium or calcium in other cans.

No change in the color of the meat resulting from the addition of E. D. T. A. was observed. Therefore, E. D. T. A. has a preventive effect for the formation of struvite in the canned foods.

However, as a decrease in the reactivity of E. D. T. A. was observed from the result of Experiment 1, the using dose of E. D. T. A. is 0.85~1.7 % per can (net content: 200 *g*) of canned crab, considering from the loss of 60 % of the reactivity. This dose must be tried practically to prevent the formation of the struvite in the canned foods. But here the approximate using dose has been determined.

Summary

The authors have observed the formation of the crystals in canned crab or canned salmon to which gelatine, agar, or S. L. D. was added in order to raise the specific

viscosity. Thus it was clearly demonstrated that the higher the specific viscosity in the juice of the cans became, the less the number of the formed crystals became. However, when the agar, gelatine or S. L. D. needed for preventing the formation of the larger crystals was added, the contents had poor merchandise value. The amounts of agar, gelatine or S. L. D. needed for preventing the crystal formation were determined.

The formation of the crystals has been said to be inevitable under the condition of the existence of the components of the crystals, because the solubility of $MgNH_4PO_4 \cdot 6H_2O$ crystal was rather small[4]. In previous paper[3], the authors have investigated the mechanism of the formation of the crystals and made it clear that the size of the formed crystals may be rendered as small as possible by rapid cooling of the can after heating. However, in the use of such a method, it is practically impossible completely to prevent the formation of the crystals. For the purpose of the prevention of the formation of the crystals, it will be preferable that some one sort of the components of the crystals exchange into a soluble compound. Here, in order to prevent the formation of the crystals owing to the changing of the magnesium of the compnents into the soluble complex salt, various amounts of sodium hexametaphosphate, Mascolin "M", Mascolin "T" or E. D. T. A. were added to the canned crab or the canned salmon, and the states of the formation of the crystals were observed. Then the added amount of various complex ion-making reagents which were needed for the complete prevention of the formation of the crystals were determined. According to the results obtained, in the canned crab or canned salmon, to which 0.11~0.22 % of sodium hexametaphosphate, when 0.1~0.28 % of Mascolin "M" or Mascolin "T", and 0.34~0.67 % of E. D. T. A. were added, the formation of the crystals was prevented. The influence of the complex ion-making agents upon the commercial qualities of the cans was varied with the added amount. In the canned crab, when the added amount of sodium hexametaphosphate was over 0.11 %, the meat became pale yellow in color, and bitter to the taste. In the above described canned crab after it was opened a white substance precipitated in the can, and the merchandise value declined. In the canned salmon, when the added amount of Mascolin "M" was over 0.28 %, the meat was scarcely changed in taste, but a part of the meat became pale brown in color. In such cans, the meat was elastic and the phenomenon of meat crumbling did not occur. In the canned salmon to which Mascolin "T" was added, the meat became discolored and pale. When the added amount of the reagent was below 0.28 %, the possibility of the formation of visible crystals was larger.

Literature cited

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3) ——————. (1957). *Ibid.* 8 (3), 130-146.
4) ——————. (1957). *Ibid.* 7 (4), 300-305.