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B. F. Goodrich Chemical Company

A DIVISION OF THE B. F. GOODRICH COMPANY

DEVELOPMENT CENTER

"smoke"

RESULTS OF THE EXPOSURE OF TEST RATS TO THE COMBUSTION PRODUCTS FROM B.F.G.C.C. PRODUCTS

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Abstract

This report presents a summary of the background leading up to our first animal combustion-exposure experiments, the current philosophy behind this kind of testing and current limitations with the testing.

Twelve key materials involving the following product lines (Eston, Abson, PVC, Hi-Temp) were chosen for this initial evaluation. All experiments were carried out at U. S. Testing using a modification of their testing protocol. In summary, ten out of the twelve submitted materials performed worse than wood. One smoke retarded PVC formulation was much superior to wood.

An analysis of the data indicates that 5 out of the 10 materials were worse than wood because of the amount of combustion products produced; the remaining 5 samples were worse than wood because of the kinds of combustion products produced.

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I. Introduction: Problem Development

The need to obtain bioassay data on the combustion products from BFG plastic materials has been increasing significantly over the past two years. Federal programs aimed at the toxicity of combustion products from synthetic materials, in general, have all involved both analytical and bioassay measurements. This activity has increased very significantly in 1974-75 with federally sponsored programs at University of Utah, University of Pittsburgh, Harvard University, the National Bureau of Standards, the University of Michigan and the Federal Aviation Administration. Specific programs at these institutions have already been discussed⁽¹⁻⁴⁾. The following pertinent information has developed from all of these programs:

- (1) toxicity defined in terms of analytical measurements is meaningless without substantive animal exposure data and,
- (2) animal exposure experiments generally involve brief exposures (15 minutes - 60 minutes) accompanied by high gas concentrations (1,000 - 10,000 ppm).

Earlier this year, I carried out a survey of pertinent animal exposure capabilities around the country and proposed in-house, in-depth testing⁽⁵⁾. Since we do not have the in-house resources to carry out such a program, it was decided that an outside testing approach should be considered⁽⁶⁾. One of the facilities surveyed by me⁽⁵⁾ seemed to fit this approach, so a program was developed to expose the combustion products from 12 key BFGCC products to test animals^(7, 8).

The purpose of this report is to summarize the results of these first exposure experiments.

II. Desired Testing Protocol

Current research involving the exposure of test animals to combustion gases appears to have the following characteristics:

- (1) smoldering combustion - flaming combustion is usually avoided because it invariably leads to hyperventilation (from CO₂), anoxia (from O₂ depletion) and thermal stress. Also, it is recognized by many that the smoldering products of combustion (generated by intense flaming combustion elsewhere) are generally responsible for life loss in a fire. This concept is still the subject of much current debate within the fire research community.

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(2) sample size and exposure volume?

It is obvious that the rate and degree of animal intoxication is very strongly dependent upon combustion gas concentration in the exposure experiment. This, in turn, is dependent upon the amount of sample that is consumed and the volume into which the combustion products are dispersed. Typically the ratio of mass lost during combustion to the total volume of exposure is measured. Ratios currently used by combustion toxicologists range from 50 to 500 mg/liter. In general, very little animal response is recorded below this range (i.e., 0% response) while extremely intense responses are recorded above this range. To put this engineering ratio in perspective, it should be noted that the ratio for the NBS Smoke Chamber is 10 - 20 mg/liter. This value indicates the reason why the NBS Smoke Chamber is generally not used as a toxicity chamber. Recently, the University of Utah has extended this mass/volume ratio in the NBS Chamber by increasing the output of the radiant heater to 5.0 watts/cm² thereby increasing the mass loss in a typical sample. They have observed significant mortality induced by PVC combustion products for a m/v ratio of 30 - 40 mg/liter⁽⁹⁾.

(3) exposure time

Experiments described in the literature on the exposure of test animals to combustion products have ranged in exposure times from 5 minutes to 4 hours. Current research seems to be settling into the 15 minute to 60 minute exposure range. Clearly the four hour exposure is not representative of a real fire hazard; in fact, any exposure over 1 hour may not be relevant to the hazard that is being modelled.

(4) response measured

Historically, the end point in a combustion inhalation experiment has been animal mortality. Recently research has been directed toward animal incapacitation, which in turn is monitored through "avoidance response" experiments. Typically an avoidance response is elicited from the animal through an external stimulus (i.e. electrical shock); once incapacitation in the animal is attained, in this case through combustion gas exposure, the animal then no longer avoids the external stimulus.

Philosophically, an avoidance response experiment is much preferred to a mortality experiment since the fundamental hazard in a developing fire is the incapacitating syndrome (or syndromes) that precedes death. Unfortunately, the research on avoidance response in combustion toxicology is in its infancy. Therefore, typically,

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animal mortality is monitored in a combustion inhalation experiment. These measurements are usually of the following type:

- (i) time to 50% mortality for a fixed mass of material or
- (ii) variable mass to induce 50% mortality for a fixed exposure time.

Economics usually decide which experimental approach will be taken. Experimental approach #2 is more definitive but much more costly. An improvement on approach #2 was made at the University of Michigan recently in which the mass-of-material range for inducing a 0 - 100% mortality range (fixed exposure time) was determined⁽³⁾.

III. The U. S. Testing Protocol

A. Procedure

It is obvious from the above discussion that as we get into this area of testing and establish data on BFG products, the following information would be most desirable in order of descending priority:

- (1) incapacitation/biological examinations
- (2) mortality
 - (a) multiple dose (mass range) - multiple response (mortality range) curve,
 - (b) multiple dose (mass range) - single response (50% mortality) point,
 - (c) single dose - single response point.

The cost, associated with these levels of testing, ranges from \$8,000 - \$15,000 for (1) to \$250 for (2c). Obviously the knowledge obtained from any testing protocol is more or less proportional to the amount of money spent.

In an attempt to minimize cost and yet establish a baseline that is representative of the testing that is now going on around the country, U. S. Testing Co., Inc. was chosen for our first animal exposure experiments. In the U. S. Testing protocol, the following procedures are carried out:

- (1) 10 test rats are placed in a 40 liter animal exposure chamber (glass),

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- (2) the test sample is exposed to radiant heat in the absence of an igniting flame in a 20 liter combustion chamber,
- (3) the time of exposure is variable; the test is stopped when one half of the animals are dead or one hour whichever occurs first,
- (4) The test has been designed so that wood induces 50% mortality for some period of time under 60 minutes,
- (5) combustion gases formed in the combustion chamber are circulated through the animal chamber at a rate of 8 liters/minute (4 liters/minute raw combustion gases + 4 liters/minute outside air),
- (6) materials are evaluated with respect to the time to 50% mortality,
- (7) U. S. Testing recommends an exposure temperature of 275°C and that materials be evaluated on an equal volume basis.

A schematic of the U. S. Testing procedure is shown in Figure 1 along with pertinent parameters relating to the test. Photographs of the combustion chamber with radiant panel (Figure 2) and the animal exposure chamber (Figure 3) are also shown.

B. Discussion of Procedure, Limitations and Testing Philosophy

Before discussing the U. S. Testing procedure and limitations thereof (as viewed by the author), it must be emphasized that a "standard test method" for combustion toxicological testing does not exist. Indeed further modifications of the procedure described above will be made as the entire science of combustion toxicology grows and matures. Thus the procedure described above should not be considered sacrosanct. In an effort to discuss the U. S. Testing procedure, its relevancy to other testing procedures, and its limitations, I pose the following questions which have been directed to me by a number of people:

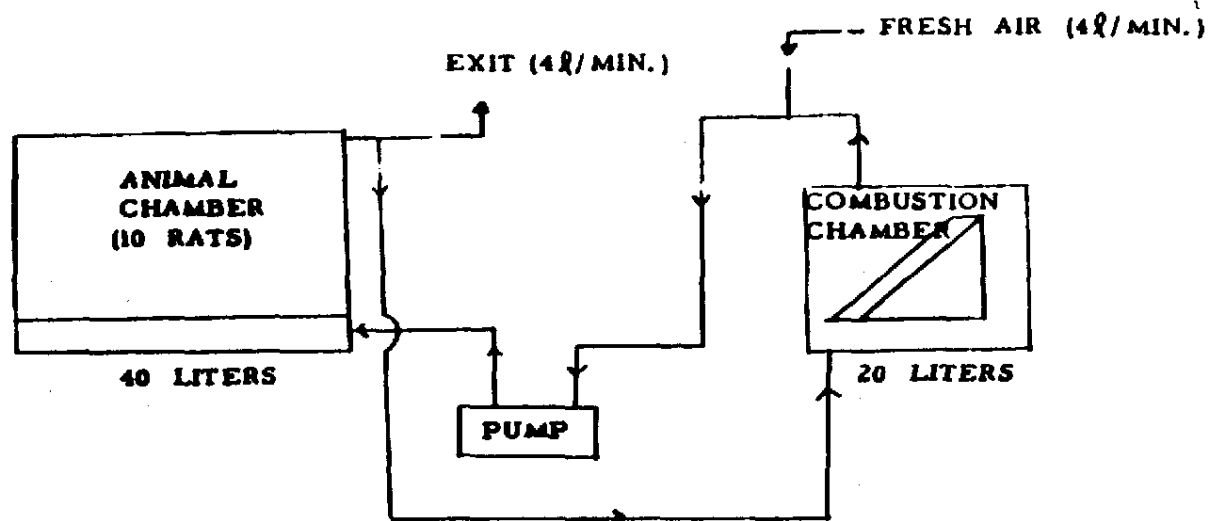
- (1) Since fires involve flaming combustion, why does the procedure call for smoldering combustion?

As noted before, flaming combustion leads to experimental problems (heat stress, anoxia, hyperventilation) with the test animals. Secondly, an intense fire will create a thermal front or wave that will create significant pyrolysis in materials closeby.

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Figure 1

U. S. TESTING PROTOCOL



CIRCULATION RATE: 8 LITERS/MIN.

EXPOSURE TEMPERATURE: 400°C

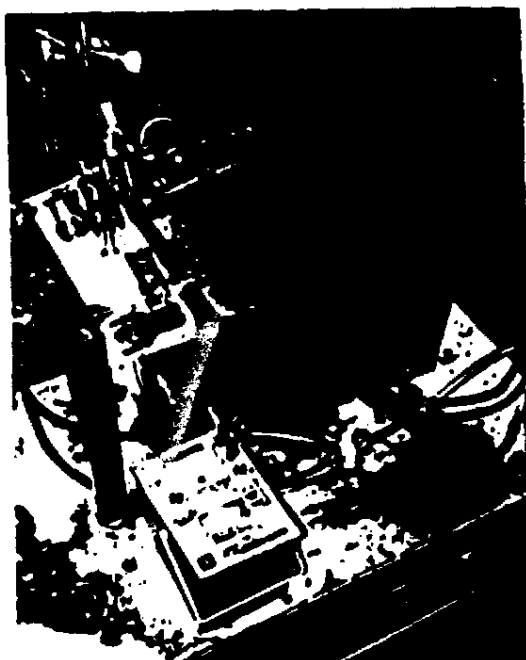
MASS MATERIAL EXPOSED: ~150g

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Figure 2

Photograph of U. S. Testing's Combustion Chamber (20 liter volume)



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Figure 3

Photograph of Animal Exposure Chamber (40 liter volume)
and Combustion Chamber



- A - animal exposure chamber
- B - combustion chamber
- C - 150 gram sample of Hi-Temp

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Another question arises with respect to the fact that heat stress, anoxia and hyperventilation are real problems in a fire and probably should be modelled. At this point we can only guess at the importance of these three effects. Certainly hyperventilation caused by CO_2 is much more important than heat stress (a statistically significant group does not die from burns) or anoxia (Fristrom's work at Johns Hopkins showed that in a full-scale fire, oxygen depletion is not an important hazard except in and very near to the fire room).

(2) Why is the exposure temperature 275°C?

In my opinion, this is the weakest part of the procedure. U. S. Testing feels that this is a good model for a low intensity fire or the early stages of a fire and thus describes the initial gas hazards in a fire. Frankly, I don't feel that this argument is entirely valid and I strongly suspect that an exposure temperature of 275°C will be rejected by most in the fire community. Historically, inhalation combustion experiments have usually involved exposure temperatures in the 450°C - 550°C region. The NBS Smoke Density Chamber is based on an exposure flux of 2.5 watts/cm² or approximately 580°C.

(3) How sensitive are the test results to exposure temperature?

I feel that this may be the most important variable in an inhalation experiment. For example with respect to smoke, which is only one "product of combustion", it has been shown that in changing the flux from 2.5 to 5.0 watts/cm², the ranking of materials will change significantly. Recently, Zinborn has stated (though I have not yet seen the data) that the combustion products from wood are more lethal when generated at low fluxes (1.0 - 2.0 watts/cm²) than at high fluxes (2.5 - 5.0 watts/cm²).

(4) How relevant is the U. S. Testing model to the current state-of-the-art?

Based on the following attributes of the U. S. Testing procedure, I believe that this protocol is as good (i.e. relevant) as any of the others:

- (a) combustion is based on both a radiant heater and a significant mass of material (as opposed to a bunsen burner and quartz tube),
- (b) Oxygen depletion is rigorously avoided,
- (c) the mass loss/volume ratio (100 - 300 mg/liter) is in line with other procedures,
- (d) exposure times are very reasonable,

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- (e) the experiment is based on a sizable number of animals (5 male + 5 female rats),
 - (f) the experimentalist (K. Mohrmann) is very capable in terms of understanding the response of test animals to combustion products.
- (5) How significant is this particular model or any animal exposure model to a real fire hazard?

Probably not very significant because (1) people in a fire situation are not forced to remain in a cage and (2) fires involve a mixture of materials and the interaction of materials in a fire may be more important than the performance of single materials. However, the political reality of this problem must be faced. First, it is obvious that a number of regulations are based on animal experiments that may or may not relate to man. Clearly the VCM problem relates to both yet the cyclamate ban may be (1) based on inaccurate animal experiments, (2) is not based on any actual human cancers. Secondly, there is obviously a historical precedence in using small scale experiments to regulate materials. The NBS Smoke Density Chamber has been used in regulations yet the same questions of relevancy exist with this test.

- (6) U. S. Testing judges performance on an "equal volume of material" basis. Wouldn't mass or surface area be more relevant?

This decision by U. S. Testing is currently based upon recent communications between U. S. Testing and the International Code of Building Officials (ICBO) in their (ICBO) effort to establish a testing protocol and thereby enforce the toxic gas requirement that is currently on the books. Our company feedback to and from ICBO has been very minimal so I cannot judge why this performance basis was chosen. Historically, the precedent, again relative to the NBS Smoke Chamber for material evaluation, is based upon constant surface area and end-use thickness (up to 1/2 inch). Another complication with respect to testing must be brought up. In our smoke retardant research work within the company, research-based testing is done on an equal surface area and equal mass basis (i.e. lb/g) while performance-based testing is done only on an equal surface area basis. The mass criterion in this case is a function of the particular end-use application. To make a long story short, we really have 3 bases upon which to judge materials in an animal exposure experiment:

- (i) equal area/end-use thickness
- (ii) equal area/constant volume
- (iii) equal area/constant mass

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From a performance standpoint, #1 would be most reasonable but from a research standpoint (what is causing animal mortality, why and how to correct) #3 would be desirable.

Our experiments at U. S. Testing were all carried out on an equal area/constant mass basis; it is obvious that if the performance-criterion is ultimately based upon an equal volume basis, then our current experiments will be of little value in ascertaining performance. Since wood has a much lower density than most of the plastic materials we investigated, our experiments at constant mass will have been too mild if an equal volume criterion is called for. It is obvious that the yet-to-be established ground rules will play a very significant role in the comparison test involving our materials and wood.

C. Limitations with the U. S. Testing Procedure

There are a number of limitations inherent with the U. S. Testing procedure. These are listed below and discussed in depth.

(1) basis for performance-evaluation:

This has been discussed above but it needs the attention of those who are interacting with the code groups.

(2) thermal exposure conditions:

Rather than expose the material to a constant temperature in which energy is increased or decreased during the experiment in order to maintain a constant temperature directly in front of the sample, a fixed energy input along the lines used in the NBS Smoke Chamber should be used. There are indications that U. S. Testing is moving in this direction; fixed energy inputs at 1.5 watts/cm² and 3 watts/cm² (or related values) would be highly desirable.

(3) animal's body wastes problem:

During exposure, the test rats constantly release their body wastes and these remain in the cage during exposure. This is a very important parameter; Cornish (University of Michigan) showed in 1968 that animal urine is a very efficient hydrogen chloride scrubber. I recommended to U. S. Testing that this problem be corrected. I don't believe we want inhalation combustion data that is based on experimental artifacts as described above. Unfortunately, I did not realize the significance of this problem until we were half way into our testing program at U. S. Testing.

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Thus all data in this report is based upon the presence of the animal waste artifact. This artifact will tend to positively influence the performance of those materials that produce acid gases during combustion. I cannot, at this time, ascertain the magnitude of this artifact on the test results.

IV. Test Results on B.F. Goodrich Materials

A. Materials' Selection

The objective of this study at U. S. Testing was to screen key BFG products (commercial formulations) with respect to fire retarded and non-fire retarded formulations. The choice of materials was more or less based on those product lines that would be susceptible to toxic gas regulations. For example, while our analytical studies indicate that Hycar may exhibit a problem with respect to hydrogen cyanide evolution during smoldering combustion⁽¹⁰⁾, this material was not chosen for evaluation because the significant market here is in automotive under-the-hood applications; this market will not be subjected to toxic gas regulations.

The materials chosen and comments relating to those choices are summarized in Table 1. In summary, 12 key products involving the Abson, Hi-Temp, PVC, and Estane product lines were chosen for evaluation.

B. Specific Testing Procedure

For all materials, except wood, approximately 140 - 150 grams of material was placed in the combustion chamber and exposed to 400°C in the absence of an igniting flame. The experiments were continued until 50% of the animals died (by visual observation) or 1 hour whichever occurred first. The animals were then removed from the exposure chamber, placed in wire cages, and post-observed for two weeks. All materials were evaluated relative to white pine and the basis of this evaluation was the time to 50% mortality (TLD₅₀).

C. Analytical Results

The following analytical measurements were made during the exposure experiments: mass, mass loss, minimum O₂ recorded in animal chamber during experiment and the time of death for each animal. In this section, this death data is summarized in terms of an average time to death (TLD₅₀) for a 50% population and the total death incidence (% mortality). It should be emphasized that it is impossible to carry out an experiment where an exact 50% mortality is recorded. Typically, the mortality is higher than this because some of the animals that survive the exposure are so intoxicated that recovery is not possible. The time of each animal's death for all experiments is recorded in the Appendix.

A summary of all analytical data is contained in Table 2.

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Table 1

MATERIALS FOR ANIMAL TESTING VIA COMBUSTION TOXICOLOGY

<u>Material</u>	<u>Comment</u>
<u>PVC/CPVC</u>	
Geon 8750	Control
8750 + 35 phr Al. hydrate + 6 phr B/N ⁽¹⁾	Current low smoke (near commercialization) PVC compound
8750 + 35 phr Al. hydrate	Another low smoke compound nearing field testing
8750 + 1.5 P/8.5 N ⁽²⁾	Per D. Dickens recommendation
8804 Blk 288	Non-fire retarded flexible jacketing compound
8737 Blk 289 ⁽³⁾	A representative fire retarded flexible formulation
3010	Hi-Temp compound
85721 Nat. 020	Expanded formulation
<u>ABS</u>	
89129 ⁽⁴⁾	Current fire retarded Abson compound
820X16 + lubricant	Identical to 89129 except does not contain fire retardants; A:B:S ratio is identical to that in 89129
<u>Estane</u>	
X430	These two compounds are a result of new fire retardant technology; polymer modification has been carried out to improve drip resistance; these are near commercialization.
X430 + drip/fire retardant ⁽⁵⁾	
<u>Non-Plastic Controls</u>	
pine wood	As per U. S. Testing procedure
wool fabric	This has been included as an example of a nitrogen containing natural product; recent NBS smoke chamber studies suggest very high levels of hydrogen cyanide during smoldering combustion.

(1) Refers to 3 phr bismuth subcarbonate + 3 phr nickel oxide.

(2) 1.5 phr iron oxide + 8.5 phr iron oxide.

(3) Antimony oxide retardant.

(4) Fire retardant is based on PVC + antimony oxide composition.

(5) Based on dechlorane, antimony oxide, chlorinated polyethylene.

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Table 2
SUMMARY OF ALL DATA FROM U. S. TESTING ANIMAL EXPOSURE EXPERIMENTS

Material	Mass, g	Mass loss, g	Min. O ₂ ⁽¹⁾ in Chamber	LD ₅₀ ⁽²⁾ Minutes	% Mortality ⁽³⁾	U. S. Testing ⁽⁴⁾ Ranking
Ammon. Nitrate	149	82	19.0	6.8	100%	1
Ammon. Nitrate + T.C.	147.5	14.5	19.5	8.1	100%	3
Oil-Temp. 1010-109	147	28	17.3	15.8	70%	10
Green Ammon. Nit. 288	150	57	19.5	8.8	100%	4
Green Nit. 288 ⁽⁵⁾	145	62	15.0	14.9	100%	9
Explosive X-10	142	77	17.0	10.1	100%	5
Explosive X-10 + T.C.	149	68	17.0	8.3	50%	2
Green Nitro	146	36	19.3	41.4	80%	12
Green Nitro + 35 phr hydrated alumina + 35 phr Bi/Ni CPA	147	18.5	19.0	no deaths during exposure	0%	14
Green Nitro + 35 phr hydrated alumina	146	26	18.0	13.9	90%	8
Green Nitro + 10 phr Fe/Ni CPA	189.5 ⁽⁶⁾	28	20.5	11.1	90%	7
Green Nitro + 10 phr Fe/Ni CPA	145	37	19.5	10.8	90%	6
Wood (control)	143	26	18.8	39.0, 36.6 ⁽⁷⁾	60%	11
Wood (control)	39	10	19.0	35.5 ⁽⁸⁾	40%	13

(1) This is the minimum oxygen level that was recorded in the animal cage during exposure.

(2) Expanded data contained in Appendix.

(3) These deaths occurred during the test or immediately after.

(4) 1-worst; 14-best

(5) A fire-retarded flexible formulation.

(6) The mass of material in this run was too high; however, since we are into a "thermally thick" region, reducing the mass to 145g will probably not affect the mass loss significantly; this material will be rerun.

(7) Second value obtained by U. S. Testing at their own cost.

(8) For 40% mortality.

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D. Discussion

Of the 12 BFG products submitted by us, U. S. Testing has ranked them in the following decreasing order (see Table 2) of hazard:

Abson > f.r Estane > f.r. Abson > Geon 8804 >

Estane > Geon 85721 > Geon 8750 + 10 phr Fe/Ni >

Geon 8750 + 35 phr hydrated alumina > Geon 8737 >

Hi-Temp >> wood > Geon 8750 >>>

Geon 8750 + 35 phr hydrated alumina + 3 phr Bi/Ni CPA

Thus ten out of the twelve materials are worse than wood while one material is superior to wood and one material is far superior to wood. The worst material was Abson 820X16. This material literally exploded, (observed by W. C. Bachtel) and resulted in the generation of a rapid, highly concentrated dose of combustion gases. The situation in the animal exposure cage after 7 minutes into this experiment is shown in Figure 4; note the brown, heavy smoke - all animals were dead or near death (totally incapacitated) at this point.

A comment on the wool experiment is in order. It will be noted in Table 2 that the amount of material tested in the experiment with wool was significantly lower than all other experiments. This was done so that another "100% dead, short time to death" data point was not obtained. Thus, it absolutely can not be concluded that wool is safer than wood because the evaluation was not done on an equal mass basis. If it had been, there is no doubt in this author's mind that wool would have been one of the worst materials. However, this decision to reduce the mass of wool in the experiment was made on purely analytical grounds.

In an attempt to analyze these results, a brief review of the factors that lead to animal mortality is in order. There are two significant factors that control animal mortality in a combustion-inhalation experiment: the kinds of combustion gases and the amounts of combustion gases. If, for example, there is evidence that a large amount of combustion gases is generated and animal mortality is low then one must conclude that the toxicity of those combustion gases is low (Case I). On the other hand, if a small amount of combustion gases are generated and animal mortality is high, then one must conclude that the toxicity of those combustion gases is high (Case II). Finally, the third situation is the case where a large concentration of combustion gases are released and animal mortality is high (Case III). In this situation, one cannot conclude anything about the toxicity of the combustion gases because the detector (animal) has been overwhelmed by either a high concentration of moderately toxic gases or a low concentration of highly toxic gas in the presence

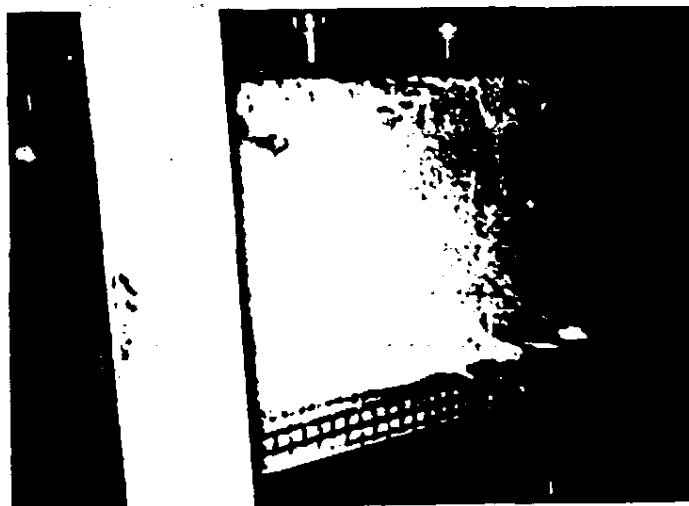
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Figure 4

Animal Exposure Chamber After 7 Minutes Into Experiment
With Abscon 820X16



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Material	Mass loss, g	LD ₅₀ , minutes
(1) Wool	10	35.5
(2) F.R. Abson	14.5	8.1
(3) Geon 8750 + CPA	18.5	no deaths
(4) Geon 8750 + hy. al.	24	13.9
(5) Wood	26	39.0
(6) H1-Temp	28	15.8
(7) Geon 8750 + 10 phr CPA	28	11.1
(8) Geon 8750	34	41.4
(9) Geon 85721	37	10.8
(10) Geon 8804	57	8.8
(11) Geon 8737	62	14.9
(12) Kacene XA30 + P.R.	68	8.3
(13) Kacene XA30	77	10.1
(14) Abson 820X16	82	6.8

of a high concentration of non-toxic gases. The significance of this final case is important in viewing our results at U. S. Testing and trying to understand why the animals died. Ideally we would like to compare materials on an equal "concentration of combustion products" basis. However, this is impossible because of the varying thermal stability of materials. Some products literally explode during the exposure while others tend to char and produce a surface that protects the underlying virgin material from the heat. An example of the former is Abson 820X16; an example of the latter is Geon 8750 + smoke retardant. The analytical measurement that allows an assessment of the quantity of the combustion products is the mass loss. Thus, if materials are assessed in light of their mass loss during combustion, something can be said about the toxicity of the combustion products and why the animals died. Fortunately the materials that were tested did exhibit a wide range in mass loss (10 grams - 68 grams). If materials are listed according to their mass loss and are then compared on a LD₅₀ basis, a number of interesting conclusions are reached. This listing is shown below:

In analyzing this list and in light of the three classifications discussed above, it is apparent that materials #10 - #14 (see list, above) fall into a Class III category. That is, these materials are hazardous, not because their combustion products are especially toxic, but rather because a high concentration of combustion products were formed. As with any Class III material, we can say nothing about the degree of toxicity of the combustion products. It is interesting to note that the average mass loss to volume ratio for materials #10 - #14 is approximately 700mg/liter* whereas it is only 120mg/liter* for wood. Clearly the low thermal stability of these materials, and not any unusual set of combustion products, is responsible for their poor performance in the test.

Materials #4, 5, 6 and 7 all exhibit about the same mass loss yet the three plastic materials (#4, 6, 7) are significantly worse than wood (#5). This is, therefore, a Case II situation in which the toxicity of the combustion products from samples #4, #6, #7 are worse than those from the wood control.

Comparing material #2 to wood (#5), the combustion products from this material are significantly more toxic than those from wood.

Along the same lines of reasoning, one must conclude then that the toxicity of the combustion products from sample #8 (Geon 8750) is less than that from the wood control.

Sample #9 (expanded vinyl) also seems to be a Case II situation. Comparing this sample to sample #8 (rigid 8750), it can be seen that the combustion products from #9 are more toxic (significantly) than those from sample #8. This comparison of sample #9 with Geon 8750 rather than with wood is necessary because of the similarity in mass losses between sample #9 and Geon 8750.

Finally, materials #1 and #3 (wool and Geon 8750 + CPA) present an interesting case. Material #3 exhibited one of the lowest mass losses and subsequently none of the animals died during the exposure. Wool fabric (#1) on the other hand exhibited the lowest mass loss yet 40% of the animals died. Either the wool fabric is very bad and the modified Geon 8750 is good or the wool fabric is moderately bad and the modified Geon 8750 is very good.

*This value was obtained by the following treatment:

$$M/V = \frac{\text{mass loss (mg)}}{V_1 + V_2 + f_3 t_3}$$

where V_1 and V_2 are the chamber volumes, f_3 is the clean air flow into the experiment (liters/min.) and t_3 is t_{LD50} (in minutes).

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In summary, the above treatment indicates that there are two classes of materials that are bad but for different reasons. One class of materials (#10 - #14) exhibits a high degree of toxicity of combustion products because a very high concentration of combustion gases are produced. This in turn is due to these materials' low thermal stability in a high temperature environment. Another class of materials (#2, #4, #6, #7, #9 (perhaps)) exhibits a high degree of toxicity of combustion products because their combustion products are more toxic than those from wood.

In the final evaluation though (regulations), it really doesn't matter why a material is worse than wood, only that it is. Yet this distinction is important to us since solutions to one problem (or class) may not be solutions to another problem.

It must again be emphasized that these experiments are in essence only a single experiment. We know very little about the reproducibility of the test (it appears to be reproducible with respect to wood) and the test will undergo modifications as the science of combustion toxicology matures. However, I believe these results, when viewed in light of current research in this field, are reasonable and suggest that a continuing and sustained effort in this area is not only justified but important to our future growth in the market that is affected by this kind of legislation.

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APPENDIX

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This section contains a more thorough listing of the animal test data than is contained in Table 2. Listed below are:

- (1) materials tested
- (2) individual animal death times
- (3) post exposure deaths and times end
- (4) two-week survival.

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Material	Animal No.:	Time of Death (minutes)										Post-Exposure Deaths (total number/hrs.)	Animal Survival (# out of 10)
		1	2	3	4	5	6	7	8	9	10		
wood		36.5	37.0	38.0	41.5	42.0	42.0					1/24	3
Absom 820X16		6.75	6.75	6.75	6.75	6.75	7.0	7.0	7.0	7.0	7.0	0	0
NI-Temp		7.5	8.0	8.0	8.5	8.5	8.5	8.0				3/0.5	0
Geon 8804 Blk 288		8.5	8.5	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	0	0
Geon 8737 Blk		14.5	15.0	15.0	15.0	15.0	15.0	15.5	15.5	15.5	15.5	0	0
Estane X430		9.0	10.0	10.5	10.5	10.5	11.0	11.0	11.0	11.0	11.0	0	0
Estane X430 + f.r.		8.0	8.0	8.3	8.5	8.5						0	5
Geon 8750		40	39	42	42.5	43.5	44.0	44.0				1/0.5; 2/48	0
Geon 8750 + 35 phr hydrated alumina + 3 phr Si/Mi			no deaths during exposure										0
Geon 8750 + 35 phr hydrated alumina		13.5	13.5	14.0	14.0	14.5	14.5	14.5	14.5	14.5	14.5	1/0.5; 1/24	0
Geon 8750 + 10 phr Fe/Mi based smoke retardant		10.5	10.5	11.0	11.5	12.0						4/0.5; 1/24	0
Geon 85721 Mat. 020		10.5	10.5	11.0	11.0	11.0	11.5	11.5				2/0.5; 1/24	0
wool (control)		20.5	21.5	30.0	70.0							1/24	5

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Even in light of these considerations, the problem is manageable. For specific plastics, the major combustion toxicological hazard can be approximated and, therefore, can be approached scientifically. While PVC may produce 60 combustion/degradation products, three of these probably account for 99% of the toxicological response in test animals: hydrogen chloride, carbon monoxide and benzene. Medical research may eventually show that aromatic hydrocarbons play a role in transporting hydrogen chloride into the biological system. Thus, analytical work on PVC products which is geared toward hydrogen chloride, carbon monoxide and total hydrocarbon analyses* will go a long way in establishing cause and effect in animal experiments.

In nitrogen containing polymers (Nycar, Abcon, Estane), there are specific combustion products again that probably contribute significantly to toxicology. Specifically hydrogen cyanide, hydrogen halides (from fire retardants), nitrile compounds, nitrogen oxides and carbon monoxide are of greatest concern. Well designed animal exposure experiments coupled with analytical data will show which of these products are of the greatest concern. From our analytical studies alone, we know that hydrogen cyanide generation from Nycar is significant⁽⁴⁾ but is negligible from non-fire retarded Estane⁽⁵⁾ under smoldering conditions.

Status at ALTC for Monitoring Combustion Gases

Over the past 4 years we have slowly built up our capabilities in the area of combustion gas monitoring. As this development took place, a problem in data handling developed. Fortunately, earlier this year we moved into our new flammability lab and attacked the problem of handling the massive amount of data that can result from combustion gas experiments. G. Smith has been given the assignment of interfacing six of our outputs to a data handling system. As of 10/1/75, this project was 95% complete. A summary of the combustion gases that we can analyze and methods of analysis and data handling are summarized in Table 1. Currently we are developing a new method of analysis for hydrogen cyanide based on electron capture gas chromatography and we need to further develop the gas chromatography-mass spectrometric method of specific hydrocarbon analyses⁽⁶⁾.

*By total hydrocarbon analysis, I mean a quantitative analysis of the total hydrocarbons not an analysis of each hydrocarbon in the mixture.

(4) M. M. O'Mara, Staff Technical Report #328, 1/22/75.

(5) M. M. O'Mara, paper presented at 1975 American Industrial Hygiene Assoc. Meeting.

(6) M. M. O'Mara, "A Method for Trapping Volatile Organic Combustion Products from the NBS Smoke Chamber for Subsequent Mass Spectrometric Identification", Staff Technical Report #335, March 10, 1975.

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Table 1
Combustion Gas Monitoring at ALTE

<u>Combustion Product</u>	<u>Principle(s) of Analysis</u>	<u>Method</u>
CO	infra-red; gas chromatography	continuous or batch
CO ₂	infra-red; gas chromatography	continuous or batch
H ₂ , O ₂	gas chromatography	batch
hydrogen cyanide	ion-electrode; wet	batch
hydrogen chloride	ion electrode	batch
nitrogen oxides	chemiluminescence	continuous
hydrogen bromide	ion electrode	batch
hydrogen fluoride	ion electrode	batch
total aliphatics	infra-red	continuous
total aromatics	infra-red	continuous
specific hydrocarbons, nitriles, chlorinated hydrocarbons, aldehydes, etc.	gas chromatography mass spectrometry	batch

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Manpower

Over the past year I have withdrawn from the area of combustion product analyses (more or less) and we have devoted our smoke chamber to smoke retardant studies in support of line group activity. To re-establish ourselves in this needed area of technology, Bob Yount has been assigned to the flammability area. A continuous sustained effort can now be carried out in the combustion gas area. In addition to this, I have committed approximately 50% of my time to this area so that both support programs (development) and new methods technology (research) can be carried out simultaneously.

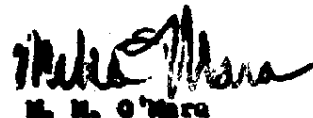
Immediate Objectives

Our immediate objectives in this area are the following:

- (1) Finish up final phase of joint NRC-G.E. corrosion study,
- (2) Develop electron capture-hydrogen cyanide method for Abeam and Ectane studies,
- (3) Further develop gas-chromatographic-mass spectrometric analysis of hydrocarbons, nitriles, etc. formed in NRC Smoke Chamber,
- (4) Begin studies of materials submitted to U. S. Testing, especially those that generated very toxic combustion gases,
- (5) Communicate in-house data that has already been collected on certain condensed-phase additives in rigid PVC.

Long Range Objectives

It is very important that our analytical studies be coupled to in-house development programs dealing with this problem area. Therefore, our long range objective is to interface with Corporate Research, Chemical Company New Products and Technical Center development programs in the most efficacious way possible.


M. N. O'Hara

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