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B.F. Goodrich Chemical Company
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RESEARCH AND DEVELOPMENT REPORT

1978 INTERNATIONAL SYMPOSIUM ON

FLAMMABILITY & FIRE RETARDANTS

TORONTO, ONTARIO, CANADA

by

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THE B. F. GOODRICH CO.

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Cleveland

J. Tinsall
R. Setava
J. Pace
H. Fiedberg
A. Ambrose
F. J. Bonet
R. A. Krueger
D. Kent
H. Rot
H. A. Maginathan
A. Anvil

Brooklyn

E. S. McRown
W. Krueger
D. Harts
R. Taylor

ALTC

M. M. O'Mara
G. Smith - R. Yount
C. Tomanak
R. Brown
R. R. Bloor/J. Somers

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May 30, 1978

SUMMARY

This was a very interesting and stimulating conference. The emphasis was distinctly on the flame and smoke performance of thermoplastics. Fabric and foam problems were not given as much coverage. The presentations from academia were very poor. There was a general lack of interest in the physics of fire.

This was strictly a Canadian-American affair. The announced European papers were withdrawn to be presented at Copenhagen in mid-July.

The best and most pertinent paper was presented by Lum of Bell Labs. He studied HCl and benzene evolution by thermally decomposing PVC directly into a mass spectrometer inlet. He shows benzene evolves in two stages. The earlier stage comes off sight after the HCl and is ca. 8% of the benzene total. In contrast PVC smoke retarded with MoO₃ drastically reduced the second benzene stage and moved the first stage up to coincide with the HCl evolution.

The worst paper was the last--a DOT contracted study by Boeing on the characteristics of electrical wire and cable in rapid transit environs. It used very poor physical evidence and reasoning. It condemned PVC and polyolefins while touting asbestos and mica. The very important intermediate rankings were not released. The fate of this study in the hands of DOT should be followed to protect ourselves from its false evidence and poor logic.

G. Belanger of Ecole Polytechnique, Montreal. Basically working in glass reinforced polyester for the Montreal Metro on contract. Was very unsophisticated in the application of physics to a fire hazard analysis. He has evidently developed some very high performance materials using extremely high concentrations of inorganic components. He bemoaned the inability to predict performance of composites from the performance of the components.

W. A. Bolding of Kaiser Aluminum and Chemical Corp. of Pleasanton, California was introducing a substitute for processed hydrated alumina. Basically, they have a source of naturally occurring hydrated bauxite. It differs from hydrated alumina mainly in its much higher iron content (~3%) which makes it a red color. At a 22% cost reduction, then he presented flimsy evidence of ca 22% less effective material. It produced buff to off-white plastics. There was very little knowledge of processing characteristics. The water of hydrated bauxite is not as tightly bound as in alumina. His main thrust was that hydrated alumina production is strictly a by-product and will not grow at the rate its use increases. They feel they have an alternative material. I feel that this material may be an adequate replacement in rug underlay but there might be a processing problem.

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May 30, 1978

Mr. Frank Roberts of the Toronto Transit system gave the paper by Bonners and Allender of Metro-Cammell Ltd., Birmingham, England. Basically a review paper, the main thrust was to appraise small, laboratory scale tests vs. the needs of overall fire safety in a transit system. Their proposal was to use the temperature at which a material has an oxygen index of 21%.

Dover Chemical Co., Ohio introduced its proprietary chlorinated resin and oil, Chlorez 760 and Paroil 160 for polystyrene and plasticized PVC, respectively. All data was UL-94. Chlorez 760 also decreased polyolefin drip.

Velsicol Chem. Corp. of Chicago was touting a proprietary fire retardant, VCC48. I was impressed with their performance data such as only a 15 phr loading in polypropylene gave a V-0 rating to a 1/16 inch sample. The additive is 7% P and 53% Br.

A. H. Gronow of American Cyanamide talked about the synergism of various phosphonium salts with ammonium polyphosphate (APP) in olefin and styrenic polymers. Apparent condensed phase activity was concluded from the similar performance in Oxygen and NaO atmosphere.

W. P. Clements and Joe Schwarcz, both of ML Industries, gave two good, separate papers on the action of Ongard II in semirigid PVC (20-30 phr DOP). Clements was mechanistically oriented. His TGA data showed Ongard II gave faster PVC decomposition at lower temperature and increased char yield in a nitrogen atmosphere. Furthermore, ca 75% of the Ongard II was left in the char and 5% was accounted for in the soot collected. They propose the smoke reduction is caused by the large decrease in benzene production when Ongard II is used. However, they had no explanation for the large dropoff in benzene reduction in going from 400°C to 500°C. Schwarcz talked mainly about the mathematics of synergism. Overall, in semirigid PVC, Ongard II was synergetic with antimony oxide in raising the oxygen index but was not synergetic in reducing the NBS smoke chamber ratings.

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May 30, 1978

I feel R. M. Lum of Bill Labs gave the best paper. He studied the vacuum pyrolysis of semiplasticized PVC (essentially unfilled wire and cable compound). The off-gases from the temperature programmed PVC samples went directly into a quadrupole mass spectrometer. There was no GC interface so very rapid scans were possible. This is really the way to do it! Maybe you have to be a monopoly to replace corroded mass discriminators! He has just completed adding computerized data acquisition, so his precision, mass range and analytic repetition are all improved dramatically. He is just now gearing up for determination of absolute yields.

He compared PVC with and without MoO_3 . His first experiments followed HCl , benzene and toluene and saturated aliphatics. Without MoO_3 , at low temperature, ca 220°C , he got HCl evolution followed by a small (ca 5-8%) fraction of benzene evolution. By 260° the major evolution of benzene, toluene and hydrocarbons occurred. The addition of MoO_3 gave a 90% decrease in benzene! But that 10% which was left came off with the catalyzed evolution of HCl at ca 200°C . In other words, the MoO_3 not only catalyzed the HCl evolution, but it also moved the benzene evolution timing up to coincide with that of the HCl evolution. Antimony oxide did not produce this effect. I asked Lum if the early benzene fraction came from plasticizer. He said limited initial rigid PVC trails looked similar.

Lum spent a great deal of effort to obtain kinetic data on HCl and benzene evolution. He would then do $\text{HCl}/d\text{PVC}$ or $d\text{H}/d\text{PVC}$ vs PVC conc. to various powers. Correlation coefficient was the entire criteria for selecting the power. The HCl evolution was dependent to the $3/2$ order. Benzene evolution went from 2nd order with $E_a = 66$ k cal/mole to a MoO_3 induced 1st order kinetics with $E_a = 37.0$ k cal/mole. Sb_2O_3 did not significantly change the results. Actually I feel his kinetic interpretations are very shaky. Even the kinetic order is not well established by the temperature programmed experiments. Isothermal experiments are planned. These experiments should give us better data.

Extended molecular mass scans show no evidence of any volatile molybdenum containing species. No residue analyses were made. Lum, Clements and Moore (of Climax) all feel their respective data are in agreement with no serious conflicts. The two step benzene evolution appears to be in conflict with the work of Erenke and Lattimer here at BFG.

Stan Martin of SRI, Menlo Park, Calif., presented the animal testing work done at SRI. This technique was done without sponsorship and did not appear to be top quality toxicological work.

Trained rats were used for testing incapacitation. Samples were burned at 4 w/cm^2 in 50/50 air- N_2 . No PVC products have yet been rated. Wood and polyamide foam are good at a 1.33 rating. Urethane foam was somewhat worse at 5-11 (which meant that there was no HCN , HCl or NOX problems). Toxicity seemed due to carbon monoxide. However polysulfone was much worse with a rating of 16. Since Martin feels that polysulfone is really much safer than wood, he feels these ratings should be normalized by some measure of burnability such as Archie Tervason's Y factor.

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May 30, 1978

Fred Moore of Climax presented no data we haven't seen except that he confirmed that at least 90% of the molybdenum remains in the char when MoO₃ is added to PVC. FR31 is a supported Mo and Zn material. All pertinent data was obtained in TGA experiments. Polyester data was absolutely minimal.

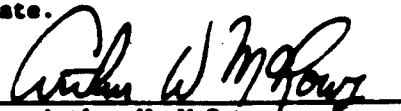
S. J. Monte of Kenrich Petrochemicals gave possibly the most dynamic talk of the meeting. Organic titanate coupling agents will solve virtually any problem! His basic lesson was that rocks don't burn. And the coupling agents can make highly inorganic filled systems behave very well. They have a wide variety of agents available. A number do not require a separate treatment of fillers--just add during regular mixing! I feel there will be definite applications in many significant markets when the technology is all worked out.

J. H. Magill of Alarie's group at Univ. of Pittsburgh was a total flop. He had nothing to say and took an hour to ramble about. I only mention this worthless paper because Alarie has such an impact with plastic toxicity studies at the NBS.

A. Taylor of Boeing gave possibly the worst paper of any merit. It was an \$89K, 1976 contract #1221 from DOT/Transportation Systems Center. Small scale lab tests for materials were used to evaluate available materials for wire and cable applications. NBS smoke chamber, electrical breakdown and some sort of toxic gas evolution were the three sole criteria used. Toxic gas evolution was the only evidence Boeing generated--they used Drager tubes! No calibration or interferences were checked for or used. Everyone knows these don't work in the presences of halides and acids and aldehydes of combustion. After using the tubes, they used a toxicity calculation of questionable validity. They used published listings on concentrations of LD50 and total death (indeterminate of exposure time) for weighting factors. Combining the three properties most heavily weighted their evaluation of toxicity.

No overall details or rankings were given until DOT release. He said PVC, polyolefins and Halar were worst and asbestos, mica and silicone rubber were the best. Overall he liked Kapton or a Kapton-silicone rubber composite best.

While I would not argue with his favorite and best choices--they have merit--I worry deeply about any rankings given materials in the more economically attractive choices. The data was very poorly obtained and yet could still be used against materials unfairly by the unsophisticate.


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