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Combustion and Toxicity: Discussion

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Dr. Shakoor (Republic of Iraq): I have read that some phosgene is liberated through the burning of poly(vinyl chloride). Is this true, and, if so, how can it be explained?

Prof. Einhorn: This suggestion has been raised with many types of polymers. I have heard about it with polyurethanes, vinylidenes, chlorides. For this to happen there must be first a gem-dichloride, that is, a compound with two chlorines on the same carbon, or a molecule capable of forming such a compound. I would like to point out that we have run a series of studies looking for phosgene and have never found it. As Dr. Woolley and others have mentioned, moisture is present and the phosgene is readily hydrolyzable. However, we have tested our methodology by the introduction of phosgene in various levels, and have then been able to detect it. After the introduction of water vapor in a wide variety of concentrations, the phosgene is then destroyed. On the other hand, with fluorinated polymers, carbonyl difluoride has been found; we and others have identified it. It is more stable in a moist environment.

Dr. Delfosse (Université des Sciences et Techniques de Lille, France): Dr. O'Mara reported a self-ignition temperature of 450°C for PVC, which is 100°C lower than the temperature we measured in our laboratory. Could he tell us the precise conditions under which this self-ignition temperature was measured?

Dr. O'Mara (B. F. Goodrich Co., Avon Lake, Ohio, USA): No, but I could obtain that information. It is a typical literature value and I believe that an ASTM test is used to make that measurement.

Dr. Lahaye (Centre de Recherche sur la Physico-Chimie, Mulhouse, France): During Dr. Smith's extremely interesting presentation, he told us that he had been able to determine the mechanism of smoke production during the combustion of PVC. Would it be possible for him to outline this mechanism, please?

Prof. D. Smith (Queen Mary College, University of London, U. K.): There is a general paper now in press (British Polymer Journal), and I gave an introductory paper relating to this topic earlier this year at a British conference in Loughborough (Society of Chemical Industry Polymer Group, January 1976). This mechanism involves quite a lot of complexity, among other things, the Diels-Alder reaction so disliked by Dr. O'Mara. Depending on the temperature of combustion, we think that three or four different reactions can take place. Basically, the mechanism is similar to that for the combustion of hydrocarbons. We feel that there is dehydrochlorination followed by cyclization within the chain; the breakdown of the chain can take many paths involving secondary degradation which can lead to smaller products such as small olefins, and also to a build-up of intermediate products by ordinary condensation processes leading to polycyclic hydrocarbons: naphthalene, anthracene, and so on. The final stage, which is well established in petroleum chemistry, is dehydrogenation.

Rather than discuss this further, I will be pleased to send anyone interested a copy of the above mentioned paper, after which we can enter into correspondence about it.

Dr. Westerberg (L. M. Erikson, Stockholm, Sweden): With regard to Dr. O'Mara's oxygen index measurements, on two slides two different values of the oxygen index were given for rigid PVC: one was 40.7 and the other 43. Is this difference due to the presence of different additives in the PVC, or to inaccuracies of the method of measurement?

Dr. O'Mara: It is not due to experimental error, but to the presence of different additives in the polymer. In one study, in which the effect of plasticizer was being investigated, we put in those additives which were also in the plasticized compounds, i.e., processing agents and metal soap stabilizer. In the rigid PVC study we used a pure PVC, with no stabilizer or processing aids. Typically, there is a range in oxygen index from 40 to 47, the reason for the variation being the presence of all the various additives which generally increase the oxygen index.

Dr. Westerberg: What is your opinion about the accuracy of this measurement? Could you give it as 0.1%, 1% or 5% accuracy?

Dr. O'Mara: The accuracy of the oxygen index measurement depends on the material being measured and the system being dealt with. For example, we have tried to measure some polyurethane films and have found that the deviation can be as high as 40%. On materials with which the char burns fairly clearly, however, the measurements can be accurate to within 2%.

Prof. Einhorn: I published an article in one of the American Chemical Society journals—I would be glad to send reprints to anyone interested.

The oxygen index test, as first developed by Martin and Fennemore, was initially presented at the Wayne State Polymer Conference in 1966, which I chaired. At that time, as combustion chemists, they were describing what that test could do. Five years later, I saw a publication in which they used the rationale that there is 21% oxygen in the air, and, if there is 27%, a material does not burn. I agree completely with Dr. O'Mara that the oxygen index test, which is perhaps the most reproducible flammability test in the world, cannot—and should not—be related to real fires in any circumstances. It can, however, by change of oxidizer, tell us nicely whether there is condensed phase or gas phase burning.

One of my doctoral students carried out a study showing that the oxygen index test will hold fairly well, at least in terms of reproducibility, in the following conditions: if the diameter is varied—which is not done in the oxygen index test—if there is steady-state combustion, and a char or whatever it is, is being formed at the same rate and eroded also at the same rate. On the other hand, if there is a char—and any materials, both solid and porous, will form a char—so that there is not a steady state, the temperature variation across the char may vary by hundreds of degrees. Further, there have been some extremely interesting studies by Deduardo and Stutts, in which they talk about top burning and the bottom burning, lift-off, wick stabilization, and other factors.

Any discussion of oxygen index must go back to Dr. Kinnouri, presently at the Department of Aerospace Engineering, Notre Dame, who—as an extremely good chemical engineer—did a heat transfer, mass transfer, and oxygen index studies. He is now able to predict completely the effect of preheating, of additives, of materials with hydrates, and others. The oxygen index is not a magic test; it can tell us whether the fire retardant being used is working in the gas phase or the condensed phase, but it should never be used to say whether or not a given material will burn. For every material that

has an oxygen index of 50 or above, I will produce another that has an oxygen index of 15—we had one material with a value of 15 which went through a 5000 gallon JP4 fire and did not burn. Conversely, for each material with a low value I could show one with a high value which will perform in the same way. Let us use this test in the way that it should be used.

Dr. Ferrero (I. C. I. France, Clamart, France): As far as fire retardancy of plasticized PVC is concerned, could Dr. O'Mara explain the advantage of replacing, in the same economic conditions, PVC with C-PVC, rather than replacing part of the phthalate plasticizer, for instance DOP, by chlorinated secondary plasticizer, in order to obtain the best fire retardant properties? Such a secondary chlorinated plasticizer could be chlorinated paraffins.

Dr. O'Mara: If I understand the question correctly, I do not think there is any interest in replacing C-PVC.

Dr. Ferrero: It was given in your example.

Dr. O'Mara: Yes, but that was merely to illustrate a point about the chemistry of the process. There are a number of reasons why C-PVC cannot be used in many applications of PVC; for example, in wiring cable, to remove PVC and put in C-PVC does not solve the smoke problem. We have shown that by changing from PVC to C-PVC there is a much less smokey polymer, but once the plasticizer is added, the level of smoke is still there, suggesting that much of the smoke problem in flexible PVC is due to the presence of the plasticizer.

Dr. Ferrero: Yes, but the economic conditions are not the same. When PVC is replaced by C-PVC, the cost is doubled.

Dr. O'Mara: That is true. What I was advocating in my paper—this relates to Dr. Smith's comment about my finding a gas phase Diels-Alder reaction so unacceptable which, in fact, is not correct—was that there are additives for PVC which can be used to reduce smoke and increase char to the extent that occurs in C-PVC during thermal decomposition. I do believe that Diels-Alder chemistry is involved in char formation (i.e., a condensed-phase Diels-Alder reaction) but not involved in benzene formation that occurs in the condensed phase. Post-chlorinating PVC results in a molecular structure that upon thermal decomposition leads to significant char formation. If the nature of this chemistry were understood, similar chemistry could be employed with PVC. I am not advocating C-PVC as an economical replacement for PVC, only as a model for improvement.

Dr. Stapfer (Ste. Metrastat, Paris, France): Can the panel tell us whether or not there is an acute need for laboratory instrumentation to measure the fire properties? I am speaking in terms of small-scale experiments where there seems to be such a need. Clearly, we are dealing with several parameters. What would be the "ideal" instrument for testing or for screening either additives or fire resistant compounds? I mean ideal in terms of a few selected parameters which would allow the investigator to get some sort of general view of the problem, even if not the total picture.

Dr. O'Mara: Relating my remarks to PVC only—because Professor Einhorn can answer it more generally, perhaps on a broader basis—for example, we know enough from animal experiments now to be certain that hydrogen chloride plays a significant role in the intoxication caused by the burning of PVC. In our laboratories, we monitor hydrogen chloride, carbon monoxide, carbon dioxide, total aromatic and aliphatic hydrocarbons by infrared spectrometry. The reason for that choice is that since we look at additives and new polymer approaches to modify the combustion process, we feel that those particular outputs will indicate when we have produced an improved product. Judgement about these measurements has to be made according to the polymer being investigated. With a nitrogen-containing polymer, for example, nitrogen oxide and hydrogen cyanide must certainly be monitored.

Prof. Einhorn: I should like to answer the question more in the aspect of the total flammability characteristics. First, it must be realized that a good and safe use in one application may be highly desirable to avoid in a second. For instance, the flammability characteristics of a carpet in a bedroom or living room as compared with the same carpet in a car driving along at 55 mph, or in an aircraft approaching Orly Airport at 3300 feet have different probabilities. We must state the probability of a material in its service life of being exposed to a heat source. Given that probability, what is the conditional probability of ignition; given ignition, will it smoke; given smoke and degradation, will it be toxic? If we consider that aspect, nobody in his right mind would use a nitrocellulose fiber for a dress because it would fail the simplest of heat or ignition tests. Thus, we have one point on a decision tree: if a material in a laboratory cannot pass a simple burner test, we rule it out because of flammability. We make the decision whether we can improve upon it and can it be done economically? If we can, we then run a simple test, perhaps something like an oxygen index, a burn-through, or a flame propagation test. Finally, when a level is reached at which we can say that the material has certain properties—no single test will tell

us this—we then move to the next level of testing. Perhaps we consider toxicity and a first-tier screening test: does it produce anything "super toxic" perhaps eight or ten times more toxic than carbon monoxide? If it does not, the material passes that first-tier test. Probably the next approach would be to try the next scale-up. It is to be a building product, this would be a corner or a room test. From the small-scale to the large-scale test, at each point, we have to weigh up the end use, the service life, and the probability of it being exposed to fire. From all these measurements we begin to develop a judgment tree, realizing cost effectiveness and risk analysis too. A carpet on the floor in this room could have its properties changed if we could have a sprinkler and detector system. This might mean that we could tolerate a more flammable carpet because we know that it would not catch fire because of these sprinkler and detector systems.

Dr. Woolley (Department of the Environment, Borehamwood, U. K.): I do not want to go much further than Prof. Einhorn and Dr. O'Mara, other than going along with what has been said about it being a matter of building up from the laboratory work within what Prof. Einhorn called the "decision tree." The further a material can go up that decision tree, the nearer we are towards obtaining a practical situation. We start by taking out a material. If we want to go to basics, this can be a box of matches or a cigarette end. We can start from this and go one step up the ladder. We climb up the ladder, and the further up the ladder, the nearer we get to the final fire hazard of that material in the situation of its intended use. That is a long, difficult tree to climb up. The further we go up it the more confidence is gained.