

Interoffice Correspondence **3M**

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Subject: Ecological Aspects of
Fluorocarbons - your memo
7/14/71

Sept. 13, 1971

RECEIVED

SEP 15 1971

ENVIRONMENTAL DIV.
POLLUTION CONTROL

TO: R. M. Adams - 220-142
FROM: H. G. Bryce - 236-1

Dr. Libby's thesis that there is "no natural sink" for fluorocarbons obviously demands some attention.

I. Definition of a Fluorocarbon

To begin with we can define a fluorocarbon, as any compound that has a significant number of -C-F bonds, such that it no longer undergoes, as a whole or in part, normal chemical, physical or biological changes. This definition embraces only stable or inert compounds. Currently these compounds would include

- | | |
|---|----------|
| 1. Fluorocarbon compounds such as chlorofluoro-hydrocarbon propellants and refrigerants world-wide. | 100.0 MM |
| 2. Polytetrafluoroethylene and polychlorotri-fluoro ethylene | 15.0 MM |
| 3. Fluoroelastomers | 2.0 MM |
| 4. 3M Fluorochemicals | |
| Inert Liquids | 0.2 |
| Fiber Treatment + Surfactants | 2.0 |
| Total (100% solids basis) | 2.2 MM |

II. Disposition of Volatile Fluorocarbons in the Environment

1. The volatile products which include all the fluorocarbon propellants, refrigerants and the inert liquids will largely end up mixed into the air atmosphere surrounding the earth.
2. On the basis of the following assumptions
 - a) Annual production world-wide 2,000 MM lbs.
 - b) All of volatile products are released to atmosphere and would be in a layer 1.0 miles thick surrounding the earth.

-continued-

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3MAD2496587

Exhibit **274**
Date: **10-26-07**
Debby J. Campeau
Stewart & Associates

CONFIDENTIAL - SUBJECT TO A PROTECTIVE ORDER ENTERED IN HENNEPIN COUNTY DISTRICT COURT, NO. 27-CV-10-28862

3M_MN00048386

Exhibit
2651

State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

2651.0001

b) continued

Annual production
2000 MM/lbs/yr = 6000 MM cu.ft./yr.

Volume of 1.0 mile layer surrounding earth
= 2×10^{19} cu. ft.

Therefore contamination of atmosphere due
to one year's production would be

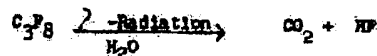
1 part in 3×10^9

or 1 ppm in 3000 years

3. There are only a few possible ways in which the volatile fluorocarbons would be removed from the atmosphere, since they do not enter into any known biological process. These processes are

a) dissolved in the ocean. It is reasonable to expect that the solubility in water could be about 0.001 ppm. max.

b) disintegrated by gamma radiation viz.



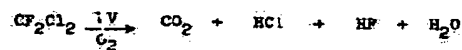
The HF and HCl would be washed into the soil and presumably end up where they started as appropriate metal salts or complexes. The half-life for this process is undoubtedly very low--so this may be insignificant.

c) Lightning

The energy available in a lightning storm would be sufficient to also break up the fluorocarbon group resulting in $\text{CO}_2 + \text{HF}$. This would be quite significant.

d) Ultraviolet radiation + Ozone

Chlorine containing fluorocarbon products would likely dechlorinate in the upper atmosphere where ultraviolet radiation is quite strong. The resulting dechlorinated products would be subject to ozone attack viz.



III. Toxicity of Fluorocarbon Gases

The completely fluorinated fluorocarbons such as CF_4 , C_3F_8 , C_6F_{18} , C_7F_{16} have a very low toxicity value and can be tolerated at very high levels in air as long as the oxygen content is not reduced, below that necessary to support normal life. Even the fluorochloro hydrocarbons are relatively non-toxic. Toxicity values referred to above are short term since no ("lifetime") data is available.

IV. Fluorocarbon plastics, elastomers

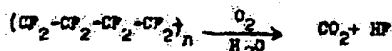
Again it must be assumed that they would not be affected to any degree by biological action.

Two things may happen to them.

- ① buried in the earth or
- ② burned in an incinerator

A piece of plastic or elastomer buried in the earth is likely to be largely intact for many thousands of years. On the other hand if a piece of the above material is burned in oxygen or air at temperatures in excess of 800°C. the decomposition would theoretically occur as follows

for example, in the case of polytetrafluoro ethylene



The HF would be returned to the soil and end up a metal salt.

V. Fluorochemical Fiber Treatments and Surfactants

As indicated above current production of these items is about 2.0 M lbs/yr. on a solids basis. These products consist of a conventional hydrocarbon backbone as functional group to which has been attached chemically certain perfluoroalkyl groups such as C_8F_{17} . Approximately 50% of the weight is the fluorocarbon group, while the rest is the hydrocarbon in make up.

7 — We can assume that about one-half of the treated textile, paper, leather etc. products will be burned in an incinerator while the other half will be buried in a landfill. As indicated previously incineration in air will result in essentially complete decomposition to CO_2 and HF. From B.O.D. and C.O.D. determinations, it is known ² that the hydrocarbon portions of these compounds are decomposed biologically.

V. --continued--

The undecomposed portion will be either a perfluoro alkyl carboxylic or sulfonic derivative or a perfluoro alkyl hydride. The perfluoro alkyl acid derivatives would be expected to be adsorbed by the soil in an ion exchange type equilibrium mechanism. However, it should be noted that the soil has a limited capacity for adsorbing these non biodegradable acidic derivatives. The perfluoro alkyl hydride would be relatively volatile and end up in the atmosphere, where their behavior would be similar to other stable fluorocarbons. Should non-degraded liquid fluorocarbons not be volatilized before mixing with ground water, this would be reason for concern.

Depending on the ratio of acids to hydride product produced, we would expect to have less than 0.5 MW lbs/yr of a fluorocarbon acid salt released to the soil. We can assume this is essentially concentrated in 100 major metropolitan areas in landfill operations, each landfill comprising an area of 10 acres, also that the soil depth is about 100 feet. The yearly level for adsorption would be about 0.5 ppm. In the soil, it is reasonable to assume that the elutriation process, should enable the soil to retain essentially 500 ppm before leaching into ground water, or surface water systems.

In any case the salts of fluorocarbon acids are only moderately toxic as the LD50 values are greater than 200 mg/kg. Hence even if they did eventually reach potable water systems their concentrations would not be sufficient to cause any real concern in view of the dilution factors involved.

CONCLUSIONS

1. At the present rate of production of gaseous or low boiling chlorofluorocarbon and fluorocarbon products world-wide, the annual production would result in only 1 part in approximately 3×10^9 parts of the earth's atmosphere.
2. Certain natural environmental processes could result in decomposition of fluorocarbon in the atmosphere. These include lightning storms, γ -radiation, ultra violet and ozone. The significance of these has not been determined.
3. Inert fluorocarbon plastic or elastomer parts, that become buried in the earth would be expected to remain there unchanged for many thousands of years.
4. Perfluoroalkyl derivatives of certain hydrocarbons are used as surfactants and as fiber treatments i.e. textiles, paper and leather. Biological activity will decompose the hydrocarbon portion but leave a relatively water soluble but inert fluorocarbon acid or derivative, which would be expected to be adsorbed by the soil.
5. Any fluorocarbon products which are subjected to incineration in air or oxygen at temperatures in excess of 850°C will be essentially decomposed to CO_2 and HF. HF will of course be adsorbed by the soil to form metal fluoride.