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TNO-report

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Migration and extraction of emulsifiers from PTFE coated
frying pans

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BACKGROUND

We want C-8 to be on the positive list of substances that are allowed by the EC as additives to PTFE. Therefore, a toxicology file must be made. The extent of tox. testing depends on the result of a migration test into food simulants: water, 3% special olive oil. If 6 dm² of PTFE surface is exposed to the food simulant and the final conc. is below 50 µg of C-8 per kg of simulant, only minor tox. testing is required.

Between 50 µg and 5 mg/kg more tests are needed. If > 5 mg --> many tests are needed. Extraction and migration tests were already done by TNO in 1979 and 1988, but gave unreliable results.

CONCLUSIONS AND PATH FORWARD

1. The Azure A (= similar to Methylene Blue) method used by TNO sofar is not suitable for this purpose, because it is not specific to C-8, and other anionic surfactants are likely to be present.
2. If we can prove that a worst case sample of PTFE corresponding to 6 dm² area and thickness x mm does not contain more C-8 than 386 ppb, then we
x
can prove by calculation that at 100% migration we will stay below 50 µg of C-8 per kg of food simulant. We agreed that this is the first step to be tested.
3. Dr Mitterberger will send to each party (DuPont, ICI, Dyneon) a 1 kg sample of 12 mm dia, 1 mm wallthickness PTFE tubing that has been sintered for 10 minutes. We all agree this is a representative worst-case material for food contact. Each party will do extraction tests with 95% ethanol C pH 9-10 and total reflux.

Tests will be done 2 hours and 8 hours, with tube cut in pieces max. 10 mm, preferably as fine as possible. Sample size 200 gram. DuPont will also run CHCl₃ extractions in parallel. Each party will perform subsequent concentration and GC analysis in his own way, with which it has the most experience. We will send each other our results before end of January.

4. Depending on the results, we will decide on further action. This will be communicated on the next APME meeting in Brussels, on 24 February 1997.
5. The contribution of 3M consists of writing the technical file for the application with the EC authorities (Mr Cox - Antwerp).

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SUMMARY

Migration tests were carried out with frying pans coated with PTFE dispersion (PTFE = polytetrafluoroethylene) put in contact with water or 3 % acetic acid for 90 minutes at 95 °C or with fat simulant HB 307 for 90 minutes at 140 °C or for 30 minutes at 200 °C. The methanol-extractable amount of residual emulsifiers (ZONYL* FSN-100, Serdox NNP 10.5 and C8-emulsifier) in the PTFE coating was determined as well.

The migration of non-ionic emulsifiers (ZONYL FSN-100 and Serdox NNP 10.5) into water or 3 % acetic acid (90 minutes at 95 °C) or into HB 307 (90 minutes at 140 °C) was found to be 0.001 or 0.002 mg/dm², which is of the order of magnitude of the detection limit.

The migration value obtained for HB 307 (30 minutes at 200 °C) is unreliable because of generation of interfering components during heating.

The migration of C8-emulsifier into water and into 3 % acetic acid (90 minutes at 95 °C) was found to be 0.005 and 0.003 mg/dm² respectively, which is of the order of magnitude of the detection limit.

The values obtained for the migration of C8-emulsifier into HB 307 (90 minutes at 140 °C or 30 minutes at 200 °C) are unreliable due to the generation of interfering components during heating.

The amount of methanol-extractable emulsifiers was found to be 0.002 mg/dm² for C8-emulsifier, 0.002 mg/dm² for ZONYL* FSN-100 and 0.001 mg/dm² for Serdox NNP 10.5, which is of the order of magnitude of the detection limit.

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After extraction of the PTFE coating with methanol at 65 °C the extractable amount of non-ionic emulsifier and of C8-emulsifier was determined with colorimetric methods of determination.

A detailed description of the various experiments is given below.

2.1 Sample material

Frying pans coated with an aqueous PTFE dispersion, ZONYL^{*} X-3551N, thickness 35-40 µm were provided by Du Pont de Nemours International S.A., Geneva, Switzerland.

It was stated that the PTFE dispersion contained non-ionic emulsifiers (ZONYL^{*} FSN-100 and Serdox NNP 10.5) and an anionic emulsifier (C8-emulsifier).

Coated frying pans with a diameter of 20 cm on bottom level were used in the migration experiments. Coated frying pans with a diameter of 24 cm on bottom level were used in the extraction experiments.

The non-ionic emulsifiers ZONYL FSN-100 (perfluorooctyl polyethoxylate) and Serdox NNP 10.5 (nonylphenol polyethoxylate) and the anionic emulsifier C8-emulsifier (ammonium perfluorooctanoate), obtained by courtesy of Du Pont de Nemours International S.A., Geneva, Switzerland, were used in the calibration and in the recovery experiments.

2.2 Migration experiments

2.2.1 Migration of non-ionic emulsifiers into aqueous food simulants
A volume of 250 ml water or 250 ml 3% acetic acid, heated to 95 °C, was brought into a PTFE-coated pan. The total area of the PTFE coating in contact with the food simulant - bottom and side wall - was 3.8 dm².

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