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Laurence Castle, Emma Bradley, Joanna Day, Jennifer Leak

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Migration of melamine from can coatings cross-linked with melamine-based resins, into food simulants and foods

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3 1 **Migration of melamine from can coatings cross-linked with melamine-based resins, into**
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5 2 **food simulants and foods**
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10 4 Emma L. Bradley*, Laurence Castle, Joanna S. Day and Jennifer Leak
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14
15 6 The Food and Environment Research Agency, Sand Hutton, York YO41 1LZ (UK)
16
17 7

18 8
19
20 9 *Author for correspondence
21

22 10 email: emma.bradley@fera.gsi.gov.uk
23

24 11 tel: +44-1904-462000
25

26 12 fax: +44-1904-462133
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34 16 **KEYWORDS:**

35
36 17 Melamine, can coatings, melamine-formaldehyde, resins, chemical migration, simulants,
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38 18 foods.
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ABSTRACT

Resins based on melamine-formaldehyde and related analogues such as methylolated melamine are used to cross-link coatings used inside food cans and on the metal closures of glass jars. Thirteen commercially coated cans and closures representing 80% of the European market, were tested using simulants under realistic industrial heat-processing conditions for canned and jarred foods. The food simulants and the retort conditions used were 3% acetic acid for 1 hr at 100°C and 10% ethanol for 1 hr at 130°C. The highest migration level seen for melamine into simulant was 332 µg/kg. There was no detectable migration of the melamine analogues cyanuric acid (<1 µg/kg) or ammelide (<5 µg/kg) from any sample. Twelve of the thirteen samples released no detectable ammeline (<5 µg/kg) but the coating giving the highest release of melamine did also release ammeline at 8 µg/kg with the higher of the two process temperatures used. Migration experiments into food simulant and foods themselves were then conducted using two experimental coatings made using amino-based cross-linking resins. Coated metal panels were exposed to the food simulant 10% (v/v) aqueous ethanol and to three foodstuffs under a range of time and temperature conditions both in the laboratory and in a commercial food canning facility using proprietary time and temperature conditions. The highest migration into a food was 152 µg/kg from the first coating processed for a long time at a moderate sterilisation temperature. The highest migration into simulant was also from this coating at 220 µg/kg when processed at 134°C for 60 mins, dropping to 190 µg/kg when processed at 123°C for 70 mins. Migration from the second coating was quite uniformly 2 to 3 times lower under all tests. These migration results were significantly higher than the levels of melamine extractable using 95% ethanol at room temperature. The experiments show that commercial canning and retorting can be mimicked in an acceptable way using laboratory tests with an autoclave or a simple pressure cooker. The results overall show there is hydrolytic degradation of the melamine-cross-linked resins to release additional melamine. There is a strong influence of the temperature of heat treatment applied with foods or simulants but only a minor influence of time of heating and only a minor influence, if any, of food/simulant acidity.

51 INTRODUCTION

52
53 Melamine (2,4,6-triamino-1,3,5-triazine, Figure 1) is a chemical with a global production
54 volume currently of about 500 Mtonnes pa. It is used in a wide variety of industrial and
55 consumer products including packaging and other food contact materials and articles. The
56 deliberate and fraudulent adulteration of food and feed with melamine in 2007 and of infant
57 milk and other milk products in 2008 caused sickness and even death in pet animals and
58 infants, mainly from kidney damage caused by crystals or stones in the urinary tract.
59 Melamine had been added to elevate the apparent protein content. Depending on the
60 purification process used, melamine may contain a number of structurally related by-products,
61 these being cyanuric acid, ammelide and ammeline (Figure 1). In the pet food scandal of
62 2007, co-adulteration with melamine plus cyanuric acid exacerbated the toxicity caused
63 because of strong complex formation leading to co-precipitation of melamine-cyanuric acid
64 crystals and stones. Ammeline, ammelide and cyanuric acid are analogous to melamine with
65 one, two and then all three amino groups replaced by hydroxyls, respectively, and so they
66 move from basic to acidic in character across the 4 analogues.

68 Melamine used to make food contact materials and articles

69 Melamine is reacted with other starting substances, principally formaldehyde, to make a
70 variety of M-F (Melamine-Formaldehyde) resins used in food contact materials and articles
71 (Figure 2). These include M-F resins used in can coatings, paper-making and adhesives along
72 with M-F plastics used to make durable articles such as cups and plates. The methylene (-
73 CH₂-) unit between the two melamine structures in Figure 2 is the formaldehyde link after
74 condensation and loss of water, H₂O. The repeat unit (M-F)_n is depicted within the brackets
75 in Figure 2.

77 In the European Union (EU), melamine is approved for use as a monomer and as an additive
78 in plastics and it has a specific migration limit (SML) of 30 mg/kg food [EC 2009]. This
79 SML was derived from a tolerable daily intake (TDI) of 0.5 mg/kg bw/day and the default
80 exposure scenario that is used for plastic food contact materials of an intake of 1 kg packaged
81 food per day by a 60 kg bw adult [SCF 1986]. There are no specific EU regulations on
82 melamine used in non-plastics (e.g. can coatings or paper/board) but an SML for plastics is
83 often taken as a presumptive standard. Both the [WHO 2009] and more recently EFSA

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3 84 [EFSA 2010] have revised the melamine TDI downwards to 0.2 mg/kg bw/day and it seems
4
5 85 likely therefore that the EU SML will be lowered too.
6
7 86

8
9 87 According to EFSA [EFSA 2010] the TDI for melamine is not applicable if there is
10
11 88 significant concomitant exposure to cyanuric acid, ammelide or ammeline, due to the
12
13 89 increased potential for formation of urinary crystals. Ammeline, ammelide and cyanuric acid
14
15 90 are not on the EU positive list of substances permitted to be used in food contact plastics.
16
17 91 Cyanuric acid (and dichlorocyanurate, which is a source of active chlorine and can ultimately
18
19 92 form cyanuric acid) are both on the Swiss inventory list of substances for printing inks [Swiss
20
21 93 Confederation, 2009]. Although on that inventory list, it is not clear if cyanuric acid or
22
23 94 dichlorocyanurate are actually used commercially or not for food packaging inks. To the best
24
25 95 of our knowledge, ammeline, ammelide and cyanuric acid are not on any other inventory list
26
27 96 of substances used by any European packaging sector, including coatings.
28

29

98 **Melamine used in coatings on metal for cans and closures**

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31 99 M-F resins and related analogues such as methylolated and other etherified melamine resins
32
33 100 can be used to cross-link coatings used inside food cans. Similar coatings can also be used on
34
35 101 the metal closures (lids) of glass jars. The coatings are cured at high temperatures and the
36
37 102 multiple reaction sites of melamine (Figure 2) allow a 3-dimensional polymer matrix to form
38
39 103 to give extensive cross-linking. The cured coatings are very thin, at typically 5 to 10 μm , so
40
41 104 that the potential for migration of residual (unreacted) melamine is expected to be low. On
42
43 105 the other hand, the contact conditions for canned or jarred foods can be very demanding,
44
45 106 including sterilisation or pasteurisation of the foodstuff in the can or jar at high temperatures
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47 107 and then subsequent long-term storage for up to several years. Consequently, the stability of
48
49 108 the coatings themselves, and of any low molecular weight melamine derivatives used as
50
51 109 precursors, needs to be considered as well as residual melamine levels.
52

53

51 **The aims of this work**

52
53 112 Since the SML of 30 mg/kg for melamine used in plastics has tended to be used as a
54
55 113 presumptive standard for non plastics packaging including coatings, there has been little
56
57 114 perceived need to study the migration of melamine from coatings into food and food
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59 115 simulants. The aim of this work was to fill this gap in our knowledge and understanding of
60
116 the migration levels of melamine from coatings and the factors that influence the migration
117
process.

118 MATERIALS AND METHODS

119

120 Ring trial samples from commercial coatings

121 Exposed simulant samples were provided in January 2010 by David Smith (Metal Packaging
122 Manufacturers Association, UK) and they were blind-coded. The simulants were a 10% (v/v)
123 solution of ethanol in water and 3% (w/v) solution of acetic acid in water. The exposed
124 simulants were the result of testing 13 commercially coated cans or closures using realistic
125 industrial heat-processing conditions for canned and jarred foods. The coated cans and
126 closures had been collected together by a joint industry group for light metal packaging (JIG)
127 comprising member companies of the trade associations CIAA (Confederation of the food and
128 drink industries of the EU), EMPAC (European Metal Packaging), CEPE (Conseil Européen
129 de l'Industrie des Peintures, des Encres d'Imprimerie et des Couleurs d'Art, covering coatings
130 and inks) and the principal European manufacturers of melamine-based coating resins. The
131 processing conditions are described more fully in the results and discussion section.

132

133 Experimental coatings

134 Two experimental coatings coded A and B were formulated by Valspar Corp. (Nantes, F)
135 using amino-based cross-linking resins that contained melamine and other melamine-related
136 substances. The amino-based resin was not the main cross-linker and was used at about 1%
137 (w/w solids basis) in the formulation. The exact composition of the amino-based resins were
138 proprietary to the resin supplier. However, it was found that the first formulation, coating A,
139 gave high levels of melamine in aqueous media at elevated temperatures and the second
140 formulation, coating B was lower in melamine release. The two coatings were applied and
141 cured industrially onto an ETP (electrolytic tinplate) metal substrate. The curing conditions
142 were 200°C PMT (peak metal temperature) for 10 minutes. The dry coating thickness was
143 about 8 µm. The coated metal panels were exposed to the food simulant 10% (v/v) aqueous
144 ethanol and to three foodstuffs coded F1, F2 and F3 under a range of time and temperature
145 conditions in a commercial food canning facility and in the laboratory.

146

147 *Industrial retorting of simulants and foods.* The industrial experiments took small sheets of
148 the coated panels and placed them into metal cans containing either food or food simulant and
149 then processed the samples using the typical industrial heat-retorting conditions of time and
150 temperature depending on the heat treatment that different food types require. Thus, two
151 0.63 dm² coated panels were cut and placed back to back into metal cans containing 10%

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3 152 (v/v) aqueous ethanol (approximately 400 mL). The cans were then sealed and retorted using
4
5 153 a static retort. Blanks were prepared and processed in the same way, with simulant but
6
7 154 without any coated panels inside. Samples and blanks were prepared in triplicate for each
8
9 155 time/temperature combination. The three (proprietary) heat treatments used for the three food
10
11 156 types F1, F2 and F3 were a relatively low temperature treatment for a long time, a medium
12
13 157 temperature treatment for a long time, and a high temperature treatment for a short time.
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15 158

16
17 159 *Laboratory retorting of simulants and foods.* The laboratory tests used either a stove-top
18
19 160 pressure cooker or a laboratory autoclave to heat the food simulant above its atmospheric
20
21 161 boiling point. The aim was to match as close as possible the time and temperature conditions
22
23 162 used industrially. Replicate ($n = 2$) test specimens were cut from each set of panels. The test
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25 163 specimens (0.2 dm^2) were immersed in 10% (v/v) aqueous ethanol (80 mL) held in a thick-
26
27 164 walled glass bottle. For heating using a pressure cooker, the exposure was for 60 or 90 mins
28
29 165 at an exposure temperatures of 109°C (using a pressure weight marked as 5 lb (2.27 kg) in
30
31 166 mass) or of 121°C (15 lb weight, 6.80 kg). The duration of the exposure was timed from
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33 167 when the required pressure was reached (i.e. when steam began to escape from the vent,
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35 168 approximately 10-15 mins after heating began). After the required exposure duration, the
36
37 169 pressure in the unit was released and the Duran bottles were allowed to cool. The exposed
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39 170 panel was then removed from the simulant. For heating in an autoclave, the exposure was for
40
41 171 20 or 60 mins at 134°C , timed from when the autoclave attained the target temperature.
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43 172

42 173 **Analysis of food simulants**

44 174 A portion of simulant was taken and internal standard ($^{13}\text{C}_3$ -melamine) was added to achieve
45
46 175 a concentration of $50 \mu\text{g/L}$. A second and third portion of simulant samples received internal
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48 176 standard and were spiked with melamine, cyanuric acid, ammeline and ammelide to achieve
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50 177 concentrations of $10 \mu\text{g/L}$ and $50 \mu\text{g/L}$ of each.
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52 178

54 179 **Analysis of food samples**

56 180 *Extraction.* The food sample was homogenised and internal standard ($^{13}\text{C}_3$ -melamine) was
57
58 181 added to a portion (1 g) to achieve a concentration of $100 \mu\text{g/kg}$. To the portion of food was
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60 182 then added water (5 mL and mix on a rotamix for 10 secs); acetonitrile (5 mL, mixed);
183 acetonitrile (30 mL, mixed) and finally water (10 mL, mixed). The whole mixture was then

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3 184 shaken for 5 mins and then centrifuged at 3500 rpm for 10 mins. A portion of the supernatant
4
5 185 was taken for analysis by LC-MS/MS. A second portion of food (1 g) received internal
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7 186 standard plus a spike of melamine, ammeline and ammelide each at a concentration of
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9 187 100 µg/kg and then extracted in the same way.
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12 189 *LC-MS/MS analysis.* All samples, 100-fold diluted samples and spikes were diluted 1:9 (v:v)
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14 190 with acetonitrile immediately prior to analysis by LC-MS/MS. The LC column was an
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16 191 Obelisk N (5 µm, 100 Å, 150 x 2.1 mm, SiELC) eluted with 0.25 mL/min 20 mM ammonium
17
18 192 acetate + 0.1% (v/v) acetic acid in water (X) and acetonitrile (Y) with a gradient X:Y of 5:95
19
20 193 up to 50:50 at 5.0 mins, held at 50:50 to 9.0 mins, equilibrate 6.0 ms at 0.3 ml/min then
21
22 194 reinject. The injection volume was 10 µL and the column was maintained at 30°C. The
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24 195 MS/MS system was a Micromass (Manchester, UK) Quattro Ultima triple quadrupole mass
25
26 196 spectrometer. Electrospray ionisation was used in the positive mode for melamine and
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28 197 ammeline with MRM transitions m/z 127->85 for quantification and 127->68 for
29
30 198 confirmation of melamine and 128->86 for quantification and 128->69 for confirmation of
31
32 199 ammeline. The MRM transition of 130->87 was monitored for the labelled melamine internal
33
34 200 standard. Electrospray ionisation was used in the negative mode for cyanuric acid and
35
36 201 ammelide with MRM transitions m/z 128->42 and 128->82 for cyanuric acid and m/z 127-
37
38 202 >84 and 127->42 for ammelide, for quantification and for confirmation respectively.
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40 203

41 204 **Analytical quality control**

42 205 Each analytical batch contained blank foods and food simulants carried through the analytical
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44 206 procedure. Each batch also contained blank samples spiked with known concentrations of
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46 207 melamine for recovery checks and results were corrected for the analytical recovery.
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210 **RESULTS AND DISCUSSION**

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212 **Choice of food simulants and foods**

213 There are no officially recognised food simulants specifically for testing can coatings. A total
214 extraction using acetonitrile solvent is a common procedure [Bradley et al., 2009]. However,
215 since we were interested in high temperature processing and the possibility of hydrolytic
216 degradation, aqueous simulants/extractants were called for. Melamine itself is a basic
217 substance and it was anticipated that acid may accelerate any hydrolysis of the coatings, by
218 reversing the condensation reaction with formaldehyde that make the M-F resins (Figure 2).
219 Therefore, for the first set of experiments 3% acetic acid was used along with 10% ethanol for
220 comparison purposes. For the second set of experiments, based on the findings from the first
221 set, only 10% ethanol was used as simulant. Similarly, 3 food types were selected for the
222 second set of experiments. The food composition and the exact thermal processing conditions
223 used were proprietary. The three food types were chosen as being typical for foods that,
224 based on their nature and composition, such as acidity (F1), fat content (F2) and presence of
225 meat or fish (F3), needed a relatively low temperature treatment for a long time, a medium
226 temperature treatment for a long time, or a high temperature treatment for a short time.

227

228 **Analytical methods used**

229 A review of the analytical methods used for melamine and related compounds in foods has
230 been published recently [Tittlemier, 2010]. The main focus of method development and
231 analysis has been on melamine and (to a lesser extent) cyanuric acid. Very little has been
232 published on ammeline and ammelide.

233

234 In this work we used LC-MS/MS. Analysis of food simulants was straightforward and
235 involved dilution with acetonitrile to make the sample compatible with the LC mobile phase
236 and then direct injection. Food samples were extracted into acetonitrile:water and centrifuged
237 prior to analysis.

238

239 An Obelisk N SiELC column was used to give adequate retention of melamine and its
240 analogues and the MS/MS was operated in the positive ionisation mode for melamine and
241 ammeline, and in the negative ionisation mode for ammelide and cyanuric acid. Isotope-
242 labelled ($^{13}\text{C}_3$ -) melamine was used as the internal standard. Measurement of cyanuric acid,
243 ammeline and ammelide was against external standards. Isotope-labelled cyanuric acid is

1
2
3 244 now available for use as an internal standard but it was not used in this work. There was
4
5 245 significant ion suppression in the case of food analysis because of the limited sample clean-up
6
7 246 used and so the injection of co-extractives. The labelled melamine internal standard
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9 247 compensated automatically for this suppression. Results for the melamine analogues were
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11 248 corrected for the analytical recovery that was determined by the analysis of spiked samples
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13 249 and this corrects for any ion suppression effects too. The apparent recovery for the analytes
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15 250 in all matrices was excellent, in the range of 89 to 108%.

16 251

17 252 **Simulant tests on commercially coated cans and closures**

18
19 253 The first set of experiments investigated migration from commercially coated cans and
20
21 254 closures in a ring-trial organised by the JIG (Joint Industry Group for Light Metal Packaging).
22
23 255 The results were summarised in [EFSA 2010].

24 256

25
26 257 *Choice of samples.* According to the JIG, many cans typically consist of a number of
27
28 258 different coatings on different parts of the can such as can ends, bodies and side-stripes.
29
30 259 Coatings are also used on the metal closures for jars and bottles. The 13 coated articles tested
31
32 260 were sourced from within the supply chain and were based on epoxyanhydride,
33
34 261 epoxyphenolic coatings or organosols, some of which contained melamine resins. The
35
36 262 coatings were said to be representative of about 80% of the current European market for 2-
37
38 263 piece and 3-piece food cans and closures for jars.

39 264

40 265 *Test conditions used.* The cans and closures were 'extracted' using simulants under realistic
41
42 266 industrial heat-processing conditions for canned and jarred foods. The food simulants and the
43
44 267 retort conditions used were 3% acetic acid for 1 hr at 100°C (denoted AA) and 10% ethanol
45
46 268 for 1 hr at 130°C (denoted E10). The exposed simulants were coded anonymously by an
47
48 269 independent party and submitted blind to 6 participating laboratories (including Fera) for
49
50 270 analysis and reporting results back to the coordinator. All 6 labs used LC-MS for the
51
52 271 analysis.

53 272

54
55 273 *Results.* The analytical results for melamine are shown in Table 1. Fera reported the most
56
57 274 complete set of results and these results are given in Table 1 along with the consensus values
58
59 275 for each coating that was assigned as the simple arithmetic mean of participants results,
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276 omitting any clear outliers. The first 8 coating systems were tested separately with AA and
277
with E10. The remaining 5 coating systems were tested with E10 only. In order to comply

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3 278 with EU anti-cartel rules governing such joint-industry projects (rules on competition laid down
4 in Articles 81 and 82 of the EC Treaty) the samples were coded anonymously and the
5 279 formulation details were not shared. In addition the cans and closures contained a mixture of
6 280 different coatings. Consequently, results cannot be interpreted in detail according to the
7 281 different coating compositions, what melamine-formaldehyde resins they may contain, the
8 282 stoving (curing) process used etc., because this information is not known. However, some
9 283 general conclusions can be drawn from the results. The highest migration of melamine was
10 284 332 µg/kg (Table 1). For the coatings that did show melamine migration, levels were
11 285 significantly higher into E10 (1 hr/130°C) compared to AA (1 hr/100°C) suggesting a more
12 286 important effect of temperature rather than acidity in causing migration. The ratio for (E10-
13 287 130°C) / (AA-100°C) was at least 2 to 6 for coatings 3, 5 and 6 (setting AA at the upper-
14 288 bound limit of detection (LoD)) and was 3, 8 and 21 for coatings 7, 8 and 4 that released more
15 289 melamine. According to the JIG, the data indicates that migration levels of melamine into
16 290 both E10-130°C and AA-100°C can exceed the residual content in the can coating, as
17 291 determined by solvent extraction by a wide margin. Thus, some decomposition of the coating
18 292 seems to occur, probably by a hydrolysis mechanism, to form additional melamine.
19 293
20 294

21 295 *Cyanuric acid.* Two laboratories including Fera tested the simulant samples for cyanuric
22 296 acid. All samples showed non-detectable levels at LoDs of 1 µg/kg (Lab 1) or 20 µg/kg
23 297 (Fera).
24 298

25 299 *Ammeline and ammelide.* Fera alone tested the samples for ammeline and ammelide and all
26 300 samples were less than the LoD of 5 µg/kg except for the E10-130°C extract of coating
27 301 number 7 which contained ammeline at 8 µg/kg. It is probably significant that this coating 7
28 302 under this test condition also gave the highest melamine migration at 332 µg/kg. It is also
29 303 probably significant that ammeline is the closest related analogue of the 3 to melamine -
30 304 differing in only one of the three amino groups replaced by hydroxyl (Figure 1) - formally a
31 305 hydrolysis. It is not clear if the very low level of ammeline results from a small degree of
32 306 impurity in the melamine used to make the amino-based cross-linking resin or if it results
33 307 from hydrolysis during the migration test. In either case, it represents just $8/332 = 2.4\%$ of
34 308 the melamine migration level.
35 309

36 310 **Food and simulant tests**

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2
3 311 The second set of experiments was conducted to compare migration levels into foods and
4
5 312 food simulants and to investigate the influence of the time and temperature of processing
6
7 313 conditions. Because, in the JIG experiments there were mixtures of coatings on the cans and
8
9 314 closures tested, it was decided to examine metal coated with only one coating, where it was
10
11 315 known that different levels of melamine could be generated in aqueous media at elevated
12
13 316 temperatures. Valspar Corp. (Nantes, F) made two experimental coatings using amino-based
14
15 317 cross-linking resins. Coating A gave a high level of melamine in aqueous media at elevated
16
17 318 temperatures whilst coating B gave a lower level. The coatings were applied to ETP panels
18
19 319 and cured industrially.
20

21 321 The migration test results are presented in Table 2. Migration levels from the test panels were
22
23 322 measured on an area-related basis ($\mu\text{g}/\text{dm}^2$) and they have also been recalculated and shown
24
25 323 in Table 2 in units of $\mu\text{g}/\text{kg}$ using the standard ratio of 1 kg:6 dm^2 . The ratio of food mass to
26
27 324 surface area can in practice vary depending on the can size, the use of coatings on metal
28
29 325 closures etc.
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31 326
32 327 The results for melamine migration reveal many features. The results using a pressure cooker
33
34 328 or a laboratory autoclave compared very well with the results using industrial food processing
35
36 329 equipment. The processing conditions used industrially were proprietary. The conditions
37
38 330 used in the laboratory experiments were chosen to match the industrial conditions as closely
39
40 331 as possible, but the match was not exact because of the limitations on the autoclave settings
41
42 332 and limited range of over-pressure weights available for the pressure cooker.
43

44 334 It should be also noted that the heating and cooling of the laboratory autoclave in particular
45
46 335 was a slow process. It took 65 mins for the autoclave to reach the set temperature of 134 °C
47
48 336 from a cold start at 22 °C, a 20 mins test period, and then an additional 50 mins to cool
49
50 337 sufficiently to gain safe access and stop the experiment. In contrast, the pressure cooker took
51
52 338 only 10-15 mins to come up to temperature since it had a lower thermal mass and a higher
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54 339 specific heat input than the autoclave, heated as it was with a stove-top gas ring. The close
55
56 340 similarity in results indicates that heat-up and cool-down times (which will differ according to
57
58 341 scale) are not very important.
59

60 343 Consistent with this observation, migration levels were not affected very significantly by the
344 time of heating. At a set temperature, migration did not change from 60 to 90 mins and even

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3 345 in going from 20 to 60 mins the increase was only ca. 50% (Table 2). There was a stronger
4
5 346 influence of temperature with a 2- to 4-fold increase in migration in going from 109°C to
6
7 347 134°C. In all cases, when the time and temperature were matched closely, the simulant 10%
8
9 348 ethanol gave at least the same and usually higher results than seen with foods. The highest
10
11 349 migration into food was 152 µg/kg from coating A into food F2 sterilised for a long time at a
12
13 350 medium retort temperature. The highest migration into simulant was also from coating A at
14
15 351 220 µg/kg when processed at 134°C for 60 mins, dropping to 190 µg/kg when processed
16
17 352 using the simulant at the same time and temperature conditions as those used for food F2.
18

19 353
20 354 Migration from the coating with a low melamine amino resin was quite uniformly 2 to 3 times
21
22 355 lower than migration from the high melamine amino resin cross-linked coating, in all the
23
24 356 combinations of food/simulant/process conditions (Table 2).
25

26 357
27 358 There was no detectable migration of ammeline or ammelide from the coatings into any of the
28
29 359 foods or simulants. The LoD was 12 µg/kg for simulant and was in the range 5 to 25 µg/kg
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31 360 for foods depending on the substance and the matrix. Cyanuric acid was not tested for.
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362 CONCLUSIONS ON MIGRATION OF MELAMINE FROM CAN COATINGS

363
364 Although the data on can coatings and closures are limited, these results show there is a
365 strong influence of the temperature of heat treatment applied in the experiments with foods
366 and stimulants, only a minor influence of time of heating, and only a minor influence, if any,
367 of food/simulant acidity. Hydrolytic degradation of the melamine-crossed-linked resins
368 clearly takes place to release additional melamine. The experiments show that commercial
369 canning and retorting can be mimicked in an acceptable way using laboratory tests with an
370 autoclave or a simple pressure cooker.

371 372 **Future research needs**

373
374 In related work on melamine-formaldehyde plastics ('melaware') used as cups and plates etc.,
375 a similar strong dependency on the temperature rather than the acidity of the simulant (food)
376 was found [Bradley et al., in press]. It would be interesting to understand which specific
377 chemical units or configurations in a M-F resin are the most labile towards hydrolysis, so that
378 synthesis of the resins used in coatings could be optimised to minimise the hydrolysis and
379 subsequent release of melamine under high temperature food processing conditions such as
380 sterilisation or pasteurisation in cans and jars. One focus of attention could be simply the
381 extent to which all the melamine units are linked into the polymer structure. For example,
382 Figure 2 shows two melamine units, one with 2 amino groups reacted into the polymer
383 structure and one with all 3 amino units reacted into the structure. So to liberate any free
384 melamine would require 2 or 3 linkages to be broken. On the other hand, any pendant
385 melamine linked via only one amino unit would of course need to suffer only a single
386 hydrolysis to liberate melamine. Other structural features may also come into play in
387 providing a fraction of melamino units that is more facile to liberate than the bulk.

388 389 390 **ACKNOWLEDGEMENTS**

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394 provided the two experimental coatings for the second set of food and simulant tests, the H. J.

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3 395 Heinz Company heat-processed those samples, and the two companies co-funded that phase
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5 396 of the work.
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432 **Table 1. Migration of melamine ($\mu\text{g}/\text{kg}$) from commercial coatings on light metal**
 433 **packaging (cans, closures) - JIG Analytical Results.**

Coating	Test conditions	Melamine migration $\mu\text{g}/\text{kg}$	
		Fera	Consensus
Coating 1	3% acetic acid 1 hr / 100°C	3.5	2.5
	10% ethanol 1 hr / 130°C	<1.5	<2
Coating 2	3% acetic acid 1 hr / 100°C	1.7	2
	10% ethanol 1 hr / 130°C	1.5	1.5
Coating 3	3% acetic acid 1 hr / 100°C	<1.5	<2
	10% ethanol 1 hr / 130°C	11	10
Coating 4	3% acetic acid 1 hr / 100°C	6.8	7
	10% ethanol 1 hr / 130°C	151	147
Coating 5	3% acetic acid 1 hr / 100°C	<1.5	<2
	10% ethanol 1 hr / 130°C	3	3
Coating 6	3% acetic acid 1 hr / 100°C	<1.5	<2
	10% ethanol 1 hr / 130°C	12	12
Coating 7	3% acetic acid 1 hr / 100°C	102	104
	10% ethanol 1 hr / 130°C	332	321
Coating 8	3% acetic acid 1 hr / 100°C	14	18
	10% ethanol 1 hr / 130°C	146	141
Coating 9	10% ethanol 1 hr / 130°C	*	327
Coating 10	10% ethanol 1 hr / 130°C	50	49
Coating 11	10% ethanol 1 hr / 130°C	95	90
Coating 12	10% ethanol 1 hr / 130°C	210	219
Coating 13	10% ethanol 1 hr / 130°C	2.5	2.5

434
 435 Coatings 1 and 2 were metal closures such as those used on glass jars for baby foods: The other
 436 samples were filled metal cans. The Consensus value is the simple mean of results from the 6
 437 laboratories participating in the ring trail, omitting any clear outliers.

438 * No Fera result - the sample vial was broken in transit and it was not replaced.

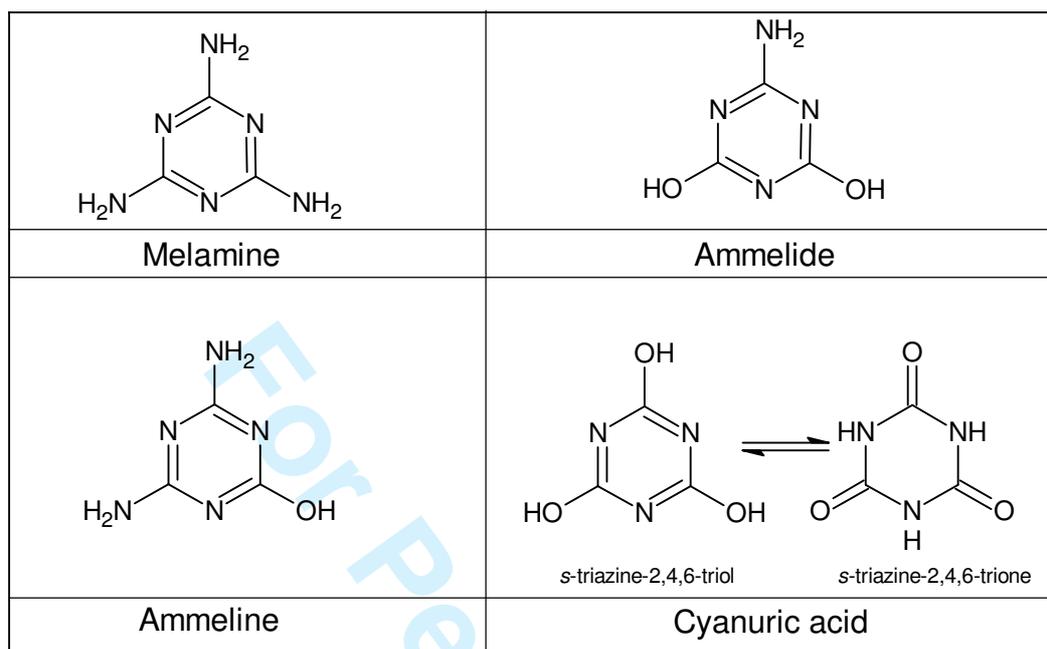
Table 2. Melamine migration from two experimental coatings into foods and food simulants using lab tests and industrial heat-retorting conditions

Food / simulant	Industry process conditions	Lab test Conditions	Melamine ($\mu\text{g}/\text{dm}^2$)	Melamine ($\mu\text{g}/\text{kg}$)	Melamine ($\mu\text{g}/\text{dm}^2$)	Melamine ($\mu\text{g}/\text{kg}$)
			Coating A		Coating B	
	temp / time	temp / time				
Food type 1	low / long		8.9	53	<3.8	<23
10% Ethanol	low / long		16	97	4.6	28
10% Ethanol		109°C / 60 mins	17	103	5.3	32
10% Ethanol		109°C / 90 mins	17	104	5.3	32
Food type 2	medium / long		25	152	9.5	57
10% Ethanol	medium / long		32	190	15	87
10% Ethanol		121°C / 60 mins	26	153	11	68
10% Ethanol		121°C / 90 mins	26	153	11	68
Food type 3	high / short		22	134	6.3	38
10% Ethanol	high / short		25	151	11	63
10% Ethanol		134°C / 20 mins	28	169	11	66
10% Ethanol		134°C / 60 mins	37	220	16	98

Simulant results are average of duplicate specimens of coated panels tested. 109 °C and 121 °C tests were conducted using a stove-top pressure cooker, 134C tests used a laboratory autoclave.

Food results are average of triplicate specimens of coated panels tested. The exact industrial retorting conditions used were proprietary.

Figure 1: Structures of melamine, ammeline, ammelide and cyanuric acid.



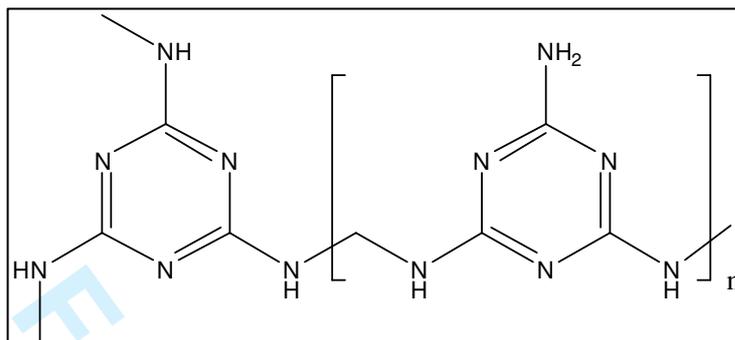


Figure 2: Schematic of a melamine-formaldehyde polymer