Environmental Health Perspectives
Vol. 11, pp. 197–202, 1975

An Industrial Approach to Evaluation of Pyrolysis and Combustion Hazards

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In addition to the usual toxicology studies necessary for the safe manufacture and use of polymers at room temperature, special studies are needed for polymers which will be used at elevated temperatures. This paper discusses various areas to be investigated and principles for deciding on test materials, tests, and test conditions, polytetrafluoroethylene (PTFE) and fluorinated polyethylene–propylene (PFEP) pyrolysis studies being used as an illustrative case history. Some limitations of animal testing also are mentioned. A toxicological spectrum relating toxicological determinants to PTFE temperature is developed.

The industrial approach to the evaluation of pyrolysis and combustion hazards of polymers should not be unique from an academic or consulting or governmental laboratory approach to the same problem. All four should be interested in evaluating these hazards for manufacturing, processing, and transportation workers, the consumer, and the environment.

The approach that I will develop can be subdivided into four, usually interrelated, areas: evaluation, simulation, education, and follow-up.

Evaluation consists of examining the proposed manufacturing process, proposed secondary fabrication processes, proposed uses and probable disposal procedures, seeking places where the polymer could be exposed to excessive heat.

Simulation is the attempted laboratory simulation of these situations to determine their hazards. Ideally, the laboratory simulation should also simulate reasonable abuse or give some idea how much abuse is possible before toxic products are evolved. Representative commercial material should be used for these evaluations.

The education phase covers educating manufacturing personnel and users about safe manufacturing and use conditions and the hazards of abuse.

The follow-up aspect consists of maintaining continuous liaison with all aspects of the polymer from manufacture to disposal or recycle. Manufacturing processes change, fabrication methodology changes, uses and abuses change and disposal or recycle methodology changes. Any of these changes may result in new opportunities for the polymer to be exposed to excessive heat. A good intelligence network that will promptly inform the toxicologist of these new opportunities for thermal degradation is extremely important.

Polytetrafluoroethylene (PTFE) and fluorinated polyethylene–propylene polymers (FEP), because of their high thermal stability as well as other unique properties, are particularly susceptible to thermal abuse. These polymers will be considered in this paper to illustrate this approach.

The manufacture of these polymers offers no opportunity for excessive heating. However fabrication, the many uses and incineration do offer many such opportunities. Uses or opera-

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tions where thermal exposure or thermal abuse might occur are: reclaiming clad metal, wire coating and stripping, nonstick cookware, scavenging melts, fabricating, coatings, fires, incineration, and machining.

The PTFE resins were the first perfluorocarbons developed commercially, and they will be discussed first. They are not thermoplastic, so instead of fabricating structures with injection molding techniques, methodology similar to powder metallurgy was used. In this methodology, a mold was filled with the resin granules, compacted and then heated to ca. 300°C for several minutes. At this temperature, the granules coalesced to form a more or less rigid mass in the shape of the mold. This is called sintering. The mold and shape were then cooled and, if necessary, the shape was then machined to the final shape or dimensions.

There are thus two opportunities in this methodology for overheating—the sintering process and machining operations.

Studies were undertaken to determine the temperature at which toxicants were evolved from PTFE and the nature of these products (*1–5*). Variables such as air flow rate and volume over the sample while heating, relative humidity of the air, sample size, and surface area probably would affect the results and it was necessary to pick a set of standard conditions. We decided to model the system after conditions used by the Underwriter's Laboratory to study the toxicity of pyrolysis products from structural materials.

The weight loss for PTFE resins varies typically from about $1 \times 10^{-3}\%$/hr at 290°C to about 4%/hr at 450°C (*6*). Under the conditions of our test, the pyrolysis products were not lethal to rats in a 4-hr exposure when the sample was heated at 400°C, but killed all rats when the sample was heated at 450°C. Analysis of the off-gases by a gas chromatographic procedure revealed only tetrafluoroethylene (TFE) at 450°C. At a sample temperature of 460°C, hexafluoropropylene (HFP) was also detected and at 475°C, perfluoroisobutylene (PFIB) was detected (*5*). The concentrations of these gases as a function of temperature are shown in Figure 1. Since the 5-hr approximate lethal concentration (ALC) of TFE is 45,000 ppm (v/v) (*7*) and the 4-hr ALC of HFP is ca. 3000 ppm (v/v) (*3,8,9*) these off-gases could not account for the toxicity seen. The 4-hr ALC of octafluoroisobutene (PFIB) is 0.5 ppm (*2*), but PFIB was not detected at 450°C. Other investigators had reported octafluorocyclobutane (OFCB) and hexafluoroethane (HFE) as pyrolysis products from PTFE under various conditions (*2*). We did not detect them. Our analytical method for these five fluorocarbons was reliable to 0.1 ppm with amounts as low as 0.03 ppm detectable, so if they had been present, we would have detected them. OFCB and HFE have 4-hr ALC's for rats of >800,000 ppm (*10,11*), i.e., if all the nitrogen in the atmosphere they breathed for 4 hr was replaced with either of these, it would not be lethal. Obviously, these possible pyrolysis products would be toxicologically insignificant, compared to HFP and PFIB.

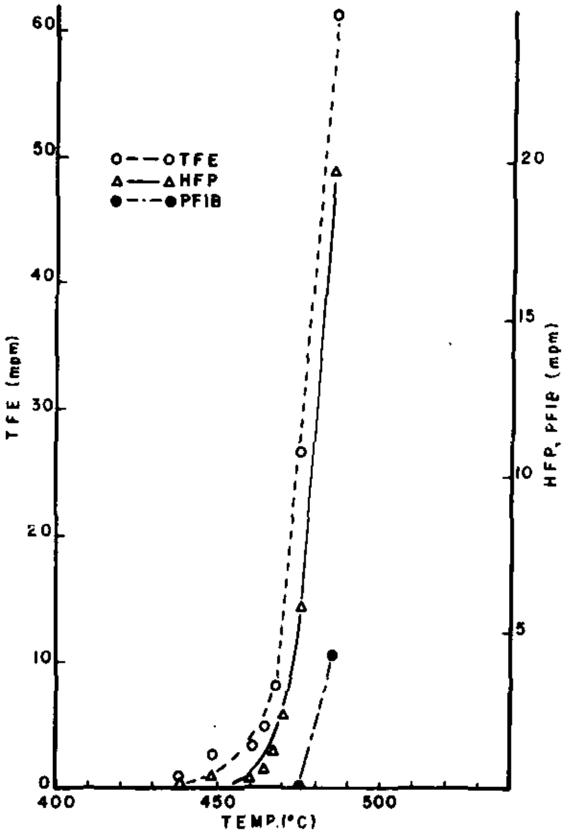

FIGURE 1. Evolution of (○) tetrafluoroethylene, (Δ) hexafluoropropylene, and (●) perfluoroisobutylene from polytetrafluoroethylene resin as a function of temperature.

We did detect some hydrolyzable fluoride, but it was not present in sufficient concentration to account for the toxicity seen, if it was any known material containing hydrolyzable fluoride. Other experiments also indicated it was not the lethal agent.

Further experiments indicated that the lethal agent at this temperature was a particulate material which could be removed by filters with a 0.2 μm pore size (*5*).

From these experiments, it appeared to be safe to sinter PTFE at 300°C. Ventilation and respirators would provide adequate protection in the event of any overheating; at least at temperatures up to ca. 500°C.

As most toxicologists are aware, animal studies do not reveal everything about the toxicological effects of a chemical and the toxicity of PTFE and FEP pyrolysis products is a dramatic illustration of this fact.

Workers carrying the hot sintered shapes from the ovens to cooling benches found that if they carried them close to their chest, they developed a condition which came to be known as the "shakes" (J. H. Foulger, Haskell Laboratory project report, E. I. du Pont de Nemours and Co., Inc., unpublished). If they carried them at arm's length, they developed no symptoms. The "shakes" were characterized by typical influenza symptoms: chills, spiking fever, achy feeling, tightness of chest, headache, cough, weakness in legs, and malaise. They lasted 18–48 hr. Recovery was complete and without any residual effects or aftereffects. No animal species has yet been found that responds to PTFE or poly-FEP fume the same way as humans, so definitive studies on the etiologic agent(s) have not yet been possible. Cavagna et al. (*12*) have reported some of the clinical signs in rabbits pretreated with an aerosol of dilute acetic acid and then exposed to the polymer fume. We have not been able to duplicate their findings. We also have evaluated squirrel monkeys, dogs and cats as possible models for "polymer fume fever" as the "shakes" are now called, but have not yet found a suitable model (*13*).

The etiologic agent is not known, but sublimate or particulate has been suggested [J. H. Foulger, Haskell Laboratory project report, E. I. du Pont de Nemours and Company, Inc., unpublished; and *(12)*]. Particulate is formed whenever PTFE or FEP is heated to temperatures where weight loss occurs. It probably is partially degraded polymer.

The similarity of symptoms, clinical signs and their onset and duration between metal fume fever and polymer fume fever is consistent with particulate as the etiologic agent for polymer fume fever (*14*). In the former, the syndrome is caused by inhaling fume from a hot metal such as zinc. In the latter, it is caused by inhaling the fume from a hot polymer. The obvious common element is a small, hot, possibly "activated" particle (*12*). No facile explanation is presently available for the absence of similar fume fevers when fumes from other polymers are inhaled. We do not know of any deaths from polymer fume fever.

Although the causative agent is not known, protective steps are known: ventilation, use of respirators, or use of furnace cooling.

This problem was thought to be solved after pinpointing the probable cause of polymer fume fever and prescribing the appropriate protective steps, but sporadic outbreaks of polymer fume fever continued to occur, even when proper precautions were taken. Thorough investigation of these incidents showed that they occurred only in pipe and cigarette smokers working with the powdered resin or in other operations where their tobacco could become contaminated with polymer particles. Following this lead, controlled human studies were carried out in which volunteers smoked cigarettes spiked with various amounts of a low molecular weight PTFE in a cigarette. It was found that as little as 0.4 mg of this polymer caused polymer fume fever in nine of ten volunteers (*11*).

The educational phase of the program has almost eliminated polymer fume fever from the industrial scene, but occasional cases are still reported to us. They are always found to result from not following handling precautions in du Pont's freely distributed bulletin on safe handling practices for these resins (*6*). There is also an American Industrial Hygiene Association Hygienic Guide on Teflon (*15*).

Machining operations using high speeds and dull tools could possibly heat the PTFE enough to cause polymer fume fever in a machinist bending over his work (*6*). However, such machining conditions also give parts that will be out of specification when they cool. This, plus the educational approach have virtually eliminated polymer fume fever from this area. Even under the worst imaginable machining conditions, the PTFE would not be heated to 450°C, so the other toxicological aspects are unimportant here.

Wire coating with FEP enamels involves a heat-curing step. However, the knowledge already discussed is directly applicable and there are no new hazards. There are, however, two areas in wire technology where exposure to serious toxicants could possibly occur: thermal wire stripping and short circuits or overloads.

Because of the cost of copper wire, scrap is stripped of its insulation and recycled. The usual process is to overheat the insulation so that it separates from the wire and is easily stripped mechanically. No new toxicants are produced from FEP by this procedure, and the industrial hygiene answer is again to use adequate spot ventilation and to educate the workers carrying out this operation.

A short circuit or overload, particularly with some of the exotic alloy wires, could conceivably result in localized overheating of an FEP insulated wire and the release of toxicologically important pyrolysis products. Our studies indicate that it is indeed possible to evolve products which are lethal to rats from these wire enamels at elevated temperatures. However, the thermal safety margin is greater for these enamels than for alternative insulations (*6*).

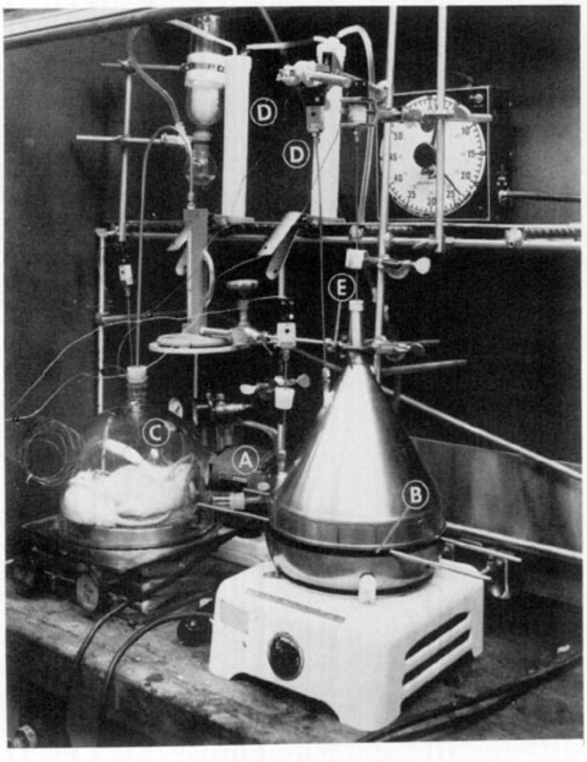

FIGURE 2. Typical exposure arrangement for evaluating the toxicity of pyrolysis products from PTFE coated frypans. The vacuum pump (*A*) draws a known volume of air through the annular space (*B*) between the frypan and the stainless steel funnel. The air then enters the exposure chamber (*C*). The air is then passed through two gas scrubbing towers containing 0.1*N* aqueous NaOH (*D*). Samples for gaseous fluorocarbon analyses are taken at (*E*).

Nonstick cookware is another application of PTFE resins where thermal degradation is possible. Before these resins could be used in this application, it was necessary to carry out extensive pyrolysis tests to be sure that no one could be injured from this use. Rats were exposed for 4 hr to the fumes from frypans coated by prototype commercial processes with prototype resins and heated to various temperatures. A 4-hr exposure seems excessive if only home use is considered, but it is not an excessive exposure if commercial use is also considered. This, in fact, is the usual inhalation exposure time for studies on commercial chemicals. A typical exposure arrangement is shown in Figure 2. A measured volume of air, drawn through the annular space between the stainless steel funnel and the frypan carries the pyrolysis products to the inhalation chamber. Aliquots of the chamber atmosphere are analyzed for gaseous fluorocarbons and hydrolyzable fluoride.

Typical temperatures for frying various foods range from 130°C for fish fillet to 280°C for steak (*16*). The approximate lethal temperature (ALT) for rats for a 4-hr exposure to the pyrolysis products from a PTFE-coated frypan is 425–450°C. Thus there is a wide safety margin under typical use conditions. The plastic handle of a frypan would decompose if the pan was kept at 280°C for long. The odor from the decomposing handle would alert the user to a problem long before there was any problem from pyrolyzed PTFE.

Considering the amount of PTFE resin on a pan, the usual frying temperatures, the possible abuse temperatures, the size and ventilation of home and commercial kitchens, we did not feel the use of PTFE-coated cookware presented any real hazard from thermal degradation products. Actual human tests indicated that even gross thermal abuse of a coated frypan would not cause polymer fume fever under use conditions.

Use experience indicates that these assessments were correct for humans. However, after the pans had been on the market for several years, we began to get sporadic reports that pet birds kept in kitchens had died after a coated frypan had been left unattended for long periods of time on a stove set at a high heat.

As a result we carried out several experiments with Japanese quail and parakeets. These are summarized in Table 1 (*17*). Because of a short supply of parakeets, fewer experiments could be carried out with these birds than with the Japanese quail. Enough experiments could be carried out, however, to demonstrate that both bird species were more sensitive to the fumes from PTFE resin than are rats. However, they are not more sensitive than rats to the fumes from the naturally occurring frying media (*11*), and both rats and these birds are more sensitive to the fumes from these media than the fumes from PTFE. The safety balance additionally favors the PTFE-clad frypan, in that corn oil or butter left unattended in a frypan on a stove, and reaching temperatures where PTFE resins would emit fumes lethal to a parakeet, would probably flash near that temperature and not only kill the bird, but possibly involve the kitchen and the entire house in a fire.

This sensitivity of some birds to inhaled materials is not a new finding. It has been long known. Probably the best known example is the classic use of a caged canary in mines to detect low oxygen levels or detect toxicants at levels below a human effect level.

The data already presented can be applied to the other possible resin overheating situations listed above and those uses will not be discussed further.

Table 1. Pan temperatures at which the pyrolysis products from PTFE-coated frypans, uncoated pans or uncoated pans containing butter or corn oil were lethal to Japanese quail, parakeets or rats exposed for 4 hr (ALT).

Test material	ALT, °C		
	Quail	Parakeets	Rats
Cast iron frypan (CI)	>450	>330	
Aluminum frypan (AL)[a]	>450		
AL+corn oil[a]	310[b]		
CI+corn oil	290[b]		
AL+butter[a]	290	≤260	250
CI+butter	260	≤260	
PTFE-clad pan	330	280	425–450

[a] Handle removed.
[b] Media flashed.

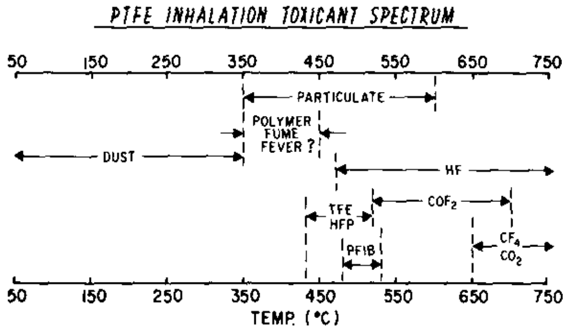

FIGURE 3. PTFE inhalation toxicant spectrum as a function of temperature (heated in air).

The toxicological spectrum of PTFE as developed in du Pont and other laboratories (*1–5*) is summarized in Figure 3 and can be applied to all known PTFE uses. As can be seen, the industrial hygiene ramifications of this spectrum are complex.

For temperatures up to about 350°C, the resin dust is the toxicological determinant. Studies have shown this can be considered a nuisance dust (*15*).

Particulate, whatever its chemical composition, is probably the principal toxic agent from about 350°C to 450°C. However, at temperatures ca. 25°C above the ALT, PFIB is formed and, at temperatures ca. 30°C above the ALT, it may be present in concentrations lethal to rats (5). At temperatures 100–300°C above the ALT, carbonyl fluoride is probably the principal toxicant (*18,19*). At these elevated temperatures, a further reaction, yielding the less toxic materials CF_4 and CO_2 is possible (*18*).

The pyrolysis product boundaries shown should be considered a range rather than a definite value. The toxicological importance of each material in the spectrum will be minimal at either end of its region and will become maximal in the center.

The relative abundance of the respective toxicants at various temperatures is, of course, a function of the reaction kinetics for the various reactions involved.

A similar spectrum exists for FEP polymers, but the evolution of the various gaseous materials commences about 50°C lower than for PTFE resins.

A strictly analogous toxicological situation pertains in the case of the pyrolysis in air of polymethylene (also known as oil) or its constituent hydrocarbons. Its toxicity at room temperature is due solely to the toxicity of the particular hydrocarbon molecule. As the temperature is raised, thermal "cracking" and rearrangement occur, and the toxicity of these products becomes important. As the temperature is increased further, carbon monoxide is formed and its toxicity usually dominates. With further increases in temperature, carbon dioxide is formed, and its toxicity is predominant. Thus, here also, the toxicological determinant depends upon the temperature of the system.

A similar temperature-dependent toxicological spectrum also exists for the naturally occurring cellulosic polymer wood, and a similar toxicological spectrum almost certainly exists for other synthetic polymers. However, most other polymers differ from PTFE and FEP in that they contain adjuvants, as does wood, which may also contribute to the toxicity or modify the pyrolysis products at any temperature.

The amount of pyrolysis and the pyrolysis products may also vary with the pyrolysis atmosphere. For example, we have found that the weight loss of PTFE heated in nitrogen at 450°C was less than half that of PTFE heated in air. As might be expected, the pyrolysate, on a weight-of-polymer-heated basis, was less than half as toxic to rats (5). We also have evidence that particulate evolved from PTFE heated in a nitrogen atmosphere is chemically different from particulate evolved from PTFE heated in an oxygen atmosphere. Since we do not yet have an animal model for polymer fume fever, we have not been able to determine whether or not this particulate can cause polymer fume fever.

In summary, to evaluate all the pyrolysis and combustion hazards from a polymer on a continuing basis, one must: try to anticipate all (human) exposures; simulate these in the laboratory; use the actual product in all tests, if possible; maintain close liaison with the market; keep an open mind; and remember that pyrolysis products vary with temperature and additives and also with pyrolysis atmosphere.

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