DEPARTMENT OF HEALTH & HUMAN SERVICES — Public Health Service

Memorandum

Date June 28, 1985

From Food Additive Chemistry Evaluation Branch, HFF-458

Subject FAP 5B3870 - Minnesota Mining and Manufacturing Co. (3M). Perfluoroalkyl Acrylate Copolymer as an Oil and Water Repellent for Paper. Submission dated 5/17/85.

To Petitions Control Branch, HFF-334
Attention: B. Anderson

The petition is proposing an amendment to 176.170 (not explicitly stated) to provide for the use of the polymer of:

1. Ethanaminium, N,N,N trimethyl 2-[(2-methyl-1-oxo-2-propenyl)-oxy]-, Chloride. CAS No. 5039-78-1

2. 2-Propenoic acid, 2-methyl-, oxiranylmethyl ester, CAS No. 106-91-2 (Glycidyl Methacrylate, GMA)

3. 2-Propenoic acid, 2- ethoxyethyl ester. CAS No. 106-74-1 (Ethoxy Ethyl Acrylate, EEA)

4. 2-Propenoic acid, 2 [[(heptadecafluoroctyl) sulfonyl] methylamino] ethyl ester. CAS No. 25268-77-3. (MeFOSEA)

Maximum level of use in paper would be 0.5 weight percent. Conditions of use could range from C through H, Table 2, 176.170 (c). The polymer would not be used with alcoholic foods.

Preliminary work on this polymer was previously submitted to FDA. DCH's 7/18/83 memo to A. Laumbach, HFF-334, as well as the Memorandum of Conference 9/20/83 should be consulted. These should be placed in the petition jacket.

Identity

Structures of the various monomers were listed in our 7/18/83 memo. Adjuvants which would be used in the polymerization reaction [illegible]

A typical polymer is prepared using the following recipe:

[redacted]

Minor components expected to be present are given in Table I.

Table I.

	Compound	CAS Reg. No.
1.	[redacted]	
2.		
3.		
4.		
5.		
6.		
7.		
8.		

[redacted]

3M should have the CAS Registry No. assigned to the complete polymer. This can be done by writing to Chemical Abstracts Service. The infrared spectrum of the polymer should be submitted as well as an estimate of molecular weight. Petitioner should also submit a draft of the proposed regulation.

Specifications of the polymer and starting materials are given in Appendix A. The specification for maximum residual MeFOSEA is 0.5%.

Use and Intended Technical Effect

3M's polymer, known commercially as (b)(4) is said to provide oil, grease and water resistance when used as a coating on paper products. It is intended to replace 3M's current product, (b)(4) regulated in 176.170 under the name ammonium bis(N-ethyl-2-perfluoroalkylsulfonamido ethyl) phosphates. This compound does not produce water repellency

unless auxiliary chemicals are present. Although methods for determining oil and water resistance are present in the petition, no technical effect data are present and should be submitted. The proposed polymer will be sold as a 40% aqueous latex. It can be added at the wet end of the paper making process, at the size press, or at the calender stack.

Migration

Paper was extracted according to the following protocol suggested on the basis of the 9/20/83 meeting:

Heptane:	150°F/2 hrs; 120°F for 22 hrs.
Water:	210°F/2 hrs; 120°F for 22 hrs.
3% Acetic Acid:	210°F/2 hrs; 120°F for 22 hrs.

The basis weight of paper extracted was 55 pounds per 3000 ft^2, the petitioner claims that paper treated with 0.5% solids on fiber was not completely penetrated by water, 3% acetic acid or corn oil. This was demonstrated by using soluble dyes, but no data are reported. If penetration is not complete, both sides of the paper could be used in the calculations. Generally we would assume complete penetration when paper with that basis weight is extracted. However the intended technical effect of the polymer is to retard absorption of liquids, so incomplete absorption is quite possible. DCH will accept 3M's argument pending receipt of technical effect information. Available data concerning dye absorption should be submitted.

The actual extractions were carried out on paper having 23% polymer, a 46-fold exaggeration. The petitioner has calculated that results from paper treated in this manner can be made equivalent to corresponding results from 300 pound (per ream) paperboard treated at the 0.5% level by dividing the former by 8.3; (page 000020).

Most components could be determined by either gas chromatography or HPLC. For those components that could be determined by GC, extracts were injected directly into the chromatograph. For [redacted] the solvent was evaporated and replaced with an equal weight of solvent suitable for HPLC.

Results are shown in Table I. Heptane values have been divided by five. Considering the type of uses envisioned (pizza cartons, paper plates) this assumption is warranted. All migration values have been scaled to 300 pound weight paper having 0.5% polymer in the manner described above.

Table II

Compound	Heptane	Water	3% Acetic Acid
MeFOSEA	0.036 ppm	0.007 ppm	0.007 ppm
MeFOSE Alcohol	0.163	0.029	0.026
MeFOSE Amide	0.001	0.007	0.007
MeCarboxamide	0.001	0.007	0.007
EEA	0.001	0.007	0.007
GMA	0.001	0.007	0.007
	0.002	0.072	0.070

(Examination of these results shows that most of the values are quantitation limits.)

In addition the oligomeric compound "MeFOSE/MeFOSEA Adduct", as well as total fluoride were determined. Concentrations are shown in Table III.

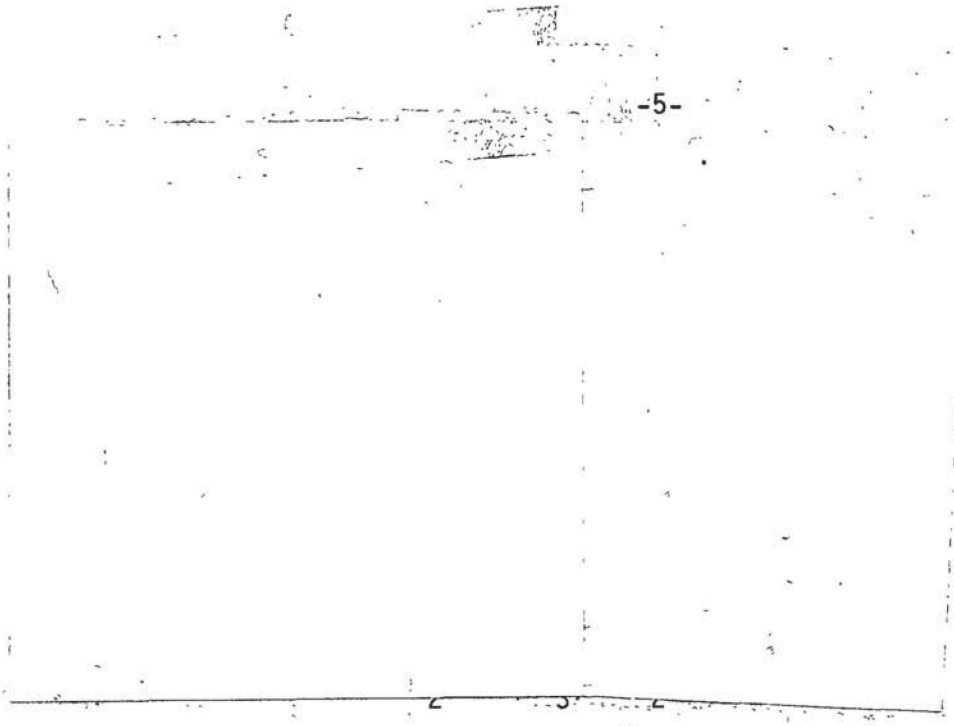
Table III

	Exaggerated Extraction (ppm)			Levels in Food (ppm)		
	Heptane	Water	3% Acetic Acid	Heptane/5	Water	3% Acetic Acid
MeFOSE/MeFOSEA Adduct	66.6	<1.0	<1.0	0.128	0.014	0.014
Total F^-	154.7	0.75	0.93			

Structures for MeFOSE/MeFOSEA Adduct as well as the eight minor components are given in Table IV.

Table IV

MeFOSE/MeFOSEA Adduct	$C_8F_{17}SO_2N(CH_3)C_2H_4O_2CCH_2CH_2O(-)$ $C_2H_4N(CH_3)O_2SC_8F_{17}$
MeFOSE Alcohol	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$
MeFOS Amide	$C_8F_{17}SO_2N(CH_3)H$
MeCarboxamide	$C_7F_{15}CON(CH_3)H$



The adduct is the condensation product of MeFOSEA and MeFOSE alcohol, from which FOSEA is prepared. The structure is reportedly consistent with NMR and IR. The adduct can be prepared as a pure standard.

Analyses

Total fluoride was determined by absorption of molecular aluminum fluoride, formed by passing organic fluorine over aluminum nitrate in a furnace. The method has been validated in previous submissions to FDA.

MeFOSEA/MeFOSE was determined by GC using electron capture detector (ECD). Measureable adduct was determined in the aqueous extracts, but the predominant peaks were in heptane. Spiking/recovery data were acceptable. Chromatographic peaks are well resolved.

MeFOSEA was determined in the same way. As with the adduct, measurable levels were observed in the aqueous extracts but heptane levels predominated. Percent recoveries were acceptable for the heptane extracts, but were high for the aqueous extracts. The reason for the high recoveries is that levels in the unspiked extracts ("<0.5") were apparently counted as 0, where in reality they were a fraction of 0.5 ppm. We note that MeFOSE alcohol recoveries were generally lower, ie, closer to 100%. In this case aqueous levels were higher and were subtracted from the spiked levels. MeFOSE alcohol was determined in the same manner as the first two species.

MeFOSEA/MeFOSE adduct, MeFOSEA, and MeFOSE are volatile components which yielded a total of 96 ug/g Fluoride (calculated directly in the extract, not converted to ppm in food). The petitioner has characterized the non-volatile residue from evaporation of the heptane extract by NMR peak area measurements and has calculated that the residue contains 50 ug fluoride arising from nonvolatile oligomers. The total of volatile and nonvolatile fluoride of 146 ug/g is close to the analytical result of 155 ug/g.

If we assume that 155 - 96 or 59 ug/g is the contribution due to fluorine-containing oligomers, we calculate that the migration level in fatty food should be 0.12 ppm. Since fatty food migration predominates, we calculate a concentration in the diet of 5 ppb for F^- oligomers. Since fluorine constitues about 37% of the polymer, 5 ppb fluoride would correspond to about 14 ppb oligomer.

As shown in Table II, Ethoquad 18/25 is extracted to a greater extent than the other components of the polymer. The compound is a quaternary ammonium salt, so the highest levels are expected in aqueous solvents. (The structure was given in our 7/18/83 memo.) As indicated above, analysis was by an HPLC method. Percent recoveries are acceptable, but the chromatogram peak in the water extract lies on a shoulder. The method would not be acceptable for a regulatory analysis but is adequate for review purposes.

[illegible] nt. The petitioner has not reported analyses on the compound itself but has analyzed paper directly for this compound by placing a sample of treated paper directly in the GPC cavity, allowing 3 minutes for equilibration, then moving the cavity contents into the capillary with carrier gas. No [illegible] of 17 nanograms/in^2, which would correspond to a level lower than 1 ppb in the diet. In the same experiment it was found that no 2-ethoxyethanol was present at 34 ng/in^2. The latter compound is a known impurity in EEA. The analytical method, and chromatograms of both spiked and unspiked paper are reported on pages 000250-000262 of the petition. No calculation is present which relates spiking levels to concentrations in paper, but in view of the low levels involved, DCH does not intend to pursue the matter further.

The remaining compounds listed in Table II occur at very low levels. Our comments concerning their analyses are given in the following table:

Table VI

MeFOSE Amide	Low levels detected in each solvent
MeCarboxamide	Low levels detected in water and heptane
EEA	Very low levels in each solvent GC signals possibly noise.
GMA	Small amounts GMA found in 3% acetic acid extract. Could be noise or an impurity.

Table VI (con't)

Interference in the blanks at HPLC retention time for the compound. Assigned quantitation limit of 5.0 ppm (0.070 ppm in food) is acceptable. No observable compound peak in chromatograms of the extracts.

Concentration in the Daily Diet

Although strictly speaking the consumption factor for coated paper (0.21) should be applied to the migration values, the anticipated use should only be a small subset of coating applications. The projected usage is expected to increase to about 250 tons annually. Current annual use of styrene- butadiene latex amounts to 94,000 tons, for example. For this reason 3M is justified in using the consumption factor of 0.1 in its calculations. The daily diet for those components which were definitely found to be present are given in Table VII.

Table VII

Compound	Concentration in Daily Diet	EDI
MeFOSEA	1.9 ppb	5.7 ug/day
MeFOSE Alcohol	8.3	25
MeFOSE Amide	8.4	1.2
MeCarboxamide	0.4	1.7
MeFOSE/MeFOSEA Adduct	6.0	18
Oligomers (as F)	5	15

Conclusion

The petition is not acceptable for filing. The following information should be submitted:

1. The CAS Name and Registry Number of the polymer. If not known, this information can be obtained from Dr. Kurt Loening, Director of Nomenclature, Chemical Abstracts Service, Ohio State University, Columbus, Ohio 43210

2. The average molecular weight of the polymer.

3. An infrared spectrum of the polymer.

4. Data which show that the polymer produces the intended technical effect.

5. A draft of the proposed regulation.

6. A brief discussion of the chemistry of the [illegible] and its breakdown products.

7. Available data which show penetration of dye solutions into treated paper. This is the justification for using both sides of paper in the calculations.

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