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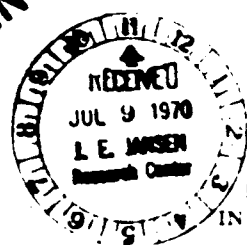
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RESEARCH REPORT

METAL-METAL SYNERGISM  
IN FLAME RETARDANT SYSTEM

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# Metal-Metal Synergisms in Flame Retardant Systems

BY

J. F. Coleman and T. F. Niemann

## SUMMARY

We have found a synergistic action between antimony trioxide ( $Sb_2O_3$ ) and other metal compounds which we believe can reduce the required amount of  $Sb_2O_3$  in fire retardant formulations. The oxides of titanium, zirconium, and salts of lead and tin are of special interest. The addition of 0.5-5.0 phr (0.5-5.0 phr) of one or more of these synergistic metal compounds reduces the required amount of  $Sb_2O_3$  now used.

Due to the limited scope of this work, this metal-metal synergism was demonstrated only in a formulation similar to our existing system, Abcon. The antimony trioxide-metal compound system was also tested in PVC or chlorinated PE are used as the halogen source. These systems should also be effective in other formulations where antimony trioxide is used with a halogen source.

Stannic oxide is an effective flame retardant when used with a halogen source. Iron oxide-halogen systems also show synergism. Of the other metal oxides and salts studied, none showed synergism with added  $Sb_2O_3$ .

Durability of the flame retardant system with the mixture of metal compounds with one or more synergistic metal compounds are used together.

When part of the  $Sb_2O_3$  is replaced with one of the synergistic metal compounds, heat distortion temperatures and Izod impact values do not change from control values. However, some changes in the resin. We did not evaluate the effects of these changes on physical properties. Nor did we investigate the effect of particle size, distribution or form on the efficiency of the system.

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### CONCLUSION-

Based on this limited study using a flame calorimeter, we conclude

1. The levels of antimony trioxide now used in flame retardant formulations can be reduced to lower levels by the addition of low levels of metal compounds which are synergistic with antimony trioxide and with a halogen source.
2. Oxides or salts of titanium, iron, lead and tin are synergistic effective with low levels of antimony trioxide in the presence of a halogen source.
3. The antimony trioxide-metal salt systems are effective when PVC or chlorinated polyethylene is used as a halogen source.
4. The antimony trioxide-metal salt systems should also be used wherever antimony trioxide is now used with a halogen source.
5. Stannic oxide might be used as an antimony trioxide replacement if economics demand it.
6. Iron oxide might also be used as an antimony trioxide replacement in compositions where color is not important.
7. Combinations of two or more metal salts with at least one halogen source should impart durability to the flame retardant effect.
8. At the levels tested, oxides or salts of niobium, cobalt, nickel, zinc, cadmium, zirconium and bismuth show little synergistic effect with low levels of antimony trioxide and a halogen source.
9. At the levels tested, oxides of titanium, lead, bismuth, iron, copper, zinc, cadmium, zirconium and nickel, by themselves, are not as efficient as antimony trioxide.
10. Metal containing additives, such as thermoplasticizers, may increase the flammability of polymer blends.

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### RECOMMENDATIONS

Based on this brief survey, we recommend:

1. The use of lower levels of  $\text{Sb}_2\text{O}_3$  with low levels of synergists such as compounds such as salts of Ti, Sn, Fe and Pb to achieve the same level of protection now using  $\text{Sb}_2\text{O}_3$ -halogen source for flame retardancy.
2. Further research should be started to determine the effect of the compound particle size, distribution and form on its effectiveness as flame retardant synergist.
3. Additional metal oxides or salts should also be evaluated with  $\text{Sb}_2\text{O}_3$  or alone in halogen-containing polymer systems.
4. The use of thermal analyses of flame retardant systems should be increased to give additional information on the mechanism of action.
5. The effects of all metal-containing additives, including the synergists, must be considered when testing for flame retardancy.

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## INTRODUCTION

The use of antimony oxide ( $\text{Sb}_2\text{O}_3$ ) as a flame-retardant in a halogen-containing system is well known. The combination of a halogen and phosphorus with nitrogen is also known and used. The halogen source required for the first type of flame-retardant may be present in the polymer (PVC,  $\text{PVC}_2$ , etc.) or may be an aliphatic or aromatic halides.

It is generally accepted that the flame-retardant action of a halogen source is due to the formation of antimony trihalide or antimony oxychloride. This volatile chloride can then directly affect the mechanisms of the burning.

We feel that other volatile chlorides can also be used in flame-retardant systems if they can be formed at or near the metal salt and the halogen source. This reaction must occur very near the temperature of the flame. Since it has been found that volatile halide forms at too low a temperature, it is not available at the higher flame temperature. If the halide is formed at too high temperatures, it likewise is not available at the flame temperature. The metal used should be present in a form which can form a volatile halide at or near the burning temperature of the polymer.

The textile industry has developed a number of flame-retardant systems for flame-resistance to textiles. These include the use of antimony trioxide and a halogen source,<sup>2-5</sup> and mixtures of titanium, zirconium, and a halogen source,<sup>6-10</sup> and mixtures of titanium, zirconium, and a halogen source,<sup>11,12</sup> zinc,<sup>13,14</sup> and silicon compounds.<sup>15,16</sup> Other materials employed as flame retardants. Other materials employed as flame retardants to textiles or plastics include the use of antimony trioxide in combination with compounds containing nitrogen, phosphorus, and silicon. Flame-retardant polymers have been prepared by the reaction of antimony trioxide with oxides of metals such as Sb, P, C, F, and Zn. Organotin polymers have been prepared by the reaction of antimony trioxide with organotin compounds.

Due to the increasing cost of antimony trioxide, we decided to investigate the use of other metal salts to decrease our antimony trioxide requirements.

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# PROCEDURES AND METHODS

We wanted to study these metal-metal synergisms in a known, available commercial self-extinguishing formulation. The recipe for tests we used the following recipe, which is similar to B. F. G. 89129 Nat. 022:

|                 |             |
|-----------------|-------------|
| 105EP PVC       | 25.0 parts  |
| Thermolite 31   | 1.5 parts   |
| Tyrl SAN        | 45.0 parts  |
| 820X17          | 30.0 parts  |
| Stearic Acid    | 1.0 parts   |
| Metal Compounds | 1-8.0 parts |

To this basic recipe we added up to 8.0 parts antimony trioxide and from 0.5 to 8.0 parts of other metal compounds both with and without the  $Sb_2O_3$ . The ingredients were charged as listed and then dry blended in an Oster blender for one minute. The samples were then milled for five minutes at 320°F and compression molded at 350°F into 2 x 5 x 1/8" bars. These bars were cut into 1/2 x 5 x 1/8" property bars and used for flammability, heat distortion and Izod impact tests.

## Materials

|                                   |                                                                              |
|-----------------------------------|------------------------------------------------------------------------------|
| Abeon 89129                       | - BFG commercial self-extinguishing ABS, Nat. 022<br>Lot No. 0.0203-1        |
| K-10                              | - Commercial chlorinated polyethylene QX 2243, 10,<br>36% Cl                 |
| Geon 105EP                        | - BFG commercial PVC, Lot 28 132-2                                           |
| Tyrl SAN                          | - Dow Chemical Co., MX4582.02 Crystal 2, Lot EE<br>90312 Blend               |
| 820X17                            | - BFG ABS toughener, Lot 000024-12                                           |
| Thermolite 31                     | - PVC Stabilizer (S-8)                                                       |
| Stearic Acid                      | - Eastman Organic Chemicals                                                  |
| Calcium Stearate                  | - Lubricant (L-3)                                                            |
| Lead Laurate                      | - Lubricant                                                                  |
| Antimony Oxide                    | - M & T Chemical Co. (Pigment F-9)                                           |
| Titanox, Subpig-<br>mentary Grade | - Titanium Pigment Corporation (courtesy M. Danna)                           |
| Titanox RANC-1                    | - Titanium Pigment Corporation                                               |
| Tribase                           | - 3PbO·PbSO <sub>4</sub> powder (M & T Corporation)                          |
| Virflux PB-5                      | - Titanium Pigment Corporation (grain size 100,<br>ore courtesy of M. Danna) |

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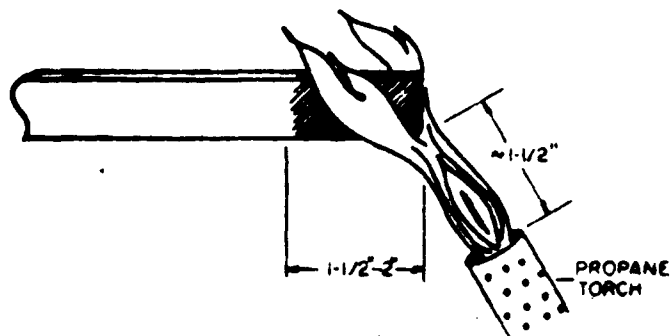
|                                          |                                                  |
|------------------------------------------|--------------------------------------------------|
| Black Iron Oxide                         | - Pigment 104, $\text{Fe}_3\text{O}_4$           |
| Red Iron Oxide                           | - Pigment 107, $\text{Fe}_2\text{O}_3$           |
| Yellow Iron Oxide                        | - Pigment 1322, hydrated $\text{Fe}_2\text{O}_3$ |
| Zinc Oxide                               | - Allied Chemical Co., Reagent Grade, P          |
| Zinc Phosphate                           | - Fisher Scientific Co., Purified                |
| Bismuth Trioxide                         | - Allied Chemical Co., Reagent Grade             |
| Aluminum Oxide                           | - Fisher Scientific Co., Reagent Grade           |
| Cupric Oxide                             | - Allied Chemical Co., Reagent Grade, Powder     |
| Stannic Oxide                            | - Allied Chemical Co., Reagent Grade, Powder     |
| Stannous Octoate<br>(Carstan 8 Catalyst) | - Carlisle Chemical Works, Inc.                  |
| Nickel (ous) Oxide                       | - Fisher Scientific Co., Reagent Grade           |
| Zirconium Oxide                          | - Fisher Scientific Co., Purified                |
| Cadmium Oxide                            | - Fisher Scientific Co., Certified               |

#### Flammability Tests

The flammability of each sample was determined by applying a propane torch flame at a 45° angle to the cross-section area of a horizontally suspended  $1/2 \times 1/8 \times 5$ " molded bar. The head of the torch was held at a distance of about 1 1/2 inches from the end of the sample. The flame front therefore covered the sample cross-section and the length of the bar for about 1 1/2-2 inches behind the cross section.

FIGURE 1

#### SCHEMATIC DIAGRAM OF FLAMMABILITY TEST APPARATUS



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The flame was applied for ten seconds and then removed. The time for the sample to extinguish was measured. If the sample did not extinguish, it was allowed to cool for ten seconds, and the flame was re-applied for ten seconds. This procedure was repeated up to four times or until the sample burned.

We also obtained the Oxygen Index of a number of the samples. Differential Scanning Calorimetry (DSC) runs were also obtained for a few selected samples.

## RESULTS AND DISCUSSION

### Metal Oxides or Salts with a PVC Halogen Source

#### Antimony Trioxide

Samples were prepared following the basic recipe with from 0.0 to 8.0 parts  $Sb_2O_3$ . The results of the flammability testing are listed in Table I. A number given under "First Flame," etc., is the time in seconds required for that sample to extinguish after the flame is removed. Other terms are self-descriptive. The same applies to all the other tables.

TABLE I

### FLAME RETARDANT PROPERTIES OF ANTIMONY TRIOXIDE

| Sample No.   | Parts $Sb_2O_3$ | First Flame | Second Flame |
|--------------|-----------------|-------------|--------------|
| 4074-1       | ---             | Burns       | ---          |
| 4080-13      | 1.0             | Burns       | ---          |
| 4080-14      | 2.0             | <1          | Burns        |
| 4080-15      | 3.0             | <1          | ---          |
| 4076-7       | 4.0             | <1          | ---          |
| 4080-16      | 4.0             | <1          | 2.5          |
| 4080-17      | 5.0             | <1          | ---          |
| 4076-8       | 6.0             | <1          | ---          |
| 4074-2       | 8.0             | <1          | ---          |
| Abscon 89129 | 8.0             | <1          | ---          |

Antimony trioxide does have a measurable effect on the self-extinguishing properties at low levels. But around 5 to 6 parts per hundred, any long-term benefits.

### Titanium Dioxide

TABLE II

#### FLAME RETARDANT PROPERTIES OF TITANIUM DIOXIDE

| Sample No. | Parts<br>Subpig | Parts<br>RANC-1 | Parts<br>$Sb_2O_3$ | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame |
|------------|-----------------|-----------------|--------------------|--------------|--------------|--------------|
| 4074-3     | 1.0             | 0.0             | 0.0                | Burns        | ---          | ---          |
| 4074-4     | 3.0             | ---             | ---                | Burns        | ---          | ---          |
| 4074-5     | 3.0             | 2.0             | ---                | Burns        | ---          | ---          |
| 4074-6     | 3.0             | 7.0             | ---                | Burns        | ---          | ---          |
| 4074-7     | ---             | 5.0             | ---                | Burns        | ---          | ---          |
| 4074-8     | ---             | 10.0            | ---                | Burns        | ---          | ---          |
| 4080-1     | 0.5             | 0.0             | 1.0                | 1.5          | 8.0          | Burns        |
| 4080-4     | 1.0             | ---             | 1.0                | 8.5          | 4.0          | Burns        |
| 4080-2     | 0.5             | ---             | 2.0                | 2.0          | 5.0          | Burns        |
| 4076-1     | 1.0             | ---             | 2.0                | 2.0          | 8.0          | Burns        |
| 4076-4     | 3.0             | ---             | 2.0                | <1.0         | Burns        | ---          |
| 4080-7     | 0.5             | 0.5             | 2.0                | <1.0         | 2.0          | Burns        |
| 4080-9     | ---             | 0.5             | 2.0                | <1.0         | 3.0          | Burns        |
| 4080-11    | ---             | 1.0             | 2.0                | 8.0          | 2.0          | Burns        |
| 4080-3     | 0.5             | ---             | 3.0                | <1.0         | 2.0          | Burns        |
| 4080-6     | 1.0             | ---             | 3.0                | <1.0         | 4.0          | Burns        |
| 4080-8     | 0.5             | 0.5             | 3.0                | <1.0         | 2.0          | Burns        |
| 4080-10    | ---             | 0.5             | 3.0                | 1.0          | 2.0          | Burns        |
| 4080-12    | ---             | 1.0             | 3.0                | <1.0         | 2.0          | Burns        |
| 4076-2     | 1.0             | ---             | 4.0                | <1.0         | 2.0          | Burns        |
| 4076-5     | 3.0             | ---             | 4.0                | <1.0         | 2.0          | Burns        |
| 4076-3     | 1.0             | ---             | 6.0                | <1.0         | 2.0          | Burns        |

Although neither type of titanium dioxide appears to be a flame retardant by itself, both types show synergistic effects at levels of  $Sb_2O_3$ .

We observed a trend towards increased flammability as more titania was added. For example, sample 4074-4 with 3 parts  $\text{TiO}_2$  burns on the second flame application. Sample 4076-1 with 1 part  $\text{TiO}_2$  extinguishes after 8 sec and 4076-2 with 0.5 parts  $\text{TiO}_2$  extinguishes after 5 sec on the second flame application. We obtained the best results in our flame test when either 0.5 parts active subpigmentary, or 1.0 parts RANC-1 titanium dioxide was incorporated into the recipe with 3.0 parts  $\text{Sb}_2\text{O}_3$ .

#### Lead Salts

We incorporated lead salts into the basic recipe by replacing the 3 parts Thermolite 31 PVC stabilizer with 3.0 parts Tribase ( $3\text{PbO} \cdot \text{PbSO}_4$ ) and the 1.0 part stearic acid with 1.0 part of lead laurate. No other levels of lead compounds were tested.

The data in Table III shows that the most efficient lead-antimony ratio is 4 parts lead salts and 4 parts antimony trioxide. The use of 4.0 parts lead salts alone does not efficiently reduce the sample flammability.

TABLE III

#### FLAME RETARDANT PROPERTIES OF LEAD COMPOUNDS

| Sample No. | Parts Lead | Parts Subpig. $\text{TiO}_2$ | Parts $\text{Sb}_2\text{O}_3$ | 1st Flame | 2nd Flame | 3rd Flame |
|------------|------------|------------------------------|-------------------------------|-----------|-----------|-----------|
| 4094-1     | 4          | ---                          | 0                             | Burns     | ---       | ---       |
| -2         | 4          | ---                          | 1                             | <1.0      | Burns     | ---       |
| -3         | 4          | ---                          | 2                             | <1.0      | 3.5       | Burns     |
| -4         | 4          | ---                          | 3                             | <1.0      | <1.0      | Burns     |
| -5         | 4          | ---                          | 4                             | <1.0      | 1.0       | ---       |
| -6         | 4          | 0.5                          | 1                             | <1.0      | Burns     | ---       |
| -7         | 4          | 0.5                          | 2                             | <1.0      | 1.5       | Burns     |
| -8         | 4          | 0.5                          | 3                             | <1.0      | 2.0       | ---       |

The combination of 4.0 parts lead salts, 3.0 parts  $\text{Sb}_2\text{O}_3$ , and 0.5 parts subpigmentary titanium dioxide is also efficient but does not show improvement over just 0.5 parts subpigmentary titanium dioxide and 3 parts antimony trioxide (sample 4080-3, Table II).

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Iron Oxides

We tested three different pigment grades of iron oxides — black magnetic (Pigment 104), red (Pigment 107) and the partially hydrated yellow (Pigment 1322). Samples 4102 1-3 and 4102 5-7 were compounded without any Thermolite 31 PVC stabilizer since iron oxide is a PVC stabilizer at ambient and processing temperatures.<sup>24</sup> And rather than 1.0 part stearic acid, 1.0 part calcium stearate was used for lubrication in all the iron recipes.<sup>24</sup> In Table IV, samples 4102 1-3 show that 3 and 5 parts of iron oxide do inhibit burning to some extent. But 4102-4 shows that 3.0 parts of iron oxide plus the Thermolite 31 stabilizer level normally used gives a

TABLE IVFLAME RETARDANT PROPERTIES OF IRON OXIDES

| Sample No. | Parts<br>Iron<br>Oxide | Type<br>Iron<br>Oxide | Parts<br>$\text{Sb}_2\text{O}_3$ | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame | 4th<br>Flame |
|------------|------------------------|-----------------------|----------------------------------|--------------|--------------|--------------|--------------|
| 4102-1     | 1.0                    | 104*                  | ---                              | Burns        | ---          | ---          | ---          |
| -2         | 3.0                    | 104*                  | ---                              | 36.0         | Burns        | ---          | ---          |
| -3         | 5.0                    | 104*                  | ---                              | 28.0         | 24.0         | Burns        | ---          |
| -4         | 3.0                    | 104                   | ---                              | 2.0          | 21.0         | 39.5         | ---          |
| 4104-1     | 1.0                    | 107                   | ---                              | 23.0         | 11.0         | 45.0         | ---          |
| -2         | 3.0                    | 107                   | ---                              | 14.0         | 17.0         | 40.0         | ---          |
| -3         | 5.0                    | 107                   | ---                              | 2.0          | 9.0          | 44.0         | ---          |
| 4105-1     | 1.0                    | 1322                  | ---                              | 2.0          | Burns        | ---          | ---          |
| -2         | 3.0                    | 1322                  | ---                              | 4.0          | 12.0         | 35.0         | ---          |
| -3         | 5.0                    | 1322                  | ---                              | 2.0          | 13.0         | 37.0         | ---          |
| 4102-5     | 1.0                    | 104*                  | 3.0                              | 1.0          | 2.0          | 4.0          | ---          |
| -6         | 3.0                    | 104*                  | 3.0                              | 1.0          | 3.0          | 2.0          | ---          |
| -7         | 5.0                    | 104*                  | 3.0                              | 1.0          | 2.5          | 2.0          | ---          |
| -8         | 3.0                    | 104                   | 3.0                              | <1.0         | 1.0          | 4.0          | ---          |
| 4104-4     | 1.0                    | 107                   | 3.0                              | <1.0         | 2.0          | 4.0          | ---          |
| -5         | 3.0                    | 107                   | 3.0                              | 1.0          | 3.0          | 8.0          | ---          |
| 4105-4     | 1.0                    | 1322                  | 3.0                              | <1.0         | 2.5          | 3.5          | ---          |
| -5         | 3.0                    | 1322                  | 3.0                              | <1.0         | 1.0          | 2.0          | ---          |

\*No Thermolite 31 added

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system that is self-extinguishing in a shorter period of time. From the data we conclude that the organotin stabilizer is also synergistical with either with the halogen alone or with the iron oxide-halogen combination. The red iron oxide (107) and yellow iron oxide (1322) also decrease the burning rate when Thermolite 31 is present. However the combination of iron oxide with 3.0 parts of  $Sb_2O_3$  is a very effective flame retardant system. Samples of these systems (4102-5-8, 4104-4, 5, 4105-4, 5) are all self-extinguishing through four flame cycles. Samples 4102-5-7 exhibit this effect without the organotin stabilizer, and 4102-8 shows further improvement with the Thermolite 31 in the recipe. All iron-containing samples were very high colored. All the iron oxide-containing samples had increased char areas caused by "blowing" of gases through the hot char. Afterglow was noticed on the longer-burning samples.

#### Iron-Titanium Oxide

Virflux PR-5 is a ground, naturally occurring ferrotitanate of titanium dioxide the ferrotitanate is not effective in the absence of  $Sb_2O_3$ . However, when small amounts of the ferrotitanate and 3.0 parts of  $Sb_2O_3$  are added to the basic recipe, the resulting samples have decreased flammability. Again, as with titanium dioxide, only a 0.5 part addition is

TABLE V

#### FLAME RETARDANT PROPERTIES OF A FERROTITANATE

| Sample No. | Parts<br>Virflux PR-5 | Parts<br>$Sb_2O_3$ | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame |
|------------|-----------------------|--------------------|--------------|--------------|--------------|
| 4096-1     | 1.0                   | ---                | Burns        | ---          | ---          |
| -2         | 3.0                   | ---                | Burns        | ---          | ---          |
| -3         | 5.0                   | ---                | Burns        | ---          | ---          |
| -4         | 0.5                   | 3.0                | < 1.0        | 1.0          | 1.0          |
| -5         | 1.0                   | 3.0                | < 1.0        | 2.0          | 3.0          |
| -6         | 2.0                   | 3.0                | < 1.0        | 3.0          | 4.0          |
| -7         | 3.0                   | 3.0                | < 1.0        | 4.0          | 5.0          |
| -8         | 4.0                   | 3.0                | < 1.0        | 5.0          | 6.0          |

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Zinc Oxide and Zinc Phosphate

TABLE VI

## FLAME RETARDANT PROPERTIES OF ZINC SALTS

| Sample No. | Parts ZnO | Parts ZnPO <sub>4</sub> | Parts Sb <sub>2</sub> O <sub>3</sub> | Parts Fe <sub>2</sub> O <sub>3</sub> | 1st Flame | 2nd Flame | 3rd Flame | 4th Flame |
|------------|-----------|-------------------------|--------------------------------------|--------------------------------------|-----------|-----------|-----------|-----------|
| 4114-1     | 1.0       | ---                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -2         | 3.0       | ---                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -3         | 5.0       | ---                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -4         | 1.0       | ---                     | 3.0                                  | ---                                  | <1        | 2         | 45        | ---       |
| -5         | 3.0       | ---                     | 3.0                                  | ---                                  | 1         | 3         | 50.5      | ---       |
| -6         | 5.0       | ---                     | 3.0                                  | ---                                  | <1        | 3         | Burns     | ---       |
| 4115-1     | ---       | 1.0                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -2         | ---       | 3.0                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -3         | ---       | 5.0                     | ---                                  | ---                                  | Burns     | ---       | ---       | ---       |
| -4         | ---       | 1.0                     | ---                                  | 3.0                                  | 12        | 11        | 18        | 25        |
| -5         | ---       | 3.0                     | ---                                  | 3.0                                  | 27        | 6         | 44        | ---       |
| -6         | ---       | 5.0                     | ---                                  | 3.0                                  | 23        | 7         | 50        | ---       |
| -7         | ---       | 1.0                     | 3.0                                  | ---                                  | <1        | <1        | 4.5       | Burns     |
| -8         | ---       | 2.0                     | 3.0                                  | ---                                  | <1        | 1         | 2.5       | Burns     |

Zinc oxide and zinc phosphate alone do not efficiently decrease the flammability of the resin system. With 3.0 parts Sb<sub>2</sub>O<sub>3</sub> added, the zinc phosphate systems can pass three flame cycles while the zinc oxide systems pass only two flame cycles. A combination of zinc phosphate and zinc oxide also decreases the flammability of the system, but the times to extinguish are rather long.

Bismuth, Aluminum and Copper Oxides

The oxide of bismuth alone decreases the flammability of the resin system, but the times to extinguish are long. The oxides of aluminum and copper do not effectively decrease the resin flammability at the levels tested. With 3.0 parts of Sb<sub>2</sub>O<sub>3</sub> present, along with a 3.0 part level of any of the metal oxides, the materials can still be classified as self-extinguishing after four flame cycles.

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**TABLE VII**  
**FLAME RETARDANT PROPERTIES OF BISMUTH, ALUMINUM**  
**AND COPPER OXIDES**

| Sample No. | Parts $\text{Bi}_2\text{O}_3$ | Parts $\text{Al}_2\text{O}_3$ | Parts $\text{CuO}$ | Parts $\text{Sb}_2\text{O}_3$ | 1st Flame | 2nd Flame | 3rd Flame | 4th Flame |
|------------|-------------------------------|-------------------------------|--------------------|-------------------------------|-----------|-----------|-----------|-----------|
| 4116-1     | 3.0                           | ---                           | ---                | ---                           | 39.5      | 41.0      | 49.0      | Burns     |
| -2         | 5.0                           | ---                           | ---                | ---                           | 25.0      | 5.0       | 32.0      | Burns     |
| -3         | 3.0                           | ---                           | ---                | 3.0                           | 3.0       | 1.0       | 1.0       | 35.0      |
| -4         | ---                           | 3.0                           | ---                | ---                           | Burns     | ---       | ---       | ---       |
| -5         | ---                           | 5.0                           | ---                | ---                           | 60        | Burns     | ---       | ---       |
| -6         | ---                           | 3.0                           | ---                | 3.0                           | <1        | 1.5       | 4.0       | 16.0      |
| -7         | ---                           | ---                           | 3.0                | ---                           | Burns     | ---       | ---       | ---       |
| -8         | ---                           | ---                           | 5.0                | ---                           | Burns     | ---       | ---       | ---       |
| -9         | ---                           | ---                           | 3.0                | 3.0                           | <1        | 39.5      | 4.0       | 17.0      |

TiO<sub>2</sub> Oxide

**TABLE VIII**  
**FLAME RETARDANT PROPERTIES OF STANNIC OXIDE**

| Sample No. | Parts $\text{SnO}_2$ | Parts $\text{Sb}_2\text{O}_3$ | 1st Flame | 2nd Flame | 3rd Flame | 4th Flame |
|------------|----------------------|-------------------------------|-----------|-----------|-----------|-----------|
| 4247-4     | 1.0                  | ---                           | 45.0      | ---       | ---       | ---       |
| -5         | 2.0                  | ---                           | 23.0      | 27.0      | 39.0      | ---       |
| -6         | 3.0                  | ---                           | 14.0      | 20.0      | 9.0       | 58.0      |
| 4235-4     | 4.0                  | ---                           | 4.0       | 8.0       | 4.0       | 20.0      |
| -5         | 5.0                  | ---                           | 1.0       | 7.0       | 3.0       | 11.0      |
| -6         | 6.0                  | ---                           | 1.0       | 4.0       | 9.0       | 27.0      |
| 4247-7     | 2.0                  | 1.0                           | <1.0      | 2.0       | 4.0       | 35.0      |
| -8         | 3.0                  | 1.0                           | <1.0      | 1.0       | 6.0       | 29.0      |
| -9         | 1.0                  | 2.0                           | <1.0      | 1.0       | 5.0       | 13.0      |
| -10        | 2.0                  | 2.0                           | <1.0      | 1.0       | 8.0       | 13.0      |
| 4235-7     | 2.0                  | 2.0                           | 1.0       | 1.0       | 9.0       | 13.0      |
| -8         | 4.0                  | 2.0                           | <1.0      | <1.0      | 4.0       | 3.0       |
| -9         | 6.0                  | 2.0                           | 1.0       | 1.8       | 4.0       | 10.0      |
| -10        | 3.0                  | 2.0                           | 1.0       | 1.5       | 3.0       | 1.0       |
| -11        | 4.0                  | 3.0                           | <1.0      | 1.2       | 5.5       | 10.0      |
| -12        | 6.0                  | 3.0                           | 1.0       | 1.3       | 2.0       | 1.0       |

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Stannic oxide alone appears to be an efficient flame retardant with a halogen source at about 4.0 to 6.0 parts. It does not self-extinguish as quickly as does an equivalent weight of antimony oxide (see Table I). However it is more efficient through more total flame cycles than antimony oxide. When low levels of stannic oxide are combined with low levels of antimony trioxide a combination of the effects is seen. Sample 4235-8, containing 1 part of  $\text{SnO}_2$  and 2 parts of  $\text{Sb}_2\text{O}_3$ , is self-extinguishing through four flame cycles in under 4 seconds per cycle. This is an improvement over 6 parts of either oxide alone (Tables I, VIII). The major drawbacks to the use of stannic oxide are an increased smoke emission problem, and the cost of stannic oxide which is now about competitive with antimony trioxide. However, the use of low levels of tin oxide to impart durability to the flame-retardant property cannot be overlooked.

#### Tin, Titanium and Antimony Oxides

**TABLE IX**  
**FLAME RETARDANT PROPERTIES OF TIN WITH TITANIUM**  
**AND ANTIMONY OXIDES**

| Sample No. | Parts $\text{SnO}_2$ | Parts RANC-1 $\text{TiO}_2$ | Parts $\text{Sb}_2\text{O}_3$ | 1st Flame | 2nd Flame | 3rd Flame | 4th Flame |
|------------|----------------------|-----------------------------|-------------------------------|-----------|-----------|-----------|-----------|
| 4248-1     | 1.0                  | 0.5                         | ---                           | Burns     | ---       | ---       | ---       |
| -2         | 1.0                  | 1.0                         | ---                           | 26        | 11        | Burns     | ---       |
| -3         | 2.0                  | 0.5                         | ---                           | 22        | 46        | ---       | ---       |
| -4         | 2.0                  | 1.0                         | ---                           | 22        | 27        | 25        | ---       |
| -5         | 3.0                  | 0.5                         | ---                           | 7         | 2.5       | 7         | ---       |
| -6         | 3.0                  | 1.0                         | ---                           | 2         | 21        | 32        | ---       |
| -7         | 4.0                  | 0.5                         | ---                           | 11        | 3.0       | 1.0       | ---       |
| -8         | 4.0                  | 1.0                         | ---                           | 15        | 5.0       | 4         | ---       |
| 4249-1     | 1.5                  | 0.5                         | 1.5                           | <1        | 5.0       | 7.1       | ---       |
| -2         | 1.5                  | 1.0                         | 1.5                           | 2         | 1.3       | 5.5       | ---       |
| -3         | 2.0                  | 0.5                         | 2.0                           | <1        | <1        | 7         | ---       |
| -4         | 2.0                  | 1.0                         | 2.0                           | <1        | 2.0       | 4         | ---       |
| 4247-10    | 2.0                  | ---                         | 2.0                           | <1        | 1.0       | 5         | ---       |

The use of titanium dioxide with tin dioxide does not appear to make the system much more efficient. In fact, when titanium dioxide is added to an efficient stannic oxide system, it decreases the efficiency of the system.

Stannous OctoateTABLE X

## FLAME RETARDANT PROPERTIES OF STANNOUS OCTOATE

| Sample No. | Parts<br>Sn Octoate | Parts<br>Sb <sub>2</sub> O <sub>3</sub> | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame | 4th<br>Flame |
|------------|---------------------|-----------------------------------------|--------------|--------------|--------------|--------------|
| 4254-1     | 3                   | ---                                     | 3.0          | 45.0         | Burns        | ---          |
| -2         | 4                   | ---                                     | 3.0          | 43.0         | 67.0         | ---          |
| -3         | 3                   | 1                                       | <1           | 51.0         | 52.0         | 11.0         |
| -4         | 2                   | 2                                       | 1.0          | 8.0          | 84.0         | ---          |
| -5         | 2                   | 4                                       | 1.0          | 1.0          | 14.0         | 48.0         |

Stannous octoate is less effective than stannic oxide either alone or with antimony trioxide. It is of interest because it is an organometallic (like the Thermolite 31) rather than a metal oxide. Stannous octoate appears to be too volatile since its effectiveness decreases rapidly with the increasing number of flame cycles. A less volatile organotin compound might be more effective.

Cadmium and Zirconium OxidesTABLE XI

## FLAME RETARDANT PROPERTIES OF CADMIUM AND ZIRCONIUM OXIDES

| Sample No. | Parts<br>CdO | Parts<br>ZrO <sub>2</sub> | Parts<br>Sb <sub>2</sub> O <sub>3</sub> | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame |
|------------|--------------|---------------------------|-----------------------------------------|--------------|--------------|--------------|
| 4251-1     | 2            | ---                       | ---                                     | Burns        | ---          | ---          |
| -2         | 4            | ---                       | ---                                     | Burns        | ---          | ---          |
| -3         | 6            | ---                       | ---                                     | Burns        | ---          | ---          |
| -4         | 2            | ---                       | 1                                       | 40           | 67           | ---          |
| -5         | 2            | ---                       | 2                                       | 1.0          | 13           | Burns        |
| -6         | 3            | ---                       | 1                                       | 32           | 32           | 36           |
| 4252-1     | ---          | 2                         | ---                                     | Burns        | ---          | ---          |
| -2         | ---          | 4                         | ---                                     | Burns        | ---          | ---          |
| -3         | ---          | 6                         | ---                                     | Burns        | ---          | ---          |
| -4         | ---          | 2                         | 1                                       | 1.0          | Burns        | ---          |
| -5         | ---          | 2                         | 2                                       | 1.0          | 2.0          | Burns        |
| -6         | ---          | 3                         | 1                                       | 1.0          | 6.0          | Burns        |

Cadmium and zirconium oxides alone are not effective flame retardant synergists in this halogen-containing system. When combined with levels of  $Sb_2O_3$ , there is some positive effect seen, but the flaming time of these samples is still too high.

#### Nickel Oxide

Although nickel oxide alone is not an efficient flame retardant, it does add some durability to a system with low levels of  $Sb_2O_3$ . The flaming times are rather long after the second flame cycle. However, the samples containing nickel oxide did "blow" to form higher volumes of less dense char.

TABLE XII

#### FLAME RETARDANT PROPERTIES OF NICKEL OXIDE

| Sample No. | Parts<br>NiO | Parts<br>$Sb_2O_3$ | 1st<br>Flame | 2nd<br>Flame | 3rd<br>Flame | 4th<br>Flame |
|------------|--------------|--------------------|--------------|--------------|--------------|--------------|
| 4253-1     | 2            | ---                | 53.0         | ---          | ---          | ---          |
| -2         | 4            | ---                | 63.0         | ---          | ---          | ---          |
| -3         | 6            | ---                | 2.0          | Burns        | ---          | ---          |
| -4         | 2            | 1                  | 5.0          | 20           | 26           | 86           |
| -5         | 2            | 2                  | <1           | 2.0          | 30           | 49           |
| -6         | 3            | 1                  | 1.5          | 54           | 26           | 56           |

#### Metal Oxides with Chlorinated PE Halogen Source

To further demonstrate the utility of two of these metal-metalloid systems, we prepared a polymer blend containing chlorinated polyethylene (K-10, 36% chlorine) with a total halogen content of 14.4% Cl.

|               |            |
|---------------|------------|
| Recipe: K-10  | 40.0 parts |
| Thermolite 31 | 1.5 parts  |
| SAN           | 36.0 parts |
| 820X17        | 24.0 parts |
| Stearic Acid  | 1.0 parts. |

Property bars were prepared and tested for flammability in the standard way. The results in Table XIII show that the titanium dioxide-triiron trioxide and iron oxide-antimony trioxide synergistic systems are effective in reducing the flammability of this polymer blend.

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**TABLE XIII**  
**EFFECT OF SYNERGISTIC SYSTEMS**  
**USING CHLORINATED POLYETHYLENE**

| Sample No. | Parts $\text{Sb}_2\text{O}_3$ | Parts RANC-1 $\text{TiO}_2$ | Parts $\text{Fe}_2\text{O}_3$ | 1st Flame | 2nd Flame | 3rd Flame | 4th Flame |
|------------|-------------------------------|-----------------------------|-------------------------------|-----------|-----------|-----------|-----------|
| 4117-1     | ---                           | ---                         | ---                           | Burns     | ---       | ---       | ---       |
| -2         | 3                             | ---                         | ---                           | <1        | <1        | 2.0       | ---       |
| -3         | 3                             | 1                           | ---                           | 1.0       | 4.0       | Burns     | ---       |
| -4         | 3                             | ---                         | 3                             | 1.0       | 2.5       | 6.0       | 0.0       |

#### Oxygen Index Data

The Oxygen Index ( $\text{a}_{\text{O}_2}$ ), or Limiting Oxygen Concentration (LOC) is a commercially available test method for rating the flammability of plastics. The Oxygen Index is the per cent oxygen in a  $\text{N}_2/\text{O}_2$  mixture required to just sustain combustion of a polymer sample under the test conditions. Correlation with flammability under actual use conditions has not been established. This test is described elsewhere.<sup>1, 25</sup> We have obtained the oxygen index for the samples which we felt were the best self-extinguishing materials that we prepared. This data was obtained on a GE Oxygen Index Flammability Gauge in our laboratory.

A comparison of the Oxygen Index data and the data from the propane torch test shows a major difference in the results obtained by different testing methods. The lower burning temperatures in the candle-like oxygen index test enhance the effectiveness of iron oxides as flame retardants. This is because the iron oxide-halogen system is effective at lower temperatures than  $\text{Sb}_2\text{O}_3$ - or  $\text{SnO}_2$ -halogen systems. Likewise, the  $\text{SnO}_2$  systems appear to be more flammable in this less severe test since a higher temperature is required to efficiently generate the  $\text{SnCl}_4$  than the  $\text{FeCl}_3$ . The more severe propane torch test reverses this order. Thermal analyses support both these test methods.

#### Differential Scanning Calorimetry (DSC)

DSC data were obtained for samples of PVC, ABS/PVC blend, and ABS/PVC blend containing 1) 3 parts  $\text{Sb}_2\text{O}_3$ , 2) 3 parts  $\text{Sb}_2\text{O}_3$  and 1 part

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TABLE XIV  
OXYGEN INDEX ( $n_{O_2}$ ) OF EXPERIMENTAL SAMPLES

| Sample No. | Parts<br>$Sb_2O_3$ | Other<br>Additive(s)  | Parts<br>Other(s) | $n_{O_2}(\pm 0.5)$ |
|------------|--------------------|-----------------------|-------------------|--------------------|
| 4123-1     | 8†                 | ---                   | ---               | 27.7               |
| -2         | 0                  | ---                   | ---               | 24.0               |
| -3         | 3                  | ---                   | ---               | 23.8               |
| -4         | 8                  | ---                   | ---               | 27.7               |
| -5         | 3                  | Subpig $TiO_2$        | 0.5               | 24.5               |
| -6         | 3                  | RANC-I $TiO_2$        | 1.0               | 24.5               |
| -7         | 3                  | Virflux PR-5          | 2.5               | 24.6               |
| -8         | 4                  | $Pb^*$                | 4.0               | 24.9               |
| -9         | 3                  | $Pb^*$                | 4.0               | 24.2               |
| -10        | 0                  | $Fe_2O_3^*$           | 3.0               | 30.7               |
| -11        | 0                  | $Fe_2O_3$             | 3.0               | 29.8               |
| -12        | 3                  | $Fe_2O_3$             | 3.0               | 31.4               |
| -13        | 3                  | $Fe_2O_3$             | 3.0               | 31.6               |
| -14        | 3                  | $Fe_2O_3 \cdot XH_2O$ | 3.0               | 31.8               |
| -15        | 0                  | $SnO_2/TiO_2$         | 3.0/0.5           | 23.2               |
| -16        | 1                  | $SnO_2$               | 3.0               | 24.6               |
| -17        | 2                  | $SnO_2$               | 2.0               | 25.0               |

† Ahsen 89129

\*As 3.0 parts Tribase and 1 part lead laurate

\*No Thermolite 31 added

3) 3 parts  $SnO_2$ , 4) 3 parts  $SnO_2$  and 1 part  $TiO_2$ , and 5) 3 parts  $Fe_2O_3$ . Preliminary runs show that the  $Sb_2O_3$ ,  $SnO_2$  and  $Fe_2O_3$ -containing systems exhibit different reaction pathways during decomposition. The indications are that  $Fe_2O_3$  promotes earlier PVC decomposition than  $Sb_2O_3$  or  $SnO_2$ . The addition of  $TiO_2$  appears to retard the action of  $Sb_2O_3$  making this combination more effective at the burning temperature. The  $TiO_2$  also appears to retard the reaction of  $SnO_2$  with HCl from the PVC making this combination less effective until higher temperatures are achieved. This data helps to explain why iron oxide systems have a higher Oxygen Index (Table XIV) than the  $Sb_2O_3$  or  $SnO_2$  systems in this thermally less severe candle type test. It also explains the low Oxygen Index for the  $SnO_2$  and  $SnO_2-TiO_2$  samples since these would not become synergistically active until high temperatures.

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are obtained. Further work should be done with DSC, TGA and DTA as complementary test methods for understanding flame retardant mechanisms.

#### Physical Properties of Some Compounded Systems

The only properties, other than flammability, that we tested were the heat distortion temperature (264 psi, unannealed) and notched Izod impact at room temperature. These are listed in Table XV for several of the systems. The Table is incomplete since not all systems were tested. However it does show that these properties are not detrimentally effected when low levels of metal salts are added to the basic recipe.

TABLE XV  
EFFECT OF ADDITIVES ON PHYSICAL PROPERTIES OF POLYMER BLEND

| Sample No. | Parts $\text{SnO}_2$ | Other Additive(s)               | Parts Other(s) | HDT, °C (264 psi) | Izod Impact Ft-lbs/in notch |
|------------|----------------------|---------------------------------|----------------|-------------------|-----------------------------|
| 4100-0     | 0.0                  | ---                             | ---            | 74-78*            | 2-2.2                       |
| 4100-1     | 0.0                  | Virflux PR-5                    | 1.0            | 75.5              | 6.0                         |
| 4100-2     | 0.0                  | "                               | 0.5            | 80.0              | 3.7                         |
| 4100-3     | 0.0                  | Lead*                           | 4.0            | 76.5              | 5.8                         |
| 4100-4     | 0.0                  | Lead*                           | 4.0            | ---               | 3.4                         |
| 4100-5     | 0.0                  | $\text{Fe}_2\text{O}_3$ †       | 3.0            | 77.0              | 3.7                         |
| 4100-6     | 0.0                  | $\text{Fe}_2\text{O}_3$         | 3.0            | 74.0              | 3.2                         |
| 4100-7     | 1.0                  | $\text{Fe}_2\text{O}_3$         | 3.0            | 76.0              | 2.5                         |
| 4100-8     | 0.0                  | $\text{Fe}_2\text{O}_3$ (#104)  | 3.0            | 74.0              | 5.7                         |
| 4100-9     | 1.0                  | $\text{Fe}_2\text{O}_3$ (#104)  | 3.0            | 75.0              | 4.1                         |
| 4100-10    | 0.0                  | $\text{Fe}_2\text{O}_3$ (#1322) | 3.0            | 75.0              | 5.4                         |
| 4100-11    | 1.0                  | $\text{Fe}_2\text{O}_3$ (#1322) | 3.0            | 76.0              | 3.0                         |

\* As tribase and lead laurate

† Without Thermolite 31

  
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