

## Flammability of Epoxy Resins

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### Synopsis

Flammability determinations have been made for epoxy resin formulations. The oxygen index, defined as the volume fraction of oxygen in an oxygen/nitrogen atmosphere that is required just to sustain steady candlelike burning of a stick of the material, has been used as the measure of flammability. The formulations selected for study were those for which the chemical composition of the ingredients was known at least approximately and for which uniform cast slabs ( $1/8$  in. thick) could be readily prepared. They covered a range of compositions of commercial interest. The results have been interpreted in terms of a proposed model for candlelike burning. Effects due to resin composition, cure conditions, fillers, and flame-retardant additives are discussed.

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### Selection and Preparation of Samples

The samples for burning were approximately  $6 \times 3.2 \times 80$  mm. in size. They were cut from cast slabs about  $20 \times 20 \times 0.32$  cm.

The resin formulations for casting were mixed at elevated temperatures (60–90°C.) and de-aerated with stirring under a vacuum of 25–30 mm. Hg for a minimum of 15 min. Fillers were dried at 125°C. for 24 hr. and incorporated into the resin formulation immediately on removal from the drying oven. Precautions were taken to insure intimate wetting of the filler with the resin mixture. It was necessary to add the flame-retardant additives in the final stage of the de-aeration step because of their cure-accelerating properties. The completed mixture was cast into preheated

molds consisting of two flat aluminum plates with a U-shaped Teflon spacer and cured for the required time in an air-circulated oven. On completion of the cure cycle the casting was removed from the mold and cleaned with acetone, to remove the silicone release agent employed.

### Experimental

The technique for the determination of oxygen indices has been discussed previously.<sup>1,2</sup> The sample was mounted vertically from the bottom end along the axis of a Pyrex glass chimney about 3½ in. O.D. A uniform mixture of oxygen and nitrogen passed upward through the chimney at a free-stream velocity of about 7 cm./sec. The sample was vigorously ignited at the top end with a hydrogen diffusion flame, which was then withdrawn. The volume fraction of O<sub>2</sub> in an oxygen/nitrogen mixture that just sustained burning for the entire length of the stick was taken as the oxygen index,  $n_{O_2} = [O_2]/([O_2] + [N_2])$ . It was reproducible to within ±1%. A material with an oxygen index of ≥ 0.27 would usually be considered self-extinguishing.

### The Combustion Model

The model to be used for discussing our results has been presented previously.<sup>1-3</sup> According to this model, the molten or solid polymer enclosed by the candlelike diffusion flame does not react directly with the surrounding gas; it merely pyrolyzes in the heat from the flame. The pyrolysis products in general include solids and gases. The latter move outward and react with atmospheric gases to produce the visible flame some distance away from the polymer surface. The solids tend to accumulate as a char or ash. This model has been supported by temperature and gas-composition measurements made inside flames at reduced pressure above several polymers.<sup>2</sup>

In steady burning, the rate of generation of fuel gases by pyrolysis must equal their rate of consumption in the flame. Following Fenimore and Jones, we say that the rate of generation of fuel gases is independent of the detailed nature of the gaseous flame reactions; it depends only on the heat flux from the flame. Then a material added to the polymer that inhibits burning by making the generation of pyrolysis gases more difficult (i.e., by affecting the condensed-phase reactions) should be effective regardless of the particular oxidant and flame reactions in the gas phase. For example, it has been shown that Cl incorporated into polyethylene makes the material more difficult to burn both in O<sub>2</sub>/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub> atmospheres. This with other evidence<sup>1</sup> indicates that Cl affects the pyrolysis reactions.

On the other hand, an inhibitor that is effective in O<sub>2</sub>/N<sub>2</sub> but not in N<sub>2</sub>O/N<sub>2</sub> is most likely to act by poisoning the gaseous flame reactions in O<sub>2</sub>/N<sub>2</sub>. The use of Sb compounds in chlorinated polyethylene is such a case.

The nitrous oxide test has been used here for investigating the mode of action of several inhibitors in epoxy formulations. The index is defined as follows:

$$n_{N_2O} = [N_2O]/([N_2O] + [N_2])$$

### Data

Oxygen index values for unfilled formulations containing no flame retardants are summarized in Table I. They are also plotted against the overall O/C atom ratio in Figure 1. Indices for other polymers are also shown.

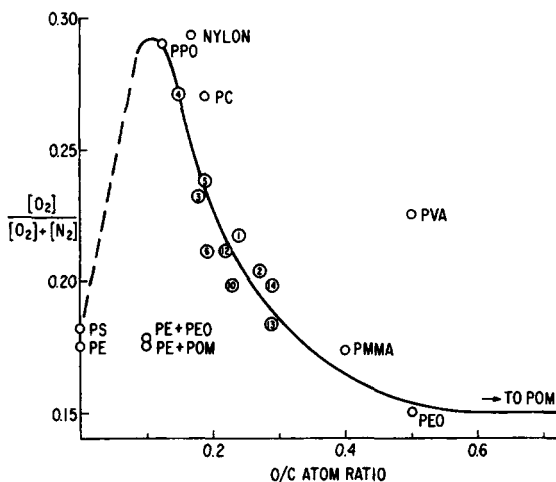


Fig. 1. Numbered points refer to FRS epoxy samples in Table I. PE, polyethylene; PMMA, poly(methyl methacrylate); PS, polystyrene; PVA, poly(vinyl alcohol); PPO, poly(2,6-xylenol); PEO, poly(ethylene oxide); PC, polycarbonate POM, polyoxymethylene.

Oxygen indices are given in Figure 2 for a particular resin-hardener formulation with several filler materials. Nitrous oxide indices for the samples containing hydrated alumina are shown in Figure 3.

Indices obtained upon addition of triphenyl antimony are summarized in Table II. Corresponding indices for the addition of triphenyl phosphorus are given in Table III. They are plotted in Figures 4 and 5.

### Effect of Resin Composition and Cure

Samples A, B, C, and D of Table I were identical with 1, 2, 3, and 4, respectively, except for cure time and temperature. It is seen that the measured indices for each pair were nearly independent of the cure conditions. This seems consistent with previous work on polyethylene, in which it was found that the oxygen index was nearly independent of the

TABLE I

Sample	Resin	Hardener <sup>a</sup>	Cure, hr./°C.	Atoms				$n_{02}$
				C	H	O	N	
Standard epoxy	Epon 826	HHPA (75), DMP-30 (1)	16/125	1.00	1.18	0.26		0.198
Small char accumulated slowly.								
KRP-1	Epon 826	MNA (118)	—	1.00	1.12	0.25		0.208
Thin, hollow char fell away every couple of minutes.								
FRS-1	Araldite 6005	MNA (97), DMP-30 (1)	24/100	1.00	1.12	0.24		0.217
-A	"	"	2/100 + 2/150					0.217
Char formed hollow, brittle shell roughly the shape of the stick.								
-2	Araldite 6005	HHPA (83), DMP-30 (1)	24/100	1.00	1.19	0.27		0.203
-B	"	"	2/100 + 2/150					0.203
Flame had distinct blue leading edge. Lacy char structure formed much more slowly than for FRS-1.								
-3	Araldite 6005	TETA (13)	24/100	1.00	1.29	0.18	0.05	0.232
-C	"	"	3/100					0.227
Flame composed of many small jets. No distinct blue leading edge. Lacy char did not form shell.								
-4	Araldite 6005	TONOX (27)	24/100	1.00	1.13	0.15	0.03	0.271
-D	"	"	2/100 + 3/150					0.271
Flame composed of many small jets. No distinct blue leading edge. Hollow char accumulated very large soot mass.								
FRS-5	Araldite 6005	BF <sub>3</sub> ·MEA (3)	24/100	1.00	1.16	0.19	0.004	0.238
								+ 0.004 BF <sub>3</sub>

Big messy flame composed of jets Green BO<sub>2</sub> emission seen in H<sub>2</sub> flame above burning stick but not in polymer flame itself. Hollow brittle char formed.

-6 Araldite 6005 DMP-30 (3) 24/100 1.00 1.16 0.19 0.005 0.211  
 Only sample to show black melt run down below flame. Lacy char formed only after burning a couple of minutes.

-10 50% Araldite 6005 MNA (69), DMP-30 (1) 24/100 1.00 1.12 0.23 0.198

50% Araldite 6060

Lacy char.

-12 Araldite 6060 MNA (42), DMP-30 (1) 24/100 1.00 1.12 0.21 0.211

Lacy char formed slowly.

-13 CY-175 MNA (134), stannous octoate (1) 24/100 1.00 1.26 0.29 0.183

Large smooth flame. Distinct blue leading edge. Large quenching distance of 0.8 mm. Char slowly formed a lacy shell.

-14 ERLA 4221 MNA (142), stannous octoate (1) 24/100 1.00 1.24 0.29 0.198

Big smooth flame. Surface browned before forming brittle hollow shell, which largely retained shape of stick. Distinct blue leading edge.

<sup>a</sup> Numbers within parentheses indicate weight per hundred parts of resin for that component. All samples except the first two contained stoichiometric quantities of resin and hardener.

TABLE II  
 Triphenyl Sb in Epoxy

Sample	Br, wt.-%	Sb, wt.-%	Parts <sup>a</sup>		Atoms			Gas veloc., cm./sec.	$n_{02}$	Gas veloc., cm./sec.	$n_{02}$		
			$\phi_3\text{Sb}$	A	B	C	H					O	Br
KP-1	13.7	0	0	84.3	115.7	1.00	1.172	0.266	0.035	0.0000	0.236	7.3	0.283
KRP-12	"	0.5	2.9	84	115.2	1.00	1.143	0.256	0.034	0.0008	0.283	7.9	0.301
-13	"	1.0	5.8	84	110.2	1.00	1.138	0.253	0.035	0.0016	0.322	8.1	0.340
-14	"	2.0	11.6	84	104.4	1.00	1.127	0.245	0.035	0.0033	0.349	8.3	0.367
-15	"	3.0	17.4	84	101.4	1.00	1.117	0.237	0.034	0.0049	0.336	8.5	0.301
-17	"	4.0	23.2	84	92.8	1.00	1.105	0.230	0.035	0.0066	0.337	8.7	0.336
-2	"	4.2	24.2	84.3	91.5	1.00	1.103	0.227	0.035	0.0070	0.336	8.9	0.336
-18	"	4.5	26.1	84.0	89.9	1.00	1.099	0.225	0.035	0.0075	0.336	8.5	0.336
-19	"	4.8	27.8	84.0	88.2	1.00	1.095	0.222	0.035	0.0080	0.336	8.5	0.336
-16	"	5.0	29.0	84.0	87	1.00	1.094	0.221	0.035	0.0084	0.336	8.1	0.336
-20	"	5.5	31.9	84.0	84.1	1.00	1.089	0.216	0.035	0.0092	0.336	8.5	0.336
-21	"	6.0	34.8	84.0	81.2	1.00	1.084	0.213	0.035	0.0102	0.336	8.4	0.336
-32	0	0	0	0	200	1.00	1.182	0.260	0.000	0.0000	0.196	7.7	0.196
-39	0	0.5	2.9	0	197	1.00	1.178	0.257	0	0.0007	0.279	7.8	0.279
-40	0	2.0	11.6	0	188	1.00	1.163	0.245	0	0.0029	0.321	8.3	0.321
-41	0	4.0	23.2	0	177	1.00	1.145	0.230	0	0.0058	0.324	8.4	0.324
-42	0	6.0	34.8	0	165	1.00	1.128	0.219	0	0.0088	0.308	8.2	0.308

<sup>a</sup> A = 100 parts D.E.R. 542 (46% Br), 41.4 parts HHPA. B = 100 parts Epon 826, 74.5 parts HHPA.

TABLE III  
Triphenyl P in Epoxy

Sample	Br, wt.-%	P, wt.-%	Parts <sup>a</sup>			Atoms				Gas, veloc., cm./ sec.	Gas, veloc., cm./ sec.	$n_{C_2}$
			$\phi_3P$	A	B	C	H	O	Br			
KP-1	13.7	0	0	84.3	115.7	1.00	1.172	0.266	0.035	0.0000	7.3	0.236
KRP-22	"	0.064	1.08	84.0	114.9	1.00	1.146	0.258	0.035	0.0004	7.7	0.266
-23	"	0.127	2.16	84.0	113.8	1.00	1.143	0.254	0.035	0.0008	7.8	0.272
-24	"	0.255	4.32	84.0	111.7	1.00	1.138	0.252	0.034	0.0016	7.9	0.287
-25	"	0.384	6.51	84.0	109.5	1.00	1.131	0.246	0.035	0.0024	8.0	0.294
-26	"	0.530	8.98	84.0	107.0	1.00	1.125	0.243	0.035	0.0033	8.2	0.311
-27	"	0.630	10.7	84.0	105.3	1.00	1.123	0.241	0.034	0.0041	8.2	0.311
-28	"	0.735	12.5	84.0	103.5	1.00	1.118	0.237	0.035	0.0046	8.5	0.332
-29	"	1.03	17.5	84.0	98.5	1.00	1.107	0.230	0.034	0.0066	8.9	0.363
-30	"	1.18	20.0	84.0	96.0	1.00	1.100	0.225	0.034	0.0075	8.8	0.359
-31	"	1.47	25.0	84.0	91.0	1.00	1.090	0.217	0.035	0.0093	9.0	0.374
-32	0	0	0	0	200	1.00	1.182	0.260	0.000	0.0000	7.7	0.196
-33	"	0.065	1.08	0	198.9	1.00	1.180	0.258	0	0.0004	7.2	0.209
-34	"	0.26	4.32	0	195.7	1.00	1.174	0.254	0	0.0014	7.4	0.241
-35	"	0.63	10.7	0	189.3	1.00	1.160	0.244	0	0.0035	7.6	0.288
-36	"	0.74	12.5	0	187.5	1.00	1.156	0.240	0	0.0041	8.1	0.305
-37	"	1.03	17.5	0	182.5	1.00	1.148	0.234	0	0.0057	8.3	0.321
-38	"	1.18	20.0	0	180.0	1.00	1.143	0.230	0	0.0065	8.4	0.330

<sup>a</sup> A = 100 parts D.E.R. 542 (46% Br) 41.1 parts HHPA. B = 100 parts Epon 826 74.5 parts HHPA.

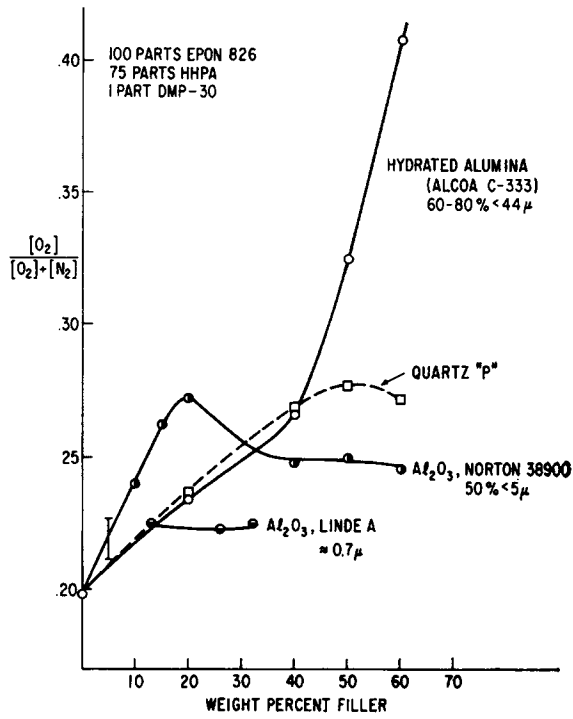


Figure 2.

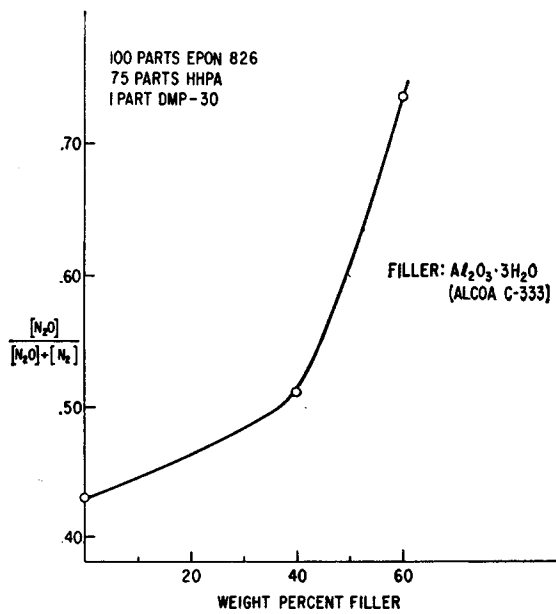


Figure 3.



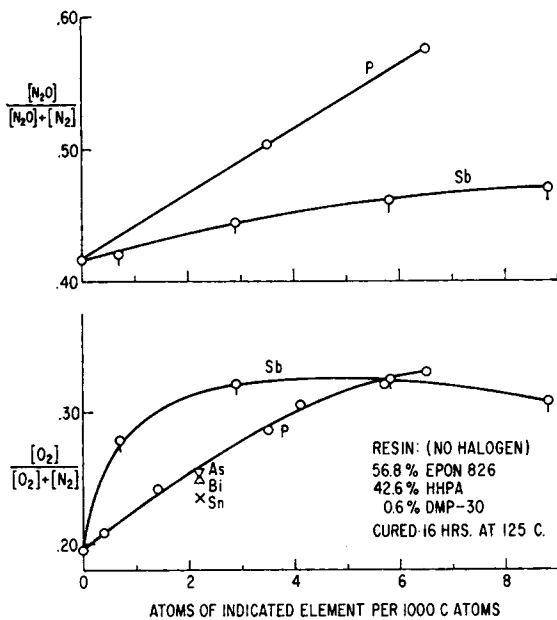


Fig. 4. Elements other than Sn added in the form of the triphenyl compound. Sn added as tributyltin acetate.

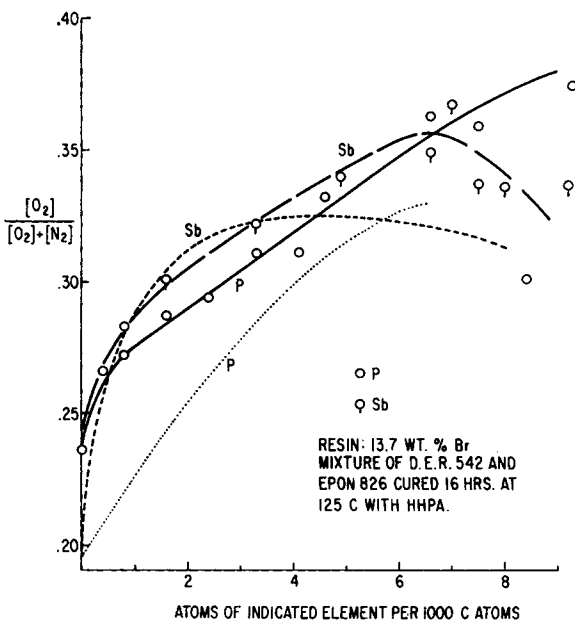
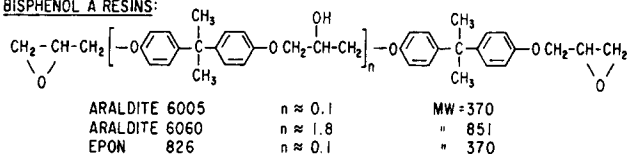


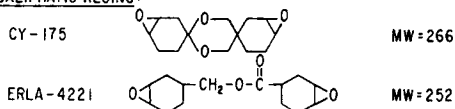
Fig. 5. Dotted and dashed lines indicate data from Fig. 4 with no halogen in the resin. P and Sb added as triphenyl compounds.

## CHEMICAL FORMULAS

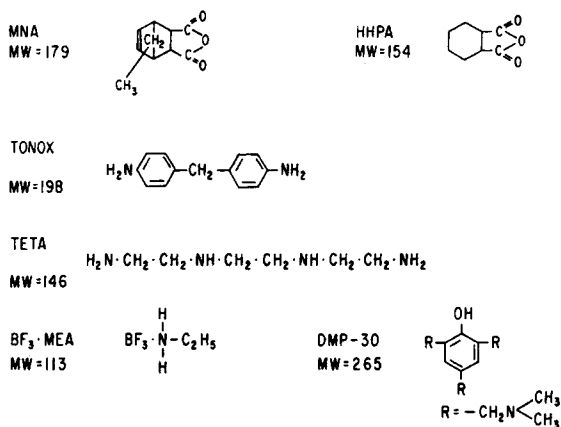
## A BISPHENOL A RESINS:



## B CYCLOALIPHATIC RESINS:



## C CURING AGENTS:



## D BROMINATED BISPHENOL A RESIN:

D.E.R. 542      MOLECULAR WEIGHT  $\approx$  750  
BROMINE CONTENT  $\approx$  46 WT. %

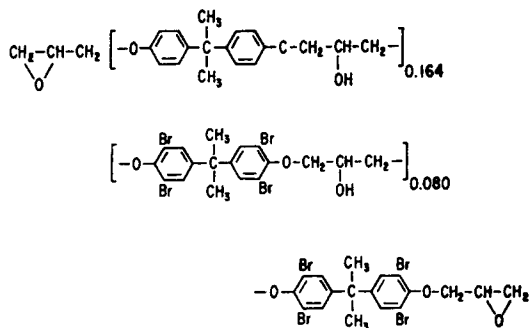


Fig. 6. Materials summary.

extent of crosslinking produced chemically (by dicumyl peroxide) or by radiation.

The bisphenol resins (Araldite, Epon) cured with acid anhydrides (MNA, HHPA) had measured indices in the range 0.198–0.217. Formulations of the same Araldite resin cured with amines (TONOX, TETA) were harder to burn, produced more soot, and had indices of 0.271 and 0.232, respectively. When cured with a small amount of tertiary amine (DMP-30) the index was 0.211, similar to the acid anhydrides. The  $\text{BF}_3$ -MEA complex gave an index of 0.238.

The cycloaliphatic resins CY-175 and ERLA 4221 cured with MNA had relatively high O/C ratios and low indices, 0.183 and 0.198, respectively.

The cure reactions are complex;<sup>4</sup> we shall not attempt to describe them in detail. However, in all formulations the expected product will be crosslinked, will contain ether and ester linkages in various ratios, and may have OH side groups. The observed indices have been plotted against the atomic ratio O/C in Figure 1. Despite the scatter there is a clear trend of decreasing index with increasing O/C. This suggests a decreasing thermal stability and increasing fuel gas formation, as the number of O atoms in the chain increases, a behavior observed for the slow pyrolysis of aliphatic polyethers.<sup>5</sup>

Indices for other polymers composed of C, H, N, and O have been added in Figure 1. The line has been sketched roughly through the indices for polymers containing oxygen atoms in the main chain. One must not infer, however, that the index is a simple function of the empirical O/C ratio; rather, it depends upon the detailed chemistry. For example, mixtures of polyethylene with either poly(ethylene oxide) or polyoxymethylene have indices of about 0.165 while PPO with nearly the same O/C ratio has an index of 0.29.

### Effect of Fillers

When inert fillers were incorporated into polymer samples and the sample burned in a candlelike manner, the inert material accumulated as an ash at the burning surface. With small filler particle sizes and high filler content (>40 wt.-%) the ash remained standing above the flame and retained the shape of the original stock. It glowed red in the flame zone and appeared to stabilize the flame (which could be quite small), so that very reproducible values of the oxygen index could be determined.

On the other hand, with less filler content the inert material accumulated and formed a crust over the burning surface. This tended to extinguish the flame. For the flame to propagate down the whole length of the stick the oxygen content of the atmosphere had to be high enough to permit shedding of the accumulated crust at intervals, after which the flame would flare up until another crust developed. The oxygen index was, therefore, determined by the complex conditions leading to periodic

shedding of the crust. The maximum in the index for Norton 38900 Alumina in Figure 2 is probably a reflection of this situation.

As seen in Figure 2, the inert fillers  $\text{Al}_2\text{O}_3$  and quartz gave significant increases in index when used in large concentrations. However, the increase was limited to about 40% for the optimum concentration of filler.

On the other hand, hydrated alumina  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  cannot be considered an inert filler. It undergoes strongly endothermic dehydration reactions at temperatures above about  $150^\circ\text{C}$ . Thus, at concentrations greater than 40 wt.-%, hydrated alumina led to a sharp increase in the oxygen index. At 60 wt.-% filler, the index of 0.41 was twice that of the unfilled resin and the standing ash was white without soot. Except for Teflon ( $n = 0.95$ ) we have not burned any other material that had so high an index without the formation of a carbonaceous char at the burning surface or soot above it.

The formulations containing  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  were also burned in  $\text{N}_2\text{O}/\text{N}_2$  atmospheres. As seen in Figure 3, the nitrous oxide index was sharply raised by high filler contents. Since  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  inhibited in both  $\text{O}_2/\text{N}_2$  and  $\text{N}_2\text{O}/\text{N}_2$  atmospheres, we conclude that it acts primarily in the condensed phase.

### Triphenyl Antimony and Triphenyl Phosphorus as Additives

Sb and P compounds are commonly employed as additives to impart flame retardance to polymers. It has been found that the triphenyl compounds of these (and other) elements can be incorporated into some epoxy formulations. The latter may or may not contain halogen. Oxygen indices and approximate empirical compositions for resins containing triphenyl Sb are given in Table II and, for the same resins, containing triphenyl P, in Table III.

In Figure 4 indices are given for a resin containing no halogen but having added triphenyl compounds. The usual oxygen index is plotted in the lower half of the figure. Antimony at an atom concentration as low as 3 Sb atoms per 1000 C atoms raised the observed index from 0.196 to 0.310, an increase of 58%, but higher Sb concentrations did not result in a further increase. Triphenyl phosphorus was an effective additive, but 5.5 atoms of P per 1000 of C were required to equal the increase in index produced by only 3 atoms of Sb. However, it appears that higher P contents should raise the index above that for corresponding Sb addition. Compounds of As, Bi, and Sn at 2.2 atoms per 1000 C atoms were slightly less effective than P.

The same Sb and P formulations were burned in  $\text{N}_2\text{O}/\text{N}_2$  mixtures; the indices so obtained are plotted in the top half of Figure 4. Despite the different gas-phase flame reactions expected for burning with  $\text{N}_2\text{O}$  the P was nearly as effective in raising the index with  $\text{N}_2\text{O}$  as with  $\text{O}_2$ . If our model discussed above is valid, this means that P inhibited in this material mostly by retarding the generation by pyrolysis reactions in the condensed phase of the fuel gases required to sustain the flame (these pyrolysis

reactions take only heat from the flame gases, and the detailed nature of the reactions generating the heat is unimportant). Previous work has shown P (in tricresyl phosphate) to be an effective inhibitor in poly(ethylene oxide) but only slightly so in polyethylene, polyoxymethylene, or poly-(methyl methacrylate). This leads one to speculate that P may work by promoting dehydration reactions in polymers containing O atoms in the backbone. In poly(ethylene oxide) this would be competing with other pyrolysis reactions that yield fuel gases. In polyoxymethylene the dehydration may be slow relative to the unzipping reactions, which yield monomer.

When the Sb formulations were burned in  $N_2O/N_2$  (Fig. 4), the increase in index for small Sb concentrations was not as great as for the same material burned in  $O_2/N_2$  nor for the same atom concentration of P burned in  $N_2O$ . Thus, our model indicates that Sb inhibits mostly by retarding gas-phase flame reactions.

Previous work has shown that triphenyl Sb added to polyethylene inhibits only slightly in the absence of Cl; three atoms of Sb per 1000 of C increased the index only from 0.175 to 0.187. It is, therefore, surprising that triphenyl Sb proved so effective in the epoxy in the absence of halogen (residual halogen in the resin was found by analysis to be only 0.15% of Cl). It is commonly suggested that Cl enhances the effectiveness of Sb by formation of a volatile chloride, which transports Sb into the gas phase, where it poisons the flame reactions. If this is the only function of the Cl, it would appear that Sb from triphenyl Sb in the epoxy must reach the flame zone without chloride formation, whereas Sb from triphenyl Sb in polyethylene does not, unless some halogen is present. Triphenyl Sb has a boiling point of  $>360^\circ C$ . and may vaporize without appreciable decomposition, carrying Sb into the flame zone. The vapor pressure of the phenyl compound is considerably lower than that of  $SbCl_3$  (b.p.  $\approx 210^\circ C$ .).

Now, according to the proposed model for candlelike flames, the stability of the leading edge of the flame is critical for sustained burning.<sup>2</sup> The fuel gases that burn in this region are derived from the initial stages of the pyrolysis of the solid polymer, which has been rather gently heated by the approaching flame. It appears quite possible that in this situation the vapor pressure of triphenyl Sb is adequate for transporting Sb in the case of epoxy but not of polyethylene. In the latter case the higher vapor pressure of  $SbCl_3$  formed early in the pyrolysis would be required. This proposed explanation appears reasonable, but more information is needed to substantiate it (note that  $Sb_2O_3$  has a vapor pressure very much lower than triphenyl Sb; if the model described above is correct, it appears unlikely that  $Sb_2O_3$  alone would ever be effective).

### **Triphenyl Antimony and Triphenyl Phosphorus in Brominated Epoxy**

In Figure 5 oxygen indices for triphenyl Sb and triphenyl P added to a brominated epoxy are plotted. Corresponding data from Figure 4 for halogen-free resin are shown by the dotted lines. The Br was incorporated

in the form of tetrabromobisphenol A in D.E.R. 542 to the extent of 13.7 wt.-% of the total formulation. This amounted to 35 atoms of Br per 1000 of C.

With no added Sb or P compounds the incorporation of Br increased the index from 0.195 for no Br to 0.235 for 35 atoms per 1000 C, or about 0.001 for each Br atom per 1000 C atoms. This increase in index per Br atom was only about 1/90 of the initial increase per Sb atom shown in Figure 4 and about 1/30 of the initial increase per P atom. Previous work on Br compounds incorporated into polyethylene has indicated that Br acts primarily by poisoning the gaseous flame reactions.

In the regions of 1 to 3 Sb atoms per 1000 C (which is of much practical interest) the indices with and without Br were nearly identical. This is consistent with the picture that the primary function of the Br is the transport of Sb into the gas phase. When such transport is already adequate, as appears to be the case of triphenyl antimony in the epoxy, the addition of Br does not further increase the index. At higher Sb concentrations Br does appear to enhance the effectiveness of Sb, but the effect is limited. The large scatter of the experimental data in this region (>5 Sb per 1000 C) is not understood.

In the case of triphenyl phosphorus the indices in the brominated resin were consistently higher. However, the effects of Br and P were not strictly additive. The effect of the P was always greater. This is consistent with the hypothesis that P acts by affecting the pyrolysis to make generation of fuel gases more difficult and that Br acts primarily by poisoning the gaseous flame reactions.

### Summary

The flammabilities of selected epoxy formulations have been evaluated through determination of oxygen indices. These have been presented. The following general statements and conclusions apply.

(1) For a given formulation the oxygen index was nearly independent of cure conditions.

(2) There was a trend to lower indices (i.e., easier burning) for increasing O/C ratio in the overall composition. Resins cured with amine hardeners had lower O/C values and were more difficult to burn than the same resins cured with acid anhydrides. The cycloaliphatic resins had the highest O/C ratios and were the easiest to burn.

(3) Although we had no objective measure of soot and char formation, it appeared that the amine-cured resins gave most soot and the anhydride-cured cycloaliphatic resins the least.

(4) Inert fillers increased the oxygen index, but the maximum increase was 40%, and high filler contents between 20 and 50 wt.-% were required for maximum effect.

(5) Hydrated alumina,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , at 40–60 wt.-% resulted in a sharp increase in index, up to twice that in the unfilled resin. At 60 wt.-% filler there was no soot or char formation. The effect was produced largely in the

condensed phase, presumably as a result of endothermic dehydration reactions.

(6) Triphenyl antimony in concentrations giving as few as 3 Sb atoms per 1000 C atoms was an effective inhibitor (index increased by 60%) without the presence of halogen.

Addition of Br to the resin did not produce a further increase in index, until the concentration of Sb was raised above 3 atoms per 1000 C; then the effect was limited. The  $N_2O$  test indicated that Sb mostly poisoned the flame reactions. It is proposed that the effectiveness of triphenyl antimony in the absence of halogen resulted from its relatively high vapor pressure and thermal stability.

(7) Triphenyl phosphorus at concentrations giving 5.5 atoms of P per 1000 of C raised the index 60%. It was effective in both  $N_2O/N_2$  and  $O_2/N_2$ ; hence, it is believed to inhibit by altering pyrolysis reactions in the condensed phase. Addition of Br to the resin resulted in a further increase in index, but the effects of Br and P were not fully additive.

(8) Triphenyl arsenic, triphenyl bismuth, and tributyl tin acetate were somewhat less effective inhibitors than triphenyl phosphorus.

(9) Br incorporated into the resin structure in the form of tetrabromobisphenol A to the extent of 35 atoms per 1000 C atoms raised the index 20%. Previous work had shown that Br inhibits in polyethylene mostly by poisoning the flame reactions.<sup>3</sup> We suspect that it inhibited in the epoxies in a similar way.

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### References

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3. F. J. Martin, *Combust. Flame*, in press.
4. H. Lee and K. Neville, *Epoxy Resins*, McGraw-Hill, New York, 1957.
5. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964, p. 232.

### Résumé

Des déterminations d'inflammabilité ont été faites pour différents types de résines époxy. L'indice d'oxygène, défini comme la fraction en volume d'oxygène, dans une atmosphère oxygène/azote, qui est requise pour maintenir une combustion stationnaire, comme celle d'une bougie, d'un bâtonnet de la substance a été utilisé comme mesure d'inflammabilité. Les résines choisies pour cette étude sont celles pour lesquelles la composition chimique des ingrédients est connue au moins approximativement et pour lesquelles une plaquette coulée uniforme (1/8 in. d'épaisseur) peut facilement être préparée. Elles couvrent un domaine de composition d'intérêt commercial. Les résultats ont été interprétés sur la base d'un modèle proposé pour la combustion semblable à celle d'une bougie. Des effets dus à la composition de la résine, aux conditions de traitement, à la charge et aux additifs retardateurs de flamme sont discutés.

### Zusammenfassung

Entflammbarkeitsbestimmungen an Epoxyharz-Typen wurden durchgeführt. Der Sauerstoffindex, definiert als Volumbruch des Sauerstoffs in einer Sauerstoff-Stickstoff-Atmosphäre, die erforderlich ist, um das ständige kerzenähnliche Brennen eines Stabes aus dem Material gerade aufrechtzuerhalten, wurde als Mass für die Entflammbarkeit verwendet. Für die Untersuchung wurden diejenigen Typen ausgewählt, von denen man die chemische Zusammensetzung der Bestandteile wenigstens annähernd kannte und aus denen man leicht einheitliche Gussplatten ( $\frac{1}{8}$  in. dick) herstellen konnte. Sie überstrichen einen kommerziell interessanten Bereich an Zusammensetzungen. Die Ergebnisse wurden auf der Grundlage eines für das kerzenartige Brennen vorgeschlagenen Modells interpretiert. Die Einflüsse der Harz-Zusammensetzung, der Härtingsbedingungen, der Füllstoffe und der flammhemmenden Zusätze werden diskutiert.

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