MDCTec services
MATERIALS ▪ DATABASE ▪ COMPLIANCE

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Augsburg, the 10.03.2017

REPORT[1] 000271-2099-4[2] *Kinetik*TEST

Migration test from PP plaques under repeated use conditions for Irganox 1076 and Metilox

Order date 13.09.2016

Sample receipt 13.09.2016

Sample no	Description	Comment	Delivery
16535	PP plaques from PP homopolymer with Irganox 1076 (CAS no 2082-79-3)	$c_{P,0}$ = 1000 ppm	by post mail
16536	PP plaques from PP homopolymer with Metilox (CAS no 6386-38-5)	$c_{P,0}$ = 500 ppm	by post mail

1 Aim

Experimental test and simulation of specific migration according to the predefined repeated use scenario by generally recognized diffusion models based on scientific evidence according to Article 18 in conjunction with Annex V (migration modelling) of the plastics Regulation (EU) No 10/2011.

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1 This report includes 3 pages plus attachments. A partial publication of the report requires the prior written consent of the contractor.
The test and/or calculation results refer solely on the samples and/or information provided by the customer and the tested and/or calculated parameters.
Reference samples or sample residues are stored for a period of 6 month as far as possible and if no deviating agreement with the contractor exists and disposed of after.

2 This report substitutes report 000271-2099-4 dated 16.02.2017

2 Material (PP plaques)

Polymer

Polypropylene, homopolymer

Diffusion properties

Diffusion coefficients of migrants in polymer determined by fitting of experimental data.

2.1 Polymer

- PP, homo
- Density: 0.905
- Diffusion coefficients were determined by fitting of experimental data. Polymer specific constants were calculated based on Piringer's approach [3] therefrom:
  D_P = 1.57 E-10 (A'_P = 9.4 τ = 1577) (Metilox with ethanol 50% at 60°C)
  D_P = 1.76 E-11 (A'_P = 9.4 τ = 1577) (Irganox 1076 with ethanol 50% at 60°C)
  D_P = 3.50 E-10 (A'_P = 10.2 τ = 1577) (Metilox with ethanol 95% at 60°C)
  D_P = 8.73 E-11 (A'_P = 11.0 τ = 1577) (Irganox 1076 with ethanol 95% at 60°C)
- ***Samples:***
  - Plaques with 63 x 63 x 1 mm
- ***Simulant:***
  - Density: 0.825 g/cm² (ethanol 50% at 60°C)
  - Density: 0.750 g/cm² (ethanol 95% at 60°C)

2.2 Migrants

(i) Irganox 1076
3-Octadecyl 3-(3,5-di-tertbutyl-4-hydroxyphenyl) propionate (CAS: 2082-79-3)
M = 530.8 g/mol
$c_{P,0}$ = 1200 ppm (determined experimentally)

(ii) Metilox
Methyl 3-(3,5-di-tert-butyl-4 hydroxyphenyl)propionate (CAS n°: 6386-38-5)
M = 292.41 g/mol
$c_{P,0}$ = 875 ppm (determined experimentally)

2.3 Partitioning

(i) Irganox 1076
3-Octadecyl 3-(3,5-di-tertbutyl-4-hydroxyphenyl) propionate (CAS: 2082-79-3)
$K_{P,F}$ = 1000 for ethanol/water 50% (determined by fitting of experimental data)
$K_{P,F}$ = 1 for ethanol 95% (determined by fitting of experimental data)

(ii) Metilox
Methyl 3-(3,5-di-tert-butyl-4 hydroxyphenyl)propionate (CAS n°: 6386-38-5)
$K_{P,F}$ = 100 for ethanol/water 50% (determined by fitting of experimental data)
$K_{P,F}$ = 0.1 for ethanol 95% (determined by fitting of experimental data)

[3] T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickley, P. Mercea, M. Milana, A. O'Brien, S. Rebre, R. Rijk, O. Piringer; "Evaluation of migration models that might be used in support of regulations for food-contact plastics."; Food Additives and Contaminants, January 2005; 22(1): 73-90

2.4 Conditions of uses

Table 1 Repeated use scenario

Week	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday		
1		00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 24h00	00h00 - 24h00		08h00 at 60° C
	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00				16h00 at 25° C
	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00				
2	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 24h00	00h00 - 24h00		
	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00				
	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00				
3	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 24h00	00h00 - 24h00		
	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00				
	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00				
4	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 08h00	00h00 - 24h00	00h00 - 24h00		
	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00	08h00 - 16h00				
	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00	16h00 - 24h00				

3 Results

3.1 Initial concentration

The initial concentration of the two migrants was determined by repeated extraction with ethyl acetate and quantified by LC/MS.

Substance	concentration [mg/kg] plastic
Metilox	875
Irganox 1076	1200

3.2 Migration investigations

The migration tests were performed under repeated use conditions by full immersion of one (1) plaque into 70 ml simulant, i.e. total contact area = 82 cm² (both sides).

The quantification of Irganox 1076 and Metilox was performed directly from the migration solution without sample workup by LC/MS based on external calibration.

The migration results for Irganox 1076 into ethanol 50% indicate that a boundary resistance at the interface exists.

3.3 Migration modeling

The SML 5.232 software [4] was used for evaluation of the experimental data by migration modeling [5].

4 AKTS AG; www.akts.com

5 B. RODUIT, C.H. BORGEAT, S. CAVIN, C. FRAGNIERE, & V. DUDLER, " Application of Finite Element Analysis (FEA) for the simulation of release of additives from multilayer polymeric packaging structures.", Food Additives and Contaminants, October 2005; 22(10): 945–955

**Table 2 Migration of Irganox 1076 in ethanol 50%
(repeated use time/temperature scenario)**

Time	Migration 1	Migration 2	Migration 1	Migration 2	Migration	Modeling
days	µg/dm²	µg/dm²	mg/l	mg/l	mg/kg	mg/kg
0,0	0	0	0,000	0,000	0,000	0,000
0,3	17,1	17,0	0,197	0,196	0,238	0,672
1,3	11,9	11,8	0,136	0,136	0,165	0,438
2,3	10,8	11,0	0,124	0,127	0,152	0,345
3,3	9,3	10,1	0,108	0,117	0,136	0,293
4,3	11,1	9,6	0,128	0,111	0,145	0,259
7,3	9,2	8,5	0,106	0,098	0,124	0,222
8,3	8,7	9,2	0,101	0,106	0,125	0,212
9,3	9,9	10,9	0,114	0,125	0,145	0,199
10,3	11,6	12,4	0,134	0,143	0,168	0,187
11,3	12,0	12,3	0,138	0,142	0,170	0,178
14,3	11,3	11,1	0,130	0,128	0,156	0,161
15,3	10,2	11,2	0,117	0,129	0,149	0,159
16,3	11,1	10,4	0,128	0,120	0,150	0,154
17,3	11,6	10,5	0,133	0,121	0,154	0,149
18,3	10,6	9,5	0,122	0,109	0,140	0,144
21,3	10,9	9,0	0,126	0,104	0,139	0,133
22,3	10,3	9,9	0,119	0,114	0,141	0,133
23,3	9,7	8,5	0,112	0,098	0,127	0,130
24,3	9,2	10,2	0,106	0,117	0,135	0,127
25,3	9,1	9,4	0,105	0,108	0,129	0,124

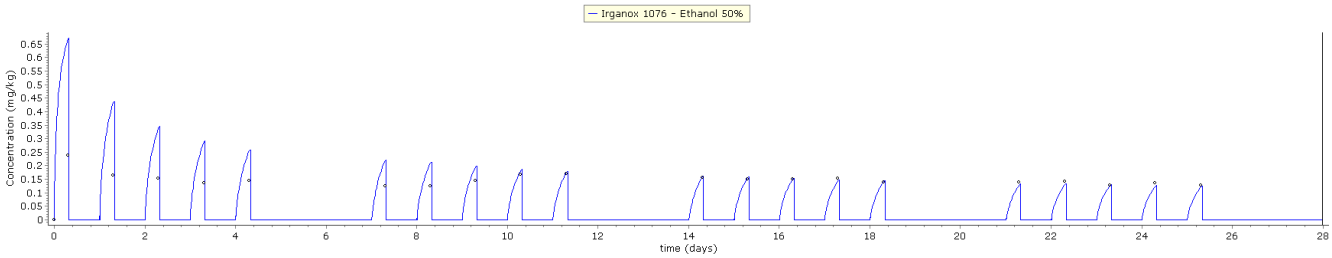

Figure 1 Migration of Irganox 1076 in ethanol 50% (K = 4500)

Table 3 Migration of Irganox 1076 in ethanol 95% (repeated use time/temperature scenario)

Time	Migration 1	Migration 2	Migration 1	Migration 2	Migration	Modeling
days	µg/dm²	µg/dm²	mg/l	mg/l	mg/kg	mg/kg
0,0	0	0	0,000	0,000	0,000	0,000
0,3	125	124	1,439	1,428	1,911	3,031
1,3	75,0	80,1	0,863	0,923	1,191	1,251
2,3	60,7	60,6	0,699	0,698	0,931	0,959
3,3	53,3	52,8	0,614	0,608	0,815	0,808
4,3	41,7	42,1	0,480	0,485	0,644	0,712
7,3	43,7	39,8	0,504	0,459	0,641	0,641
8,3	45,7	46,0	0,527	0,530	0,704	0,590
9,3	39,8	40,4	0,458	0,465	0,616	0,549
10,3	40,2	41,0	0,462	0,472	0,623	0,516
11,3	37,2	33,9	0,428	0,390	0,546	0,488
14,3	26,7	29,5	0,307	0,339	0,431	0,463
15,3	34,0	31,6	0,392	0,364	0,503	0,443
16,3	30,4	25,5	0,350	0,294	0,429	0,425
17,3	28,1	27,0	0,323	0,311	0,423	0,409
18,3	25,0	24,9	0,288	0,287	0,383	0,395
21,3	24,5	23,0	0,282	0,265	0,364	0,381
22,3	25,7	24,9	0,296	0,287	0,388	0,370
23,3	21,3	20,8	0,246	0,239	0,323	0,359
24,3	22,7	23,7	0,262	0,273	0,356	0,349
25,3	25,3	26,2	0,291	0,302	0,395	0,340

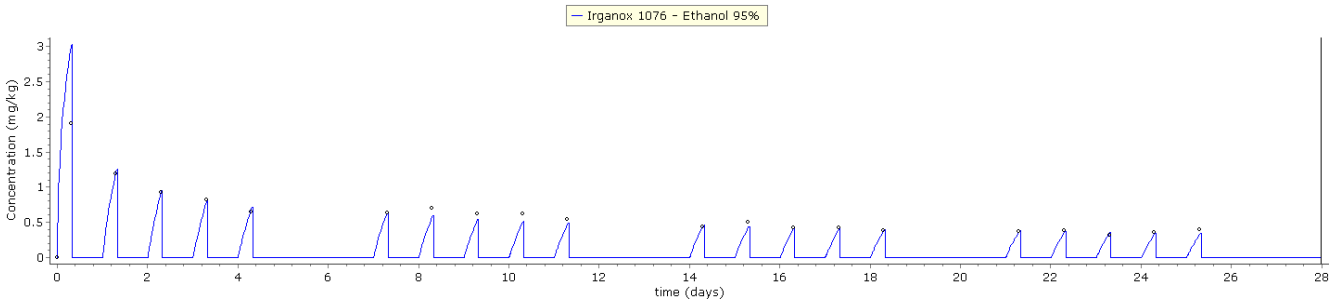

Figure 2 Migration of Irganox 1076 in ethanol 95% (K = 1)

**Table 4 Migration of Metilox in ethanol 50%
(repeated use time/temperature scenario)**

Time	Migration 1	Migration 2	Migration 1	Migration 2	Migration	Modeling
days	µg/dm²	µg/dm²	mg/l	mg/l	mg/kg	mg/kg
0,0	0	0	0,000	0,000	0,000	0,000
0,3	114	102	1,312	1,171	1,505	2,170
1,3	82,7	67,7	0,952	0,780	1,050	1,120
2,3	53,8	45,9	0,620	0,528	0,696	0,840
3,3	53,5	51,0	0,616	0,588	0,730	0,703
4,3	55,0	49,6	0,634	0,571	0,730	0,617
7,3	35,7	31,2	0,411	0,359	0,467	0,542
8,3	38,7	40,9	0,446	0,471	0,556	0,508
9,3	36,8	39,3	0,424	0,453	0,531	0,474
10,3	29,9	29,4	0,345	0,338	0,414	0,445
11,3	31,9	33,2	0,367	0,383	0,454	0,421
14,3	22,5	25,7	0,259	0,296	0,336	0,391
15,3	27,1	29,4	0,312	0,338	0,394	0,381
16,3	25,4	24,3	0,293	0,280	0,347	0,366
17,3	18,8	19,2	0,216	0,221	0,265	0,352
18,3	22,8	23,0	0,262	0,264	0,319	0,340
21,3	22,7	26,2	0,262	0,301	0,341	0,322
22,3	21,2	22,0	0,244	0,253	0,301	0,317
23,3	23,4	23,9	0,269	0,276	0,330	0,309
24,3	21,2	21,5	0,244	0,248	0,298	0,301
25,3	22,7	24,3	0,261	0,280	0,328	0,293

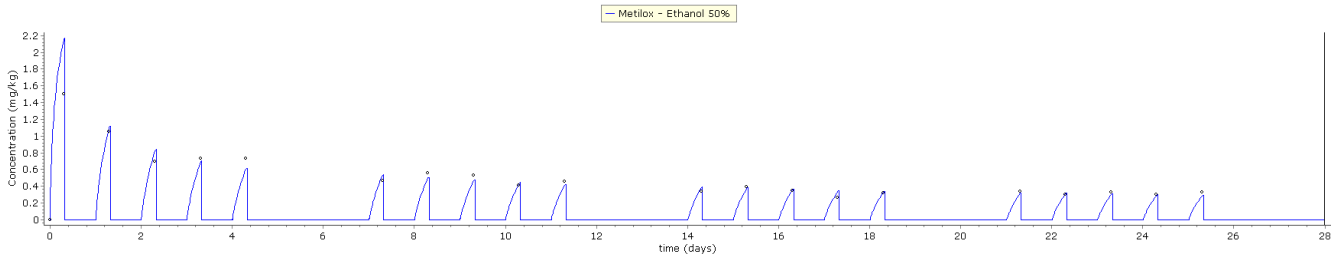

Figure 3 Migration of Metilox in ethanol 50% (K = 100)

**Table 5 Migration of Metilox in ethanol 95%
(repeated use time/temperature scenario)**

Time	Migration 1	Migration 2	Migration 1	Migration 2	Migration	Modeling
days	µg/dm²	µg/dm²	mg/l	mg/l	mg/kg	mg/kg
0,0	0	0	0,000	0,000	0,000	0,000
0,3	189	208	2,178	2,393	3,047	4,430
1,3	121	122	1,388	1,403	1,861	1,826
2,3	83,0	93,9	0,956	1,081	1,358	1,400
3,3	79,7	76,5	0,918	0,881	1,199	1,180
4,3	65,5	66,3	0,755	0,763	1,012	1,039
7,3	59,5	60,0	0,686	0,691	0,918	0,936
8,3	61,8	59,3	0,712	0,683	0,930	0,861
9,3	52,8	51,2	0,608	0,589	0,798	0,802
10,3	49,7	49,3	0,572	0,568	0,760	0,753
11,3	45,7	46,9	0,526	0,540	0,711	0,713
14,3	42,3	40,5	0,487	0,466	0,635	0,676
15,3	40,3	43,9	0,464	0,505	0,646	0,647
16,3	36,4	35,2	0,419	0,405	0,549	0,620
17,3	35,2	35,5	0,406	0,409	0,543	0,597
18,3	36,9	40,7	0,425	0,469	0,596	0,576
21,3	32,5	36,0	0,374	0,415	0,526	0,557
22,3	34,7	34,0	0,400	0,391	0,527	0,540
23,3	34,4	39,0	0,396	0,449	0,564	0,524
24,3	34,6	35,5	0,398	0,409	0,538	0,510
25,3	34,3	32,8	0,395	0,377	0,515	0,497

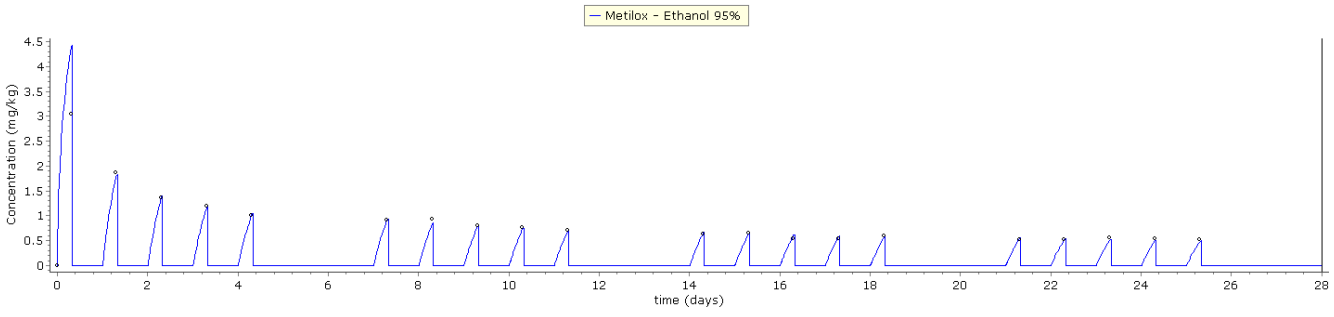

Figure 4 Migration of Metilox in ethanol 95% (K = 0.1)

4 Conclusions

Diffusion and partition coefficients were determined by fitting of experimental data. Polymer specific constants were calculated based on Piringer's approach from these diffusion coefficients.

Good agreement between experimental data and modeling results is observed.

The calculations and their evaluation are limited to the information made available by the contractor and are elaborated to the best of our knowledge and belief according to the state-of-art in science and technology.

MDCTec Services GmbH

Dr. Rainer Brandsch