Science

DDT causes feminization of gull eggs

Gull eggs exposed to the pesticide DDT at levels that were found in the environment in the early 1970's lead to male gulls with abnormal development of ovarian tissue and oviducts, say D. Michael Fry and C. Kuehler Toone of the University of California, Davis [*Science*, **213**, 922 (1981)]. Such feminization of male bird embryos affects reproductive behavior of these birds when they mature, the researchers say. They suggest that male gulls exposed to DDT as embryos may be less likely to migrate to breeding colonies—explaining the markedly skewed sex ratio of adult birds that is observed on Santa Barbara Island.

Insects may learn to respond to pheromones

An insect's response to pheromones may be learned to some extent, say researchers Bernard D. Roitberg and Ronald J. Prokopy of the University of Amherst [*Nature*, **292**, 540 (1981)]. They have studied female apple maggot flies. These flies deposit a pheromone on the surface of fruit in which they have laid eggs to keep other flies from depositing eggs in the same fruit. However, the researchers find that females that have never been exposed to pheromone-treated fruit are not inhibited by it; it is only after an initial encounter that they avoid pheromone-marked fruit. "This mechanism may provide flies with a means of reducing the cost of continually maintaining an unused information processing system," the researchers suggest.

Naturally occurring toxins found in parsnips

Parsnips, and perhaps other related vegetables such as celery and parsley, contain appreciable levels of three phototoxic, mutagenic, and photocarcinogenic chemicals that are not destroyed by normal cooking procedures, according to G. Wayne Ivie and coworkers at USDA's Agricultural Research Laboratory at College Station, Tex. [*Science*, **213**, [illegible] (1981)]. The compounds, psoralen, xanthotoxin, and bergapten, are all linear furocoumarins. Consumption of a 0.1 kg parsnip root could expose an individual to [illegible] mg of the compounds, [illegible] expected to cause [illegible] under certain circumstances, [illegible] exposure actually [illegible] humans cannot be [illegible] logic data, the researchers [illegible]

[illegible]chlorinated dibenzo[illegible]

[illegible]

[illegible] as well as dioxins in the fly ash of municipal incinerators. Now they have perfected techniques to find individual isomers of these compounds in tissue samples at the parts-per-trillion level. The turtle fat contained the compounds at a total level of about 3 ppb and the seal fat at about [illegible] ppt. Isotope ratios in the two species were nearly identical and suggest to the researchers that the source of the compounds is probably direct contamination by polychlorinated biphenyls (PCB's).

Education

Chief named to engineering faculty project

A manager for the engineering faculty shortage project of the American Association of Engineering Societies has been named by the American Society of Engineering Education, which is performing the two-year project for AAES. He is electrical engineer John W. Geils, currently director of the network design division at American Telephone & Telegraph. Geils will become a staff executive of ASEE Sept. 1. The major emphasis of the project is to develop a firm data base upon which solutions to the crisis in engineering education can be developed, with special emphasis on retaining doctoral degree engineers in faculty positions.

Technology

Nonnitrite food additive gets patent

FMC Corp.'s phosphorus chemicals division has been granted a patent (U.S. 4,282,260) for use of sodium hypophosphite to replace sodium nitrite as a suppressant of botulinus toxin formation in smoked meats. FMC says its studies show that sodium hypophosphite, which is on FDA's generally recognized as safe (GRAS) list, is as effective for this use as sodium nitrite. It has been suggested that dietary sodium nitrite increases chances of formation of carcinogenic nitrosamines in the body.

[illegible] gas turbine with synthesis gas

[illegible] gas from bituminous coal has been used [illegible] to generate [illegible] MW of electric power [illegible] turbine of Dow Chemical [illegible] company [illegible]

On the basis of the data obtained, the agency concluded that PCBs do not pose an imminent threat to homes using natural gas. The letter to transmission companies directed the firms to take steps to assure proper disposal of any contaminants found and to prevent further contamination from entering their systems or other systems they connect with.

Transmission Company Reports

EPA said it first wanted reports from the companies on the amounts found, where they were located, how workers would be protected from them, and how the companies would handle, mark, store, and dispose of them.

Next, the agency asked firms to report "all possible alternatives" for preventing the movement of PCBs into other pipe systems; estimates of the cost, effectiveness, and time needed for each alternative; an assessment of the feasibility of each method; and a discussion of the exposure potential from each method.

With that data, EPA said it would discuss with each firm the best method to put into effect.

Once a method was agreed upon, the agency said transmission companies should report the time the plan would take to be put into operation, and other data such as worker safety procedures, disposal procedures, and procedures to monitor the effectiveness of the method.

The agency additionally asked companies to report data on sources of the contamination and how it could be eliminated and monitored. If companies did not remove all contaminants from their systems, the agency directed them to submit yet another report on the length of pipe still contaminated, an estimate of the concentration of PCBs in the pipeline condensate, and a description of all possible methods for removing it.

EPA asked that companies report within two weeks of receiving the letter when they would be able to submit all the required information.

Contacting Distribution Companies

The agency also asked regional offices to contact local gas distribution companies about developing procedures to locate any PCB contamination, determine its health hazard, prevent its movement or remove it, and possibly monitor the ambient air in customers' homes for indications of contamination.

EPA headquarters said the regions should "use their best efforts" to bring all gas distributors into the monitoring and cleanup program.

The kinds of distribution companies EPA said should participate in the program were those that had compressors or any other equipment that "could be the source of PCBs," those that fogged their systems in the past, those that were supplied by a transmission company that had detected contaminants in its feed lines, and those that served a "substantial population."

"Substantial populations" were defined as portions of large cities, medium-sized cities, and "several rural counties."

Although the letter to regional offices set forth recommendations for having distribution companies report different kinds of data, the cover letter said the guidelines "are meant to be flexible."

In some cases, headquarters said, no cleanup would be necessary. It added, however, that if "any PCB exposure is found to be occurring above background levels," EPA could "require immediate action to remove the hazard, including extensive measures, if necessary."

Research

NIOSH BEGINS REPRODUCTIVE STUDY AT CHEMICAL MANUFACTURING PLANT

The National Institute for Occupational Safety and Health is conducting a health hazard evaluation of workers at a West Virginia plant which manufactures toluene diamine and dinitrotoluene, two chemicals produced at a Kentucky facility where reduced sperm counts among workers were found earlier this year.

Richard Ublar, an industrial hygienist with the International Chemical Workers Union, told BNA that his union requested the new study at the Allied Chemical Co. plant in Moundsville, W. Va., after learning of the results of the earlier investigation.

In that study, workers at an Olin Chemical Corp. facility in Brandenburg, Ky., were found to have significantly reduced sperm counts as compared with workers not exposed to toluene diamine and dinitrotoluene. The earlier study said the findings could not be considered "conclusive" in showing a reproductive effect from the two substances without further information, but at the same time it said the data should not be dismissed as insignificant (Current Report, March 20, p. 1601).

Steven Ahrenholz, the NIOSH project officer for the study, reported that the institute hopes to complete data collection by mid-July. After that, it will decide what further action to take, he added.

The Allied plant is "fairly similar" to the Olin facility in Kentucky, although the Allied plant, in addition to producing toluene diamine, also uses it on-site to manufacture toluene diisocyanate, the researcher said.

In requesting the study, the union "wanted to see if there were any particular problems" among the Allied workers in view of the Olin investigation results, Uhlar told BNA. The union also requested health hazard evaluations at two other toluene diamine facilities — an American Cyanamid Co. plant in Bound Brook, N.J., and a Mobay Co. facility in New Martinsville, W. Va.

Lead

COST/BENEFIT TERMED INAPPROPRIATE FOR EVALUATION OF CURRENT STANDARD

The concept of cost/benefit analysis "is inappropriate for an agency designed to save lives" and is an "infeasible technique" for the Occupational Safety and Health Administration's decisionmaking purposes, according to the United Steelworkers of America.

Further, the International Association of Machinists argued that such an analysis is neither implied in the Occupational Safety and Health Act nor suggested by legislative history, and "constitutes a transgression of congressional prerogative."

These comments were submitted to OSHA in response to its April 21 announcement that it was reopening the rulemaking record to conduct a cost/benefit analysis and was requesting comments on the economic and technological feasibility of provisions of the lead standard (Current Report, April 24, p. 93).

However, if OSHA decides to go ahead with the analysis, the Steelworkers want the agency to follow rulemaking procedures, making sure to publish its initial determination on the protocol it plans to use. OSHA should conduct its cost/benefit study from the view of the affected workers rather than the employer, should use its subpoena power to get the cost data it needs from industry, and in the event the

Coping ineffectively with an environmental disaster

Events following the tragic contamination of Michigan farms with PBB are spelled out in a clear and balanced account

"The Poisoning of Michigan" by Joyce Egginton, W. W. Norton & Co., New York, 1980, 351 pages, $13.95

Reviewed by Isadore A. Bernstein, professor of biological chemistry at the University of Michigan's medical school, professor of environmental and industrial health in its school of public health, and associate director for research for its Institute of Environmental & Industrial Health. Bernstein headed a scientific panel that advised the governor of Michigan following the 1973 PBB contamination there

"All the relevant institutions of democracy failed. Rather than working for the public good they operated, individually and collectively, against it—not out of malice, but simply because this was an event outside their experience and beyond their budgetary means to resolve."

With these succinct—yet sympathetic—statements, Joyce Egginton introduces her account of the accidental contamination of livestock and people in Michigan by polybrominated biphenyls (PBB). In "The Poisoning of Michigan," she has crafted a concise and sensitive report of the actions taken by individuals and organizations to identify the nature of the problem and assess its scope, to control the spread of the pollutant, to evaluate damage to life and property, and to counteract the economic and health effects of this episode. For the student of environmental health, this book can serve as the best available chronicle of Michigan's PBB affair. It provides a clear perception of the etiology and progression of the contamination and the steps which must be taken to minimize chances of repetition.

The first part of the book covers the story from late spring in 1973, when Michigan Chemical Corp. responded to an order for magnesium oxide by erroneously shipping PBB (a commercial fire-retardant mixture) to the Farm Bureau Services' feed mill near Battle Creek, to April 1974, when PBB was identified as a contaminant in feed on a dairy farm whose milk production had decreased precipitously. It chronicles the persistent efforts of one farmer to obtain the assistance of various state and federal institutions in explaining the "plague" which had enveloped his livestock. Milk production had dropped 60%. Cows were ill. Some died. Although dedication and persistence ultimately triumphed, the story emphasizes the nearly insurmountable obstacles an individual faces in confronting the various institutions of our complex society.

The second part concerns actions taken by the various government agencies and the companies involved to define the extent of the contamination, to limit its spread, and to deal with the economic and health implications of the incident in the farm areas of the state. By the time the contaminant had been identified, it had permeated through most of Michigan. The contamination was far wider than anyone imagined.

Each party dealt with the situation according to its own perceptions of the problem and in its own best interests. The Michigan Department of Agriculture (MDA) attempted to be the quiet eye at the center of a hurricane which kept increasing in intensity as the broad geographic scope of the contamination became apparent. Other state agencies kept a low profile. The federal Food & Drug Administration saw the issue as primarily a state problem. It did set what it considered a safe "action level" for PBB above which contaminated farm products could not be sold. This level was based upon estimates of the toxicity of PBB. Insufficient information was available to be certain. MDA enforced this ruling.

It was to everyone's advantage to play down the entire affair. Farmers whose herds were affected preferred not to broadcast their plights, fearing that their economic positions and their reputations would suffer. Companies found it expedient to deal quietly with insurance claimants one by one. Government agencies hid behind their duties as regulators, professing not to have the resources to obtain new pertinent information. Universities claimed to have no money to do the necessary research.

The possible effect of the contamination on the urban population of the state was generally ignored. Attention was concentrated initially on farm families. The episode was considered to be a simple agricultural problem that would be resolved by routine action. The legislative and executive branches of the state government appeared to subscribe to this view. Although not ignoring the situation, neither responded enthusiastically to requests for additional funds or new initiatives.

The right of farmers to be reimbursed for damages resulting from contamination of their livestock at concentrations of PBB above the "action level" set by FDA was never disputed. Both Michigan Chemical and Farm Bureau Services had insurance to protect themselves against liability in such incidents, and extensive payments were made to owners of quarantined livestock. The episode became controversial only over what to do with livestock that had detectable levels of PBB below the "action level." Some of these herds also were quarantined by MDA.

The third part of the book deals with the controversy over disposition of animals contaminated at low levels and with the question of possible effects of PBB on human health. Should the "action level" be lowered by the state government? What risk to the consumer's health would result from ingestion of food products containing low levels of PBB? Unlike most other facets of the episode, this aspect gained widespread public interest in the state and became known beyond the borders of Michigan.

Various influences heightened the public interest in this issue. For farmers who were considering the sale of animals that were contaminated at low levels, moral and economic questions had to be faced. Studies of "low-level" animals carried out at the

state's agricultural university and outside the state failed to show abnormalities related to low body burdens of PBB, but charges surfaced that the studies were not impartial.

For the nonfarm consumer, the possible effects of long-term retention of PBB in body fat was a consideration in deciding whether to buy Michigan farm products. For new mothers who were breast-feeding, there was a concern over the possible effects on their babies of transferring PBB in the milk. Of mothers in the lower peninsula of Michigan, 90% had detectable levels of PBB in their milk.

Aware that they would be subject to further liability if Michigan officially lowered the "action level" for PBB and thereby legally devaluated animals with levels of PBB below the national "action level," both companies lobbied against its doing so. An upcoming election made politics a factor as attempts were made to blame the state administration for "covering up what two corporations were doing to the people of Michigan" and for "telling farmers to sell sick cows to the public" so that their farms would be saved.

The final chapters describe the manner in which the "disposition" question was resolved and the social, economic, and political forces that influenced this resolution. The "action level" was lowered by legislative action. The issue of whether a body burden of PBB is detrimental to human health is also discussed. Ironically, this latter question received a "definitive" answer only in the courts, where a judge stated that "in small amounts, PBB is not toxic." From a scientific point of view, this question is still unanswered.

Some of the farm families who owned "high-level" animals and who themselves had high body burdens of PBB in their fat depots were not visibly ill, whereas some individuals with relatively low body burdens of the chemical mixture claimed health problems that could be caused by residues of halogenated hydrocarbons. It has not been possible to define a dose-response relationship between the level of PBB in the body and the state of health—a basic requirement for relating an environmental chemical and a toxic response. This state of knowledge, of course, does not support the conclusion that PBB impairs health or that small amounts of PBB have no toxic effect. It is entirely possible that the wrong parameters have been compared.

Joyce Egginton, New York correspondent of the Observer of London, obviously spent a great deal of time and effort in researching the subject and in formulating the text. Characters who played key roles in the drama are realistically and dispassionately described. The clay feet of the heroes are occasionally exposed, but no one is painted as all bad. The author tries to present each event within the perspective of its time, place, and relevance.

This is in sharp contrast with the more emotional presentation of the story in "PBB: An American Tragedy" by Edwin Chen (C&EN, April 21, 1980, page 54). Chen's book concentrates on quotations from the various protagonists to highlight the charged atmosphere in which individuals and institutions tried to cope with the problem. He provides little perspective from which to judge independently the propriety or effectiveness of these attempts.

In Egginton's book, scientific material is presented at the level of the layman but with the objectivity expected by the professional. The inadvertent misspelling of one chemical name does not detract from the aura of reliability that the scientific information exudes.

Items of human interest are dispersed throughout the book, but only occasionally do they appear to cloud the author's generally critical evaluation of the matter being described. One such lapse involves the unequivocal statement that "one Michigan general practitioner came up with a correct diagnosis" of human toxicosis from PBB. Although the physician believed that his diagnosis was correct, he never provided data to support his contention. Even today, no such data are available.

These vignettes of human activity do serve to remind the reader that the story is about individual men and women, as well as about corporations and institutions. Actions taken by particular people in accord with their personalities, prejudices, interests, and education influenced the course of events.

It was a farmer with a master's degree in chemical engineering and industrial chemical experience who led the effort to identify the contaminant, which had been fed in large quantities to his dairy herd, but who did not support the later efforts to keep "low-level" animals from the market. He concluded that consuming the meat of such animals posed no risk to the consumer. Some scientists and physicians allowed their concern for the public welfare or for the institutions they represented to affect their professional judgments. As a consequence, their pronouncements lost credibility.

Most important, people with inadequate education and with little understanding of the importance of their jobs were involved in the erroneous shipment from the chemical company to the feed mill and in the introduction of the erroneous material into the feed mixer. Interestingly, the chemical workers' union is reported to have disclaimed responsibility for the erroneous shipment since its members were on strike between Oct. 5 and [illegible], 1973, during which time the union considers the shipment to have been made. Shipping records, however, indicate that PBB went to Farm Bureau Services in May of that year. In any case, farm problems were clearly evident by September. In the final analysis, people both influenced all the events and bore the brunt of the effects.

Governmental and educational institutions of Michigan provided little effective help in the efforts to deal with the problems generated by the presence of PBB in the environment. Egginton blames the "power lines" that linked state governmental agencies and the universities for this. Personal and professional relationships among the personnel of the various organizations were close. MDA had a laboratory on the campus of Michigan State with which university scientists were involved.

Egginton charges that the university's "dependence upon the legislature for appropriations made it almost impossible to keep politics out of research, particularly agricultural research." Admittedly, the state's educational institutions are dependent on the legislature for funds, and individual staff members may have had problems with divided loyalties but, in the opinion of this reviewer, to imply that the university was a party to purposefully obfuscating the issue is clearly beyond the evidence that is presented. The presence of an MDA laboratory at Michigan State is not prima facie evidence for such collusion between the two organizations.

Egginton appreciates the difficulty in establishing that an environmental chemical causes an effect on human health and closes her book with a quotation from a Michigan legislator who said that "as time goes on Michigan people may suffer from a lot of different diseases, probably due to PBB . . . and there never will be a way . . . to prove that the poisoning of Michigan was the cause." This statement has the ring of truth. □

Researchers Providing Some Details About Hazards of Fire

Computer model to predict spread of fire and combustion gases is devised; studies of lethal gases, combinations yield surprising results

MIAMI BEACH

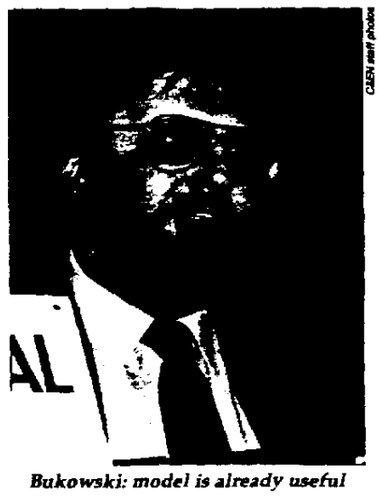
It seems like an easy question: What is it about fires that makes them hazardous to people? But detailed answers are proving extraordinarily difficult to establish. Like snowflakes, no two fires are exactly alike, and these differences greatly complicate the task of determining where their hazards come from.

Progress is being made, however. Some of that progress, from industrial, university, and government laboratories all over the U.S., was described in a day-long symposium sponsored by the Division of Chemical Health & Safety.

An initial version of a computer model that can predict the spread of fire, smoke, and toxic gases throughout a building has been developed by researchers at the National Bureau of Standards' Center for Fire Research. Though the model will be updated as better fire toxicity data come in, in its present form it is already useful to fire fighters, architects, and others concerned with the fire safety of buildings, says Richard W. Bukowski, head of the smoke hazard group at the Center for Fire Research. Smoke and toxic gases are of particular concern, because 80 to 90% of the people who die in fires succumb to smoke and gas rather than to flames or heat.

The version of the program that is now available models the build-up of a fire in one compartment, such as a room in a house, and then tracks the movement of smoke, gases, and the fire itself from that compartment throughout a one-story structure. The program presents data in graphic form—"so that you can essentially watch a picture of what is happening during the fire instead of having to pour through stacks of computer printout, tables, and graphs," Bukowski says. The current program can make predictions for essentially any number of compartments on a single floor. Development work under way will extend its capability to multiple-story buildings.

The computer program is based on data collected during 10 years of test burns—in which a piece of furniture or a room or sometimes a whole building is constructed and then deliberately burned to collect data on how fires develop and spread under different circumstances. These burns were conducted at NBS and elsewhere and cost, on average, $10,000 apiece, Bukowski says. The computer program can simulate such a burn in a few minutes at a cost of about $100. Thus, with the program it is feasible to "run" several burns under slightly varying circumstances to see what conditions make a building safer.



C&EN staff photo

Bukowski: model is already useful

"Using the computer, you can run multiple fires in a building before the building is even built, looking for sources of hazard, and then make design changes" to make the building safer, Bukowski explains. Or fires can be modeled in existing buildings to see what kinds of retrofitting might be needed. Fire departments in Phoenix and Los Angeles have expressed interest in using the system for fire fighter training.

Eventually, NBS hopes to develop a computer program that models real fires well enough to be used for setting performance-based fire codes. Most fire codes today describe the way a building must be built or retrofitted to provide adequate safety, Bukowski explains. But if accurate and comprehensive computer models can be developed, codes could be written instead to specify how a building has to perform in a fire—how long escape routes must be clear of incapacitating gases, for example—and builders could choose their own methods for providing that performance. Such a change could reduce the cost of complying with fire codes very substantially, especially in older buildings, Bukowski says.

In other work at NBS, Barbara C. Levin, head of fire toxicity research in the Center for Fire Research, and

coworkers from NBS, the American Iron & Steel Institute, and the University of Pittsburgh are developing some of the data to be incorporated into future computer programs to predict fire hazard. In particular, this group is studying the toxicity of single and multiple gases produced in fires to determine just how many of the thousands of combustion products present in fires actually contribute to fire deaths.

"We want to know if you can explain the toxicity of fires based on [just] the primary toxic combustion products or if you need to take into account some more minor or obscure combustion products that are also generated in a fire," Levin explains.

Their method is to expose male rats in groups of six to various concentrations of the major gaseous byproducts of fires for different periods of time. The animals are exposed to both single gases and to combinations of gases that would be expected to be present in an actual fire.

In some cases, all of the animal deaths can be accounted for by only considering a few of the primary combustion products, the researchers find. For example, hydrogen cyanide and carbon monoxide appear to act in an additive manner so that in the presence of just those two gases, all of the exposed animals may die, even though the concentration of each gas alone is not high enough to account for the deaths.

More striking is the effect of carbon dioxide in gas mixtures. The gas is essentially harmless by itself—levels of up to 40% (400,000 ppm) can be tolerated before any of the exposed rats die. Such concentrations are never found in real fires, Levin says, where the maximum attainable level is about 21%. However, in the presence of 5% carbon dioxide, carbon monoxide becomes twice as toxic as it is alone. The carbon dioxide appears to work by increasing the rat's uptake of carbon monoxide and by increasing and prolonging the effect of the carbon monoxide on blood acidity.

"Five per cent carbon dioxide is not an uncommon concentration in a real fire," Levin says. "So what people have thought about as a lethal amount of carbon monoxide should probably be cut in half if it is in the presence of 5% carbon dioxide."

Bertelo: estimates may be too high

But even if the assumed lethal dose of carbon monoxide is cut in half and the effect of the concentration of hydrogen cyanide found in certain real fires is considered, many of the deaths that occur in these fires still are not explained, according to William T. Lowry, assistant professor of pathology at the University of Texas Health Science Center at Dallas. Lowry has studied gas samples from about 100 fires in the Dallas area and finds many cases where the concentrations of none of the gases he measured—carbon monoxide, hydrogen cyanide, hydrogen chloride, and aldehydes—can account for the fire deaths.

Lowry's own candidate for the agent responsible for at least some of these deaths is a relatively stable free radical, as yet unidentified, which he has produced in controlled burn conditions. Under these conditions, the free radical was trapped at concentrations up to 1200 ppm, reaching this level within four minutes and maintaining it until the fire was extinguished. Such a concentration is capable of causing immediate incapacitation, Lowry says.

Studies of the lungs of rats exposed to fire gases in three test burns of houses found changes in a surface-active material located in the lining of the lung, Lowry says. This material—a surfactant made up of phospholipids, neutral lipids, and proteins—was found to undergo lipid peroxidation caused by exposure to free radicals in the fire gases. The effect was to increase pulmonary surface tension, which reduces the lung's ability to take up oxygen. Autopsies of 30 human fire victims showed similar changes "consistent with rapid incapacitation due to rapid rise in lung surface tension," Lowry says.

Preliminary studies of burn victims and fire fighters exposed to sublethal levels of combustion gases show changes in blood chemistry that suggest the presence of free radicals in the blood, Lowry says. Malondialdehyde, one product of lipid peroxidation, was also detected in the blood. Although these studies were performed on a very small number of patients, they do support the hypothesis that fires generate a free radical that has biological consequences, Lowry says.

The relationship between toxicity results obtained in test situations and what happens in real fires was examined in several laboratories. For instance, estimates of the amount of potentially lethal hydrogen chloride produced when polyvinyl chloride is involved in a fire may be much too high, says Chris A. Bertelo, a senior polymer chemist for Tenneco Polymers. In work supported by the Vinyl Institute, Bertelo measured the production of hydrogen chloride when polyvinyl chloride-coated electrical wiring was caused to burn by a power overload on the wiring. The wire was located in a 4-foot-high chamber above an 8-foot by 12-foot by 8-foot room. These conditions were intended to simulate real building conditions in which wiring is usually enclosed in walls or plenums.

Bertelo finds that even in conditions that lead to extensive decomposition of the polyvinyl chloride, as much as 30% of the hydrogen chloride formed is never released into the atmosphere. An additional 20 to 40% remains within a few inches of the site of decomposition. Less than half the hydrogen chloride produced is released into the general atmosphere. Deposition of the ma-

terial was so great near the wire, Bertelo says, that without extra circulation, the concentration in the adjacent room never exceeded 10 ppm. Separate studies by the Food & Drug Administration on baboons show tolerance levels for hydrogen chloride as high as 12,000 ppm, he adds. "It cannot be assumed that all the chlorine in polyvinyl chloride will be released as hydrogen chloride," Bertelo says. "In addition, provision must be made for the rapid decay of the product. . . . The hazard of polyvinyl chloride decomposition in fire situations is much less than originally thought."

For both wood and polyvinyl chloride, the shape of the object being burned affects the amount of smoke and toxic gases it will produce, says George V. Alexeeff, a toxicologist for Weyerhaeuser Co., Longview, Wash. A cubic piece of Douglas fir produced smoke and carbon monoxide much more slowly than did the same weight of wood in the form of shavings or a thin flat piece, Alexeeff says. Even after half an hour, when smoke production had reached its maximum for all three shapes of wood, the cube produced only about 4500 ppm of carbon monoxide, compared with 7000 to 8000 ppm for the flat piece and shavings. Similarly, in the Weyerhaeuser tests, a flat piece of polyvinyl chloride takes about 15 minutes to reach its maximum production of hydrogen chloride, compared with about 25 minutes for a cubic piece of the same weight. □

Progress reported in coupling LC and MS

The efficient coupling of liquid chromatography and mass spectrometry (LC-MS) has been a subject of continuing interest to practitioners of both arts (C&EN, Sept. 26, 1983, page 19). Evidence of recent progress in the field was presented at an LC-MS symposium sponsored by the Division of Analytical Chemistry.

There are at least two basic approaches to getting analytes out of the liquid chromatograph and into the mass spectrometer. In one, exemplified by moving belt interfaces, the solvent is evaporated from the LC eluate before the analyte passes into the mass spectrometer system. There it is ionized by conventional means. In another approach, the eluate, or a portion of it, is injected directly into an interface, where the analyte is ionized by one of several desorption techniques. The various techniques are competitive to a degree, but also complementary, because each has advantages and drawbacks, depending on the application.

At the symposium, several of the presentations focused on the mechanisms underlying the different LC-MS methods. For example, mass spectrometrist Robert J. Cotter of Johns Hopkins University noted that the thermospray technique (pioneered by Marvin Vestal at the University of Houston) is actually a desorption technique and therefore related to techniques such as fast atom bombardment (FAB), secondary ion mass spectrometry (SIMS), and electrohydrodynamic ionization (EH).

The thermospray technique is a desorption technique, Cotter explains, because the ions are formed within the buffered solvent matrix. The LC eluate enters the interface as droplets, from which the solvent evaporates until an imbalance of charges causes ejection of analyte ions. That happens, Cotter says, because the statistical imbalance of charges actually creates a high local field in the droplet.

A few years back, Cotter, working with Catherine Fenselau and other associates at Johns Hopkins, compared the relative abundances of doubly charged ions obtained with two desorption techniques: field desorption (FD) and FAB. In the absence of a field, doubly charged ions aren't easily observed, Cotter says, because they are more strongly attracted to the matrix than the singly charged ions. But in the presence of a high electric field, they should be favored. Indeed, experiments with bis-pyridinium salts showed that doubly charged ions were more abundant with FD than with FAB.

More recently, the idea was extended to comparisons of FAB and thermospray. Experiments involved tubocurarine hydrochloride, which has a divalent cation. In general, thermospray produced more modes of fragmentation, more fragment ions, and fewer molecular ions, compared with FAB. In addition, doubly charged ions were relatively abundant with thermospray, but almost completely absent with FAB. According to Cotter, the findings suggest that the ion formation mechanisms of the two processes are basically different.

In another mechanism-related presentation, Kelsey D. Cook of the University of Tennessee noted that many LC/MS interface systems exploit the LC eluate as a vehicle for solution chemical ionization, rather than expend effort to remove the solvent matrix before MS analysis, as is the case with the older moving-belt interfaces. In fact, Cook says, some of the newer moving-belt systems also rely on matrix assistance, by replacing the chromatographic solvent with a second solvent (on the belt) that facilitates FAB analysis.

With such systems, Cook says, one should consider the factors that affect how efficiently the process removes ions from a liquid matrix. They're important for quantitation of LC-MS, and also for determining the sensitivity and efficacy of other liquid desorption ionization processes, especially FAB and liquid SIMS.

In most of the LC-MS experiments to date, however, it is hard to distinguish the energetics of ion removal from the energetics of other processes taking place in the experiment, Cook says. As examples, he cites the heating that results from collisions with the hot probe used for thermospray and the ion-molecule reactions associated with chemical ionization in direct liquid introduction systems. These factors tend to complicate studies of basic mechanisms.

Electrohydrodynamic ionization, in contrast, depends on field evap-

J. JEFFERSON B-2-1 J. G. CARROZA B-1-5

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HIGHLIGHTS

1/24/84 - Someone will get back to me

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Polychlorinated Biphenyls

TRANSFORMER FIRES CONSTITUTE HEALTH RISK, PRODUCE DIOXINS, FURANS, EPA SCIENTIST SAYS

Fires associated with PCB electrical equipment constitute a "previously unrecognized health hazard by exposing persons in nonindustrial environments to toxic chemicals such as polychlorinated biphenyls, chlorinated dioxins, chlorinated furans, and other chlorinated organic compounds," according to an Environmental Protection Agency scientist.

Paul E. desRosiers, of EPA's Office of Research and Development, also found that PCB fires produce the highest concentrations of deadly polychlorinated dibenzo-p-dioxins and -furans found in the United States.

According to a paper recently submitted to the Electric Power Research Institute, desRosiers reached these conclusions after studying data from several fires involving PCB transformers and capacitors.

The information comes as EPA is attempting to determine what risks are associated with PCB transformer fires and whether federal regulations are needed to limit these risks.

Under a settlement reached with environmentalists challenging the 1982 PCB electrical equipment rule, EPA is required to issue an advance notice of proposed rulemaking in March to solicit information on transformer fires (Oct. 28, 1983, p. 1116). That information will then be used to determine whether regulations are necessary.

Dioxins and PCBs Correlated

EPA's research office is now in the process of securing soot samples from PCB electrical fires that occurred in Chicago, San Francisco, Syracuse, N.Y., and Binghamton, N.Y., desRosiers said.

The agency's analytical laboratory in Cincinnati, Ohio, will conduct a chlorobenzene isomer screen on the samples for the purpose of attempting to correlate the dioxin and furan content in soot and wipe samples with chlorobenzene and PCB content in the transformer fluid. This work should help EPA predict the amount of dioxins and furans that would be generated from the combustion of various PCB dielectric fluids, desRosiers explained.

In his paper, desRosiers noted that a 1981 study of soot from a PCB transformer fire in Binghamton, N.Y., demonstrated that dioxins and furans in the soot were biologically active. "The soot, therefore, can be considered toxic."

This is in contrast to data on fly ash from municipal incinerators. Although such fly ash is known to contain dioxins and furans, the chemicals are inactive in this form.

According to desRosiers' paper, there are 75 dioxin isomers and 135 furan isomers. Acute toxicity among the isomers can vary by up to 100,000 times, he said. By comparison, the most acutely toxic PCB isomer is only about one-fourth as toxic as the most toxic dioxin isomer — 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Chlorinated Benzenes

PCBs contain a complex mixture of furans, with up to 40 isomers being present, desRosiers said. He explained that although dioxins are not found in PCB transformers under normal conditions, they do occur when a transformer containing a mixture of PCBs and chlorinated benzenes undergoes combustion or thermal stress. The formation of dioxins is believed to be due to intermolecular reactions of chlorinated benzenes and oxygen under thermal conditions, the EPA scientist added. Thus, dioxins are produced only when chlorobenzene diluents are present in PCB mixtures, he added.

Furans, on the other hand, are found at various levels in almost all PCB transformers and capacitors, he said. However, the amount of these substances appears to increase with the age of the equipment and is generated at substantial levels when the equipment is under thermal stress.

In reviewing data from a PCB transformer fire in a 22-story office building in Binghamton, N.Y., desRosiers said analysis of soot samples found in the building showed furan isomers as high as 2,160 micrograms per gram of soot, dioxin isomers as high as 18-20 μg/g, and PCBs as high as 100,000 to 200,000 μg/g. DesRosiers said the most toxic dioxin and furan isomers were the major components within the soot, including 2,3,7,8-TCDD; 2,3,7,8-tetrachlorodibenzo-p-furan; 1,2,3,7,8-pentachlorodibenzo-p-dioxin; 1,2,3,7,8-pentachlorodibenzo-p-furan; and 2,3,4,7,8-PCDF.

"Since the tri- and tetrachlorinated benzenes comprise 35 percent of the dielectric fluid, it is not unreasonable to assume this diluent mixture represents the precursor to the PCDDs [dioxins] produced as a result of the fire," desRosiers concluded from the data.

DesRosiers also said that even after parts of the Binghamton office building were decontaminated using steam and detergents, trace amounts (nanograms per square meter) of furans and dioxins were still present.

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