



Memorandum

Date: September 27, 2006  
From: Division of Food Contact Notifications  
Chemistry Group I, HFS-275  
Subject: FCN 646: DuPont Chemical Solutions Enterprise, through Keller and Heckman, submissions of 5/31/06 and 7/19/06. Perfluorinated grease-proofing agent similar to (b) (4) for use on paper/paperboard.  
To: Division of Food Contact Notifications  
Regulatory Group II, HFS-275  
Attn: P. Honigfort, Ph.D.



DuPont Chemical Solutions Enterprise, through Keller and Heckman (K&H), has submitted a food contact notification (FCN) for use of copolymers of 2-perfluoroalkylethyl acrylate (ZFAN), 2-N,N-diethylaminoethyl methacrylate (DEAM), glycidyl methacrylate (GMA), acrylic acid (AA), and methacrylic acid (MAA) to impart oil and grease resistance to paper/paperboard, at a maximum use level of 0.37 wt-% fluorine (0.69 wt-% of the food-contact substance (FCS)) based on the weight of the paper, intended to contact all food types under conditions of use B through H. The FCS comprises 18-20 wt-% of the commercially marketed formulation (trade name (b) (4)), which is an aqueous dispersion.

The FCS is virtually identical to that which was the subject of FCNs 206, 311, and 338 and PNCs 446 and 467 (b) (4) all submitted by DuPont.<sup>1,2,3,4,5</sup> FCN 206 permitted use of (b) (4) at levels up to 0.33 wt-%, based on the weight of paper, in contact with all food types under conditions of use B through H. FCN 338 expanded the use level to up to 0.37 wt-% based on the weight of paper. FCN 311 permitted use of (b) (4) at levels up to 0.33 wt-%, based on the weight of paper, in contact with all food types in microwave susceptor packaging. (b) (4)

(b) (4)

The only differences for the subject FCS in comparison to (b) (4) are:

- 1) small amounts of AA and MAA are charged to the reactor as monomers that become part of the polymer backbone,<sup>6</sup>

<sup>1</sup> FCN 206, memorandum dated 6/10/02, K. Arvidson to J. Smith.

<sup>2</sup> FCN 311, memorandum dated 2/20/03, K. Smeds to K. Williams.

<sup>3</sup> FCN 338, memorandum to the administrative file dated 5/30/03, K. Randolph.

<sup>4</sup> PNC 446, memorandum dated 4/4/06, K. Paquette to P. Honigfort.

<sup>5</sup> PNC 467, memorandum dated 4/21/06, K. Smeds to K. McAdams.

<sup>6</sup> These two monomers were also present in the polymer backbone of Zonyl 9464 (at up to 1.6 wt-% AA units and 1.8 wt-% MAA units) due to hydrolysis of the ZFAN and DEAM side

(b) (4)

## IDENTITY, MANUFACTURE, AND COMPOSITION

## A. Identity

Chemical Name and CAS Registry No.

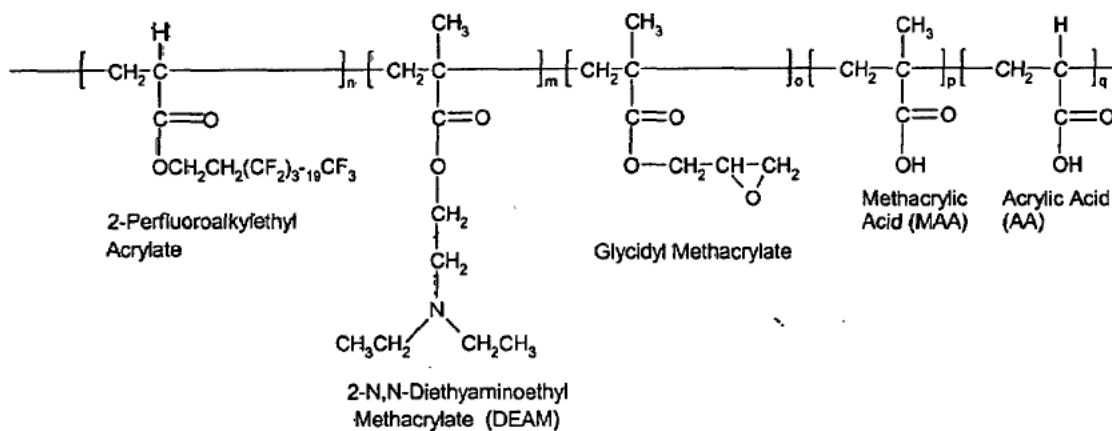
870465-08-0 2-propenoic acid, 2-methyl-, polymer with 2-(diethylamino)ethyl 2-methyl-2-propenoate, *alpha*-fluoro-*omega*-[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), oxiranylmethyl 2-methyl-2-propenoate and 2-propenoic acid

Common Names

copolymers of 2-perfluoroalkylethyl acrylate, 2-N,N-diethyl-aminoethyl methacrylate, glycidyl methacrylate, acrylic acid, and methacrylic acid

(b) (4)

(trade name for the aqueous dispersion of the FCS)

Structure

chains during high-temperature distillation of the polymer (see p. 4 of Attachment 2 to the FCN and Appendix IV to FCN 206).

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The ratios of monomer units are as follows:

ZFAN  
DEAM  
GMA  
AA  
MAA

(b) (4)



Molecular weight (b) (4)



Physical Properties/Specifications (see Part II.C.2.a of Form 3480 and Attachment 5 to the FCN, and Appendix IV to FCN 206 for the analytical methods)

(b) (4)



Data to Characterize the FCS

See Attachment 1 to the FCN for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The FCS was isolated, washed, and vacuum-dried for analysis.

The FCS is adequately identified.

**B. Manufacture**

(b) (4)



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(b) (4)



### C. Composition

The notifier provided extensive impurity profiles and specifications for the subject FCS and (b) (4) for comparison (see Attachments 3 and 5 to the FCN). The impurities were determined by gas chromatography with atomic emission detection (GC/AED) and GC with mass spectrometric detection (GC/MS) (see Attachment 3). In the vast majority of cases, the impurity levels were lower in the subject FCS, and the specifications were identical or improved for the subject FCS. The only increase was in the specification for residual DEAE from 0.4 wt-% to 0.8 wt-%; however, this increase was dealt with in our new exposure estimate for DEAE from (b) (4) in PNC 467.<sup>5</sup> The exposure estimate given in the subject FCN is based on the new, higher numbers from PNC 467. We can therefore accept the migration data and residual measurements from FCNs 206 and 338 and PNCs 446 and 467 for the subject FCN. The impurities and their relevant data are given in Table 1 below.

Because AA and MAA are added during the manufacture of (b) (4), the notifier provided new data on the residual levels of these substances in the FCS (see Attachment 6 to the FCN). AA and MAA were determined in the dried FCS by GC with a flame ionization detector (FID). The notifier provided adequate raw data to support these measurements. The concentrations of both substances were below the limit of quantification (LOQ) of the analytical method: < 40 mg/kg AA and < 20 mg/kg MAA.

(b) (4)



### D. Stability

In FCN 206, (b) (4) was shown to be stable under conditions of use B through H, based on differential scanning calorimetry and thermogravimetric analysis.<sup>1</sup> As the subject FCS

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differs only slightly in AA and MAA unit content, we expect the results to be the same for (b) (4)

#### INTENDED USE AND USE LEVEL

The FCS is intended to impart oil and grease resistance to paper/paperboard intended to contact all food types under conditions of use B through H. The FCS may be added at the wet end or the size press during papermaking. The FCS will have the same use level as (b) (4) in FCN 338: 0.37 wt-% fluorine or 0.69 wt-% of the FCS based on the weight of the paper. The FCS will be substitutional for (b) (4) and all the other authorized perfluorinated grease-proofing agents.

#### TECHNICAL EFFECT

The technical effect of the FCS in imparting oil and grease resistance to paper/paperboard was adequately demonstrated for (b) (4) in FCN 206.<sup>1</sup>

#### EXPOSURE ESTIMATES

##### A. Impurities with Previous Migration Data or Residual Measurements

As was discussed above, the uses and use levels of the FCS are the same as those for (b) (4) in FCN 338, and we have accepted migration data and residual measurements from FCN 338 (and related FCNs and PNCs) as applicable to (b) (4). Therefore, the exposures to impurities that were based on migration data or residual measurements (except as revised below) are the same as those we calculated for (b) (4) in FCN 338 and PNCs 446 and 467 (see Part II.F and II.G of Form 3480).<sup>3,4,5</sup> The results are given in Table 1.

We note that K&H used a dietary fraction (DF) value of 0.03 that they derived from Total Diet Study (TDS) data for specific foods that are packaged in grease-proofed paper rather than our recommended consumption factor (CF) of 0.05 in order to calculate exposure. We reviewed this DF in PNC 446 and determined that it was not appropriate unless the uses of the grease-proofing agent were restricted to the specific foods referenced from the TDS.<sup>4</sup> Our results therefore differ from K&H's because we continue to use our CF of 0.05 for grease-proofed paper.

##### B. MAA and AA

New residual measurements were provided for these impurities in the subject FCS (see above): < 20 mg/kg MAA and < 40 mg/kg AA. The following is an example 100% migration calculation for MAA, using the 0.69 wt-% use level of the FCS in paper, the average paper basis weight of 50 mg/in<sup>2</sup>, and our usual assumption that 10 g of food contact 1 in<sup>2</sup> of packaging:

$$\frac{20 \mu\text{g MAA}}{\text{g FCS}} \left| \frac{0.69 \text{ g FCS}}{100 \text{ g paper}} \right| \frac{0.05 \text{ g paper}}{\text{in}^2} \left| \frac{\text{in}^2}{10 \text{ g food}} \right| = 0.69 \mu\text{g/kg MAA in food}$$

The dietary concentration (DC) is calculated by multiplying the concentration in food by our consumption factor (CF) for grease-proofed paper of 0.05:

$$\text{DC} = (0.05)(0.69 \mu\text{g/kg MAA in food}) = 0.034 \text{ ppb MAA}$$

The estimated daily intake (EDI) is calculated by multiplying the DC by our assumption that individuals consume 3 kg of food per day:

$$\text{EDI} = (0.034 \times 10^{-9} \text{ g MAA/g food})(3000 \text{ g food/p/d}) = 0.10 \mu\text{g/p/d MAA}$$

The results for both impurities are given in Table 1.

C. (b) (4)

(b) (4)

#### D. Oligomers

The notifier used migration data from FCN 206, with appropriate correction factors for the use level of the FCS in the paper samples, in order to calculate the concentration of oligomers migrating to aqueous/acidic foods (see Part II.G of Form 3480). For fatty foods, the notifier used a new approach that involved using GC/AED and GC/MS to identify and quantify all the



volatile and semi-volatile fragments that were extracted from the FCS into 50% ethanol (the 50% ethanol was then extracted into 95% ethanol for analysis), assumed that these were the oligomers of MW < 1000, and added all their masses to obtain the low-molecular-weight oligomer (LMWO) concentration in the polymer sample (see Attachment 4 to the FCN). The OFAS Laboratory reviewed these data and could not accept them for the following reasons:<sup>7</sup>

- 1) The particle size of the dry polymer used in the experiment was not specified, which makes it difficult to determine how far the 50% ethanol would penetrate the polymer. The 30-min sonication time was not very aggressive for a polymer.
- 2) No spike and recovery with a surrogate chemical of molecular weight close to 1000 was used to validate any extraction procedure.
- 3) The chromatogram on p. 24 of Attachment 4 does not agree with the raw data reported in Table 1 on pp. 21-22. The tallest peak in the chromatogram does not appear to be integrated. The peak at 12.0 min was not integrated. It appears that all the largest peaks were missed.

We therefore used the exposure value for LMWO that we calculated in FCN 338 as the exposure to LMWO from the subject FCS (see Table 1). Although the same GC/AED, GC/MS technique was used to determine the LMWO in FCN 338 (Attachment 7), many of the problems pointed out by the OFAS Laboratory for the chromatogram in FCN 646 were not present. For example, all the peaks on the chromatogram were accounted for (the large peaks were for impurities already quantified, e.g., DEAM). In addition, the exposure calculated in FCN 338 is over twice that calculated from the LMWO data given in the subject FCN. As the exposure is based on 100% migration, we believe that the value from FCN 338 is sufficiently conservative to account for any discrepancies in the data.

#### **E. Cumulative Exposures**

Because none of the exposures in Table 1 exceeds those calculated for (b) (4) in FCN 338 or PNC 446 or 467 for the same uses and use levels, there will be no increase in the cumulative exposure to the LMWO or impurities. The only new exposure estimates presented in this memorandum are for residual MAA and AA (these substances were not determined in Zonyl 9464).

#### **NOTIFICATION LETTERS**

The language in the acknowledgment letter dated 7/26/06 is acceptable as written.

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<sup>7</sup> E-mail dated 6/27/06, T. Begley to K. Paquette.

Table 1. Exposures to the FCS and Its Impurities


Substance	CAS Reg. No.	Function	Exposure Estimation Method	DC (ppb)	EDI (µg/p/d)
<b>FCS oligomers of MW &lt;1000</b>	--	--	GC/AED, GC/MS of 50% EtOH extract, 100% migration, FCN 338	7.9	<b>24</b>
Diethylaminoethanol (DEAE)	100-37-8	Hydrolysis product	Migration study, PNC 467	44	130
Glycidyl methacrylate (GMA)	106-91-2	Monomer	Residual msmt., 100% migration, FCN 338	0.009	0.027
Methacrylic acid (MAA)	79-41-4	Monomer	Residual msmt., 100% migration, FCN 646	< 0.034 <sup>a</sup>	< 0.10 <sup>a</sup>
Acrylic acid (AA)	79-10-7	Monomer	Residual msmt., 100% migration, FCN 646	< 0.069 <sup>a</sup>	< 0.21 <sup>a</sup>
<b>2-Perfluoroalkylethyl acrylate (ZFAN)</b>	65605-70-1	Monomer	Migration study, FCN 338	2.9	<b>8.7</b>
<b>Telomer BA (perfluoroalkyl ethanol)</b>	--	Hydrolysis product	"	3.8	<b>11</b>
2-N,N-Diethylaminoethyl methacrylate (DEAM)	105-16-8	Monomer	"	0.14	0.42

(b) (4)

Below the LOQ of the analytical method.

### CONCLUSIONS

The exposures to the FCS and its impurities are summarized in Table 1 above. There are no increases in the cumulative exposures to the LMWO or impurities. We have no questions.

  
Kristina E. Paquette, Ph.D.

HFS-245 (Begley); Chemistry Reading File  
HFS-275:KEPaquette:436-1232:FCN646.doc:kep:9/26/06  
Init: ABBailey 9/27/06  
Final:kep:9/27/06

