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RESULTS OF DU PONTS ANALYSES OF C-8 IN HOSTAFLON TUBES

Ref : My summary of 6-dec-96 meeting in Geneva about C-8 in PTFE for food contact applications

Dear Chris,

Here are the results of our C-8 analyses on Hostaflon tubes
The conclusion is that if we agree extraction depth is less than 3 mm, only minor toxicity testing is required.
I am looking forward to the results of Hoechst and ICI.

Samples provided by Dr. Mitterberger of Dyneon:

A 1 kg of Hostaflon TF 2025 tubes 12 mm diam, 1 mm thickness
B 1 kg of same tubes, shredded by Dyneon, ca 5X5X1 mm
C samples A, cut in rings (1-2 mm) and further shredded by DuPont laboratory, ca 1 mm3.

Extractions

1. In chloroform/water

B2-1 50 grams of B refluxed for 2 hrs in a mixture of 40 ml $CHCl_3$ and 25 ml. H_2O

C2-1 50 grams of C refluxed for 2 hrs in a mixture of 40 ml $CHCl_3$ and 25 ml H_2O

2. In ethanol 99.8 %

B2-2 200 grams of B refluxed for 2 hrs in 250 ml ethanol, pH > 10 (by adding NaOH)

C2-2 192 grams of C refluxed for 2 hrs in 250 ml ethanol, pH > 10

B2-8 as B2-2, refluxed for 8 hrs in 250 ml ethanol, pH > 10

C2-8 as C2-2, refluxed for 8 hrs in 250 ml ethanol, pH > 10

Analyses

1. Methylene Blue method short description
To the 25 ml water layer was added:
-5 ml methylene blue
-1 ml 2 N H_2SO_4
This was extracted 3 times in 15 ml $CHCl_3$. The 45 ml extract was completed to 50 ml with $CHCl_3$, and extinction at 640 nm was measured on a UV-Vis spectrophotometer, and compared with a calibration line.

2. GC method short description (Du Pont ref. WW-3690)
The 250 ml ethanol was evaporated on a steam plate. This took appr. 48 hours.
The residue was esterified with 10 ml. methanol containing 1.5 mol H_2SO_4 per liter methanol at appr. 54 C during 2 hours.
To this mixture was added 10 ml hexane and 20 ml of a stock solution of 180 g/l NaCl solution in water. After shaking and phase separation 5 microliter of the hexane layer was injected on a GC capillary column with ECD detector. (50 m. 0.53 mm CP Sil 5CB fused silica). Peak area was calculated into concentration by comparison to the peak area of 1 ppm of an esterified standard solution of C-8. We used a 1 ppm C-9 solution as an internal standard to correct for variations in injection volume.

Results

B2-1	.120 ppm wt	$CHCl_3$ Dyneon shred, Me-blue
C2-1	.410 ppm wt	$CHCl_3$ DuPont shred, Me-blue
B2-2	.068 ppm wt	EthOH Dyneon shred, GC
C2-2	.097 ppm wt	EthOH DuPont shred, GC
B2-8	.065 ppm wt	EthOH Dyneon shred, GC
C2-8	.106 ppm wt	EthOH DuPont shred, GC

Discussion

1. As we discussed before, the higher numbers found with the methylene blue method are less reliable, due to:
- extinction values 0.033 and 0.066 were too low for reliable result
- there may have been other anionic surfactants in the laboratory glassware, which significantly contribute to the blue color in this low concentration range.

2. We found little difference between 2 hours and 8 hours extraction. This suggests that 2 hours of extraction should be sufficient

3. The finer shred made at the DuPont laboratory gave results that are roughly 50 % higher than Dyneon shred.

4. In the food extraction tests, 6 dm2 of PTFE surface is exposed to 1 kg of the extraction medium. If we assume the effective extraction depth is d mm, this corresponds with 0.06*d dm3 = 0.1296 * d kg of PTFE exposed to 1 kg of the extraction medium. We hope to find less than 50 microgram of C-8 per kg of extraction medium, so that only minor toxicity testing would be required. So the 0.1296 * d kg of PTFE should contain less than 50 microgram of C-8. In other words the C-8 concentration in the PTFE should be less than 386/d microgram per kg.

   If we take d = 1 mm, the concentration should not exceed 386 ppb. We find appr. 100 ppb. As you can see, d is rather important. If we decide that effective extraction depth is 4 mm, the concentration should not exceed 96 ppb, compared to actual 100 ppb.

Estimation of extraction depth

There is some indication that extraction depth is less than 1 mm. The Dyneon shredded tube pieces were flat pieces of 1 mm thickness (= tube wall thickness), and appr. 5 x 5 mm size. Apparently even though the smallest size is 1 mm, and both flat sides of the flat pieces are exposed to the extraction medium, this is not enough to take out all C-8, as evidenced by the fact that cutting into smaller pieces gave 50 % higher numbers.
Although what follows is speculative, here is a calculation of the effect of cutting:

Suppose all large pieces are exactly 5 x 5 x 1 mm, and the small ones are 1 x 1 x 1 mm. Then each large piece can be cut into 25 small ones. Each small piece has a surface area of 6 mm2, so 25 of them have a surface area of 150 mm2. This should be compared with the surface area of the large piece from which they were cut: 2 x 25 mm2 + 4 x 5 mm2 = 70 mm2. So cutting into small pieces raises the surface

area by a factor 2, and the analytical result by a factor 1.5

If the extraction depth is d mm, you can show that for 25 1 mm3 cubes, the extracted volume = 25*(6d - 12d^2 + 8d^3) mm3
= 150 d - 300 d^2 + 200 d^3

For a 1 x 5 x 5 piece the extracted volume is 70d - 44 d^2 + 8d^3. Let us assume that the factor 1.5 increase in C-8 result is fully caused by the increased extracted volume. Than we can say that:

150 d - 300 d^2 + 200 d^3 = 1.5 x [70 d - 44d^2 + 8d^3].

d can be solved by algebra, and we find d = 0.2387 mm.

At this extraction depth the increase in extracted volume of 1 mm3 pieces is exactly 1.5 times as high as the extracted volume of the same weight of 5 x 5 x 1 mm3 pieces.