DEPARTMENT OF HEALTH & HUMAN SERVICES — Public Health Service

Memorandum

Date: Feb. 10, 1983

From: Food Additive & Animal Drug Chemistry Evaluation Branch, HFF-458

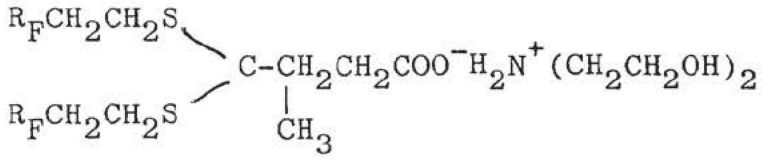
Subject: FAP 3B3700 - Ciba Geigy Corp. (CG). Pentanoic acid, 4,4-bis [(γ-ω-perfluoro-C_{8-20}-alkyl)thio] derivs., compounds with diethanolamine salt as an oil and water repellent for paper and paperboard. Submission dated 12-29-82.

To: Petitions Control Branch, HFF-334
Attn: J. Herrman, Ph.D.

The petitioner is proposing an amendment to 176.170 to provide for the use of its product at levels not exceeding 0.4% by weight. Paper containing the additive could be used in contact with non-alcoholic foods under conditions of use C through H, 176.170(c), Table 2.

Identity

CG's product is known commercially as (b) (4) and has the CAS Registry No. 71608-61-2. The structure can be represented in the following way:



The perfluoroalkyl groups, R_F, have the general formula C_nF_{2n+1}. Table I lists the components and relative proportions of the perfluoroalkyl groups.

Table I

C_6F_{13}	(b) (4)
C_8F_{17}	
$C_{10}F_{21}$	
$C_{12}F_{25}$	
$C_{14}F_{29}$	
$C_{16}F_{33}$	
$C_{18}F_{37}$	
$C_{20}F_{41}$	

(b) (4) is prepared commercially by reaction of (b) (4) [redacted]

Use & Intended Technical Effect

The formulation is used as a water and oil repellent sizing agent for paper and paperboard. It can be added at the wet-end in the manufacture of paper, but this is not explicit in the regulation. Examples of paper articles that might be treated include disposable tableware, serving trays, and packaging for refrigerated foods which may be reheated in the container at the time of use.

Data show that complete oil penetration into a sheet to which 1 mL corn oil at 230°F has been applied is delayed to a time greater than 20 minutes when 0.14% active ingredients are present. Similar data are shown with water.

Migration & Methodology

The extraction study was conducted on actual paper plates using 0.38% active ingredient. The inital concentration of (b) (4) in the paper was determined using a fluoride ion selective electrode method, described in Appendix 2. Initial concentration of additive, as (b) (4), was found to be identical (0.38%) to the added concentration.

Paper plates were cut into 4x5 inch rectangles and placed in 200 mL of the appropriate food simulating solvent. The sheet basis weight of the paper was 251.2 pounds per 3000 ft^2, the consistency of paperboard, so the area of both sides of the paper could be used in calculations.

Quadruplicate extractions were carried out under the conditions of Table I.

Table I

Water	212°F/2 hrs.
3% Acetic Acid	212°F/2 hrs.
Heptane	120°F/2 hrs.

Extract solutions were directly analyzed by aluminum monofluoride molecular absorption spectrometry (Appendices 8, 9). With this METHOD a known volume of sample solution is mixed with an aqueous $Al(NO_3)_3$ solution, AlF is formed in a carbon rod furnace and the AlF molecular absorption band at 227.45 nm is measured in an atomic absorption spectrometer.

A calibration curve constructed using both sodium fluoride standards and (b)(4) [redacted] is shown on page 000042. Although no calculation relates absorbance to a concentration in ppm (food), if we assume the reported extractant volume/surface area ratio of 5 mL/in^2 and further assume, as stated in the petition, that no concentration step occurred, the lowest point on the calibration curve is about 0.06 ppm - calculated as fluorine.

Reported migration levels (vide infra) are, with the exception of heptane, lower than this level.

The method was validated in accordance with our Validation Guidelines. Water extracts were spiked at 0.05 ppm, 0.10 ppm and 0.20 ppm. Acetic acid extracts were spiked at 1/2 these levels. Heptane extracts were spiked at 0.75 ppm, 1.50 ppm and 3.0 ppm. It is not clear that these levels refer to a concentration in food; the ? context suggests that they refer to concentrations in solution. Percent recoveries ranged from 82% to 120%. The high percentages occurred at the lowest spiking levels. In addition concentrations in the extracts were determined by standard additions (using the absorbance data from the three spiking levels). However, the absorbance at the zero spiking level was not used in the plots, and the aqueous and acidic plots appear to be non-linear. Absorbance values of extracts are reported on page 000048. "Zero" absorbance was measured for the aqueous and acidic extracts. We would like to know what minimum concentration produces a signal noticeable above the background. This is not at all clear from the discussion in the petition. No absorbance data are reported to support the claimed detection limit. In addition the petitioner should be asked to explain the relationship of the absorbance data for the heptane extract as reported on Table 2 (page 000048) to the standard additions curve; GRAPH 4. The absorbance data on the standard additions plot are much lower than ? the absorbance data reported in Table 2. The additive level of 1.7 ppm, calculated as fluorine, derived from the standard additions curve is slightly higher than the levels reported in Table 2 -- 1.4±.2 ppm.

CG's extraction results are reported in Table 3 and listed in our Table II.

Table II

Water	<0.10 ppm (in food)
3% Acetic Acid	<0.10 ppm
Heptane	1.19±.17 ppm

We note that CG is requesting use at temperatures above room temperature. The heptane extraction was only carried out at 120°F. It is our opinion that the data would support use at higher temperatures if the results are not divided by five. Otherwise use with fatty foods should be restricted to room temperature.

If we assume (pending adequate response to our questions above) that CG's results are acceptable, the concentration in the daily diet is calculated to be:

$$C_F\langle M\rangle = 0.1[0.56 \times 0.1 \text{ ppm} + 0.01 \times 0.1 \text{ ppm} + 0.41 \times 1.19 \text{ ppm}]$$

$$= 0.054 \text{ ppm}$$

The estimated daily intake would be:

$$3000 \text{ g/day} \times 0.054 \times 10^{-6} = 0.16 \text{ mg/day}$$

Conclusion

Before the additive is regulated, CG should submit the following information:

1. Absorbance data should be submitted to support the claimed detection limit. We wish to assure ourselves that 0.1 ppm additive (as fluorine) produces a discernible signal.

2. The absorbance data displayed on the standard additions curve for the heptane extracts (Graph 4) should be related to the corresponding data reported in Table 2. CG should attempt to explain why the standard additions heptane migration level of 1.7 ppm is slightly but significantly higher than the results reported in Table 2, (1.1-1.5 ppm).

Michael T. Flood

Michael T. Flood, Ph.D.

HFF-400; 450; 156
HFF-458 RF/Flood
MTFlood:lsl 2-4-83
RD Init:PSullivan Schwartz:JWHoward